Hierarchical Self-Assembly of Conjugated Block Copolymers and Semiconducting Nanorods into One-Dimensional Nanocomposites

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ABSTRACT: Semiconducting organic−inorganic nanocomposites comprising conjugated polymers (CPs) and semiconducting nanocrystals (NCs) represent an important class of functional materials. The ability to organize CPs and NCs into self-assembled nanostructures in close proximity may enable efficient charge or energy transfer between them for use in flexible electronics, light-emitting displays, and photovoltaics. Herein we report the crafting of one-dimensional (1D) functional nanocomposites composed of all-conjugated diblock copolymers and CdSe nanorods (NRs) via two consecutive self-assembly processes, namely, self-assembly of poly(3-hexylselenophene)-block-poly(3-butylthiophene) (denoted P3HS-b-P3BS) diblock copolymers into nanofibers, followed by self-assembly of P3HS-b-P3BS nanofibers and CdSe NRs to yield P3HS-b-P3BS−CdSe NR nanocomposites. Notably, P3HS-b-P3BS diblock copolymers are first rationally designed and synthesized, exhibiting a narrow optical bandgap and forming nanofibers due to strong interchain π−−π stacking (i.e., first self-assembly). Subsequently, the addition of CdSe NRs into P3HS-b-P3BS nanofiber solution results in the formation of 1D P3HS-b-P3BS−CdSe NR nanocomposites driven by the van der Waals interaction between aliphatic ligands on the surface of CdSe NRs and the hexyl side chains of P3HS-b-P3BS and the coordination interaction between the selenium of P3HS and the surface of CdSe NRs (i.e., second self-assembly). Quite intriguingly, an integrated Monte Carlo simulation and experimental study reveals that CdSe NRs are aligned parallel to the long axis of P3HS-b-P3BS nanofibers in an end-to-end mode at low concentration of CdSe. When high concentration of CdSe NRs is introduced, coexistence of the side-by-side and layer-by-layer assemblies of CdSe NRs along P3HS-b-P3BS nanofibers is yielded. Photoluminescence quenching of CdSe NRs is observed, suggesting an efficient charge transfer between CdSe and P3HS-b-P3BS. Such self-assembled conjugated diblock copolymer−quantum rod nanocomposites may find applications in optics, optoelectronics, and sensors.

INTRODUCTION

Recent research has witnessed impressive advances in organic−inorganic nanocomposites consisting of functional polymers and nanocrystals.1−3 This important class of materials combines many practical advantageous characteristics peculiar to polymers such as light weight, flexibility, low cost, and processability with unique and tunable optical, electronic, optoelectronic, magnetic, and catalytic properties of inorganic nanocrystals (NCs). They exhibit intriguing new functionalities rendered by the two dissimilar constituents and their spatial arrangement.4,5 In the latter context, the ability to enable bottom-up coassembly of polymers and nanocrystals into hierarchical architectures is of key importance as the collective properties are largely dictated by their spatial arrangements and nanoscale dimensions.6 Among various shaped functional nanocomposites, one-dimensional (1D) high-aspect-ratio conjugated polymer−nanocrystal (CP−NC) nanocomposites have been the subject of intense research as they form continuous channel for transporting charges, which is highly desirable for use in optical, electronic, and optoelectronic materials and devices.7−10

Poly(3-hexylthiophene) (P3HT) is one of most heavily investigated CPs due to its excellent solution processability and high charge carrier mobility.11,12 Recent advances in synthesis techniques render the design of a variety of P3HT-based rod−coil and rod−rod diblock copolymers (DBCPs) to realize functional assembly.13−19 P3HT-based DBCPs have been used as templates to direct n-type nanocrystals to produce p−n heterojunctions via covalent20 or noncovalent1,12 interactions, in situ gas−solid reaction,23 and so forth. Surprisingly, in contrast to P3HT, poly(3-hexylselenophene) (P3HS), a close analogue of P3HT, has been far less studied because of much more difficult synthesis and relatively poor solubility of P3HS.24 By replacing sulfur atoms in the thiophene rings with lower electronegative and more polarizable selenium

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atoms, P3HS carries some advantages over P3HT, such as smaller optical bandgap, lower oxidation and reduction potential, better interchain charge transfer, and so forth. Thus, the ability to synthesize and self-assemble P3HS-based all-conjugated DBCPs may afford them with intriguing physical properties and architectures (e.g., nanowires, nanorings, or nanoribbons), which can be readily integrated into nanocomposites when combining with NCS. It is worth noting that despite a few recent elegant studies on polyselenophene-nanoribbons, which can be readily integrated into nanocomposites when combining with NCS. It is worth noting that despite a few recent elegant studies on polyselenophene-nanoribbons, which can be readily integrated into nanocomposites when combining with NCS. It is worth noting that despite a few recent elegant studies on polyselenophene-nanoribbons, which can be readily integrated into nanocomposites when combining with NCS. 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**Experimental Section**

**Materials.** Monomers 2,5-dibromo-3-hexylselenophene and 2,5-dibromo-3-butylselenophene were synthesized according to the literature. (1,3-Bis(diphenylphosphino)propane)dichloronickel(II) (Ni(dppp)Cl2), isopropylmagnesium chloride (2.0 M solution in THF) (i-PrMgCl), cadmium oxide (CdO), tetracetylselenophenic acid (TDA), trioctylphosphine oxide (TOPO), tributylphosphine (TBP), tricyclotriphophine (TOP), and selenium powder were purchased from Sigma-Aldrich. The other reagents and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. All other reagents and solvents were used as received.

**Synthesis of Poly(3-hexylselenophene)-b-poly(3-butylselenophene) (P3HS-b-P3BS).** P3HS-b-P3BS DBCPs with various block ratios were synthesized by Grignard metathesis (GRIM) polymerization. The representative synthesis procedure for P3HS-b-P3BS with the feed molar ratio of 1:2 was as follows: two round-bottom flasks with side tubes were dried by heating under reduced pressure and cooled to room temperature. 2,5-Dibromo-3-hexylselenophene (0.63 g, 1.70 mmol) was added into flask A under N2 and then evacuated under reduced pressure to remove water and oxygen inside. After drying THF (60 mL) into the flask by syringe, the solution was stirred at 0 °C. A 2.0 M solution of i-PrMgCl in THF (0.85 mL, 1.70 mmol) was added, and the mixture was stirred at 0 °C for 30 min. The solution in flask A was then heated to 40 °C, followed by the addition of Ni(dppp)Cl2 catalyst (27.1 mg, 0.05 mmol). The resulting mixture was stirred at 40 °C for 1 h. Meanwhile, in flask B, 2,5-dibromo-3-butylselenophene (1.18 g, 3.4 mmol) was reacted with i-PrMgCl (1.7 mL, 3.40 mmol) at 0 °C for 30 min. After the reaction in flask A for 1 h, the solution in flask B was added to flask A, and the resulting mixture was reacted at 40 °C for 5 h. The reaction was quenched by adding HCl(aq) (50 wt %), and the product was precipitated using methanol. The product was then isolated via filtration, washed with excess methanol and hexane, and dried under vacuum to yield a 0.69 g deep dark solid (69% yield). Based on the ratio of the integrated areas of the two peaks at 0.88 and 0.83 ppm assigned to the resonances of terminal methyl groups in butyl and hexyl side chains, respectively, derived from 1H NMR spectra, the actual molar ratios of the P3HS and P3BS blocks of two P3HS-b-P3BS DBCP samples can be determined to be 70:30 and 31:69 (denoted HS70BS30 and HS31BS69, respectively). GPC of HS31BS69: Mn = 20900 g/mol, PDI = 1.64; HS70BS30: Mn = 21700 g/mol, PDI = 1.91. HS70BS30: 1H NMR (400 MHz, 1,2-dichlorobenzene-d4), δ (ppm): 7.04 (1 H), 2.74 (4 H), 1.67 (4.22 H), 1.47–1.18 (10 H), 0.87 (1.80 H), 0.83 (4.05 H). HS11BS69: 1H NMR (400 MHz, 1,2-dichlorobenzene-d4), δ (ppm): 7.04 (1 H), 2.74 (3.32 H), 1.67 (3.32 H), 1.47–1.18 (9.63 H), 0.87 (3.74 H), 0.83 (1.37 H).

**Synthesis of Poly(3-hexylselenophene) (P3HS) and Poly(3-butylselenophene) (P3BS) Homopolymers.** P3HS and P3BS were also synthesized in the similar way except the addition of a second monomer. The representative synthesis procedure for P3HS is as follows: a round-bottom flask with side tubes were dried by heating under reduced pressure and cooled to room temperature. 2,5-Dibromo-3-hexylselenophene (1.75 g, 4.60 mmol) was added into the flask under N2 and then evacuated under reduced pressure to remove water and oxygen inside. After drying THF (60 mL) into the flask by syringe, the solution was stirred at 0 °C. A 2.0 M solution of i-PrMgCl in THF (2.30 mL, 4.60 mmol) was added, and the mixture was stirred at 0 °C for 30 min. The solution in the flask was then heated to 40 °C, followed by the addition of Ni(dppp)Cl2 catalyst (54.2 mg, 0.1 mmol). The resulting mixture was stirred at 40 °C for 2 h. Subsequently, the reaction was quenched by adding HCl(aq) (50 wt %), and the product was precipitated using methanol. The product was then isolated via filtration, washed with excess methanol and hexane, and dried under vacuum to yield a 0.61 g of deep dark solid (61% yield). GPC: Mn = 13320 g/mol, PDI = 1.16. The P3BS homopolymers was synthesized in the same way. GPC: Mn = 8700 g/mol, PDI = 1.41. P3HS homopolymer: 1H NMR (400 MHz, 1,2-dichlorobenzene-d4), δ (ppm): 7.04 (1 H), 2.77 (4.05 H), 1.65 (4.05 H), 1.47–1.18 (13.78 H), 0.83 (5.67 H). P3BS homopolymer: 1H NMR (400 MHz, 1,2-dichlorobenzene-d4), δ (ppm): 7.04 (1 H), 2.74 (3.55 H), 1.67 (3.75 H), 1.47–1.18 (4.94 H), 0.87 (5.46 H).

**TDPA-Capped CdSe Nanorods (NRs).** CdSe NRs were synthesized according to the reported method. In a typical synthesis, CdO (0.21 g), tetracyclophosphinic acid (0.89 g) and TOPO (3.50 g) were mixed and heated to 320 °C under Ar. The mixture became a...
Scheme 1. Synthesis of P3HS-b-P3BS Diblock Copolymers (DBCPs)

Preparation of Block Copolymer Nanofibers. P3HS-b-P3BS diblock copolymers (DBCPs) were fully dissolved in toluene (1 mg/mL) at 100 °C. The solutions were then aged at room temperature for 24 h to ensure the formation of P3HS-b-P3BS nanofibers.

Formation of P3HS-b-P3BS–CdSe NR Nanocomposites. A certain amount of CdSe NRs solution (1 mL of 0.5, 1, or 2 mg/mL CdSe NRs in toluene) was added into 1 mL of the P3HS-b-P3BS nanofiber solution. The resulting mixture was then incubated at room temperature under gentle stirring (400 rpm) for 24 h to form hierarchically assembled P3HS-b-P3BS–CdSe NR nanocomposites.

Monte Carlo Simulation of Self-Assembly of P3HS-b-P3BS–CdSe NR Nanocomposites. To understand the self-assembly behaviors of the P3HS-b-P3BS (e.g., HS31BS69) nanofibers and the CdSe NRs, we performed two-dimensional (2D) Monte Carlo (MC) simulations. As the nanocomposites were observed on 2D copper wafer, the MC simulations were performed in 2D for the sake of saving computational time. All simulations were conducted on simple 2D square lattice with a dimension of 60×60 along the X and Y directions, and a = 1 is the lattice unit length. The periodic boundary condition was applied in both X and Y directions. Each lattice site was only occupied by a polymer bead or a solvent molecule because of the exclude volume interaction employed in the system. A nanofiber and a NR occupy 40 and 3 lattice sites, respectively. The volume concentration of NRs used in the system was increased from 0.023 to 0.212. There are eight nearest-neighbor sites for each lattice site in the 2D plane. The configuration of nanofiber was fixed throughout the simulation. The bond crossing was forbidden. Movements of NRs were achieved through the exchange sites between NRs and solvent. It is notable that the movements were restricted by the rigidity of NRs. In addition, the acceptance or rejection of the attempted exchange is governed by Metropolis importance sampling rule. The exchange is accepted when the energy change ∆E is negative. Otherwise, the move is accepted with a probability of p = exp[−∆E/(k_B T)], where ∆E = ∑ ij ∆N_ij, and i and j refer to NRs, nanofiber or solvent. ∆N_ij is the number difference of nearest-neighbor pairs between i and j components before and after the move; e is the interaction between components i and j. The Boltzmann constant k_B is assumed to be 1, and the temperature of the system is T = 0.07. For every simulation, 9 × 10^6 Monte Carlo steps (MCSs) were performed.

Characterization. 1H NMR spectra in 1,2-dichlorobenzene-d_6 were collected on a Bruker 400WB AVANCE III spectrometer at 100 °C. Gel permeation chromatography (GPC) was operated using a Varian PL220 GPC chromatograph equipped with one PL1110-1120 column and two PL MIXED-B 7.5 × 300 mm columns at 150 °C (1,2,4-trichlorobenzene used as the solvent). Molecular weights were determined using narrow distribution polystyrene standards. The P3HS homopolymer was characterized with GPC using an Agilent 1100 system equipped with both G1362A refractive index and G1314A UV detectors (eluent: THF; calibration: polystyrene standards). UV–vis spectroscopy was performed with a PerkinElmer Lambda 750 equipment. Photoluminescence (PL) spectra and time-resolved photoluminescence spectra were recorded on a FLS920 spectrophotometer. Grazing-incidence X-ray diffraction (GIXRD) experiments were conducted at the BL14B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF), with a fixed wavelength of 1.24 Å and a sample-to-detector distance of 35 cm. The incidence angle of the X-ray beamline was 0.15° with a 30 s exposure time. As for GIXRD analysis, the samples were completely dissolved in toluene (1 mg/mL) at 100 °C and then cooled and aged at room temperature for 24 h. The solutions were then drop-casted on precleaned silicon wafers at room temperature. The solvent (i.e., toluene) evaporated quickly within ~1 min inside fuming hood. The obtained samples were dried and stored under vacuum prior to the measurement. The transmission electron microscopy (TEM) images were obtained on a Tecnai G² 20 Twin, FEI electron microscope operated at 200 kV. The specimens for TEM were prepared by dropping the sample solution onto a carbon-coated copper grid with a filter paper placed below to absorb the excess solvent inside fuming hood. It took about several seconds to evaporate the solvent (i.e., toluene in this case). After simply drying in the fuming hood, the TEM samples were later placed in vacuum for several hours prior to the measurement. The tilt series were recorded with 1° tilting increment by the FEI explore 3D software (1/160 = 1.6; Δfocus = −1 μm) between −60° and +60° for all samples. The 3D reconstructions were performed using the Inspct 3D software. Cryogenic transmission electron microscopy (cryo-TEM) was performed using a Gatan cryo-holder operating at ~170 °C and FEI Tecnai G2 20 Twin TEM at 200 kV. High-resolution transmission electron microscopy (HRTEM), dark-field scanning TEM (DF-STEM), and energy-dispersive X-ray spectroscopy (EDS) were obtained using Tecnai G² F20 S-Twin microscope at 200 kV. Atomic force microscopy (AFM) measurements were performed using a Multimode 8 AFM Nanoscope IV in the tapping mode. Thin films for AFM were prepared by spin-coating the polymer solutions (1 mg/mL) on silicon wafer at 3000 rpm for 60 s. The X-ray photoelectron spectrum (XPS) was acquired using a PHI 3000C ESCA system, and the C 1s peak at 284.6 eV was used as a reference line. Cyclic voltammetry (CV) curves were collected using a CHI 660 electrochemical analyzer with a degassed acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu4NPf6, 0.1 M). Thin film was prepared by drop-casting polymer solution (10 μL, 10 mg/mL) onto the Pt-disk working electrode. The cyclic voltammogram was recorded using the polymer-coated working electrode and a reference electrode of Ag/Ag⁺ (0.1 M AgNO3 in acetonitrile) with a
platinum wire counter electrode at a scan rate of 100 mV/s. After the experiment was performed, ferrocene (5 mg) was added as an internal standard. The oxidation potential was calibrated against the Fc/Fc+, which is taken as 4.8 eV vs vacuum. Matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectra were recorded on an AB SCIEX 5800 using dithranol as the sample matrix. X-ray diffraction (XRD) was performed on PANalytical X’Pert PRO X-ray diffractometer using Cu Kα radiation (λ = 1.541 Å) operating at 40 kV and 40 mA.

**RESULTS AND DISCUSSION**

P3HS-b-P3BS DBCPs with various block ratios were synthesized by Grignard metathesis (GRIM) polymerization (Scheme 1). First, the monomer 2,5-dibromo-3-hexylselenophene was polymerized to yield the end-living P3HS homopolymers. Subsequently, the activated monomer 2,5-dibromo-3-butylselenophene was added to the end-living P3HS solution, forming P3HS-b-P3BS DBCPs. It is worth noting that P3HS block is needed to be polymerized first due to the poor solubility of the second P3BS block because of the shorter butyl side chains. The compositions of DBCP were determined by 1H NMR performed in 1,2-dichlorobenzene-d4 (ODCB) at 100 °C (Figure S1). The two peaks at 0.88 and 0.83 ppm are assigned to the resonances of terminal methyl groups in butyl and hexyl side chains, respectively. From the integration ratio of the two peaks, the actual molar ratios of the P3HS and P3BS blocks of two P3HS-b-P3BS DBCP samples can be determined to be 70:30 and 31:69 (denoted HS70BS30 and HS31BS69), respectively, which are close to the feed molar ratios of 2:1 and 1:2. Figure S2 shows the GPC profiles of these two DBCPs in 1,2,4-trichlorobenzene at 150 °C using polystyrene standards as calibration. The molecular weights and PDIs are 20900 g/mol and 1.64 for HS31BS69 and 21700 g/mol and 1.91 for HS70BS30 (Table S1). Notably, GPC tends to overestimate the molecular weights of polythiophenes or polyselenophenes by 20%−130% (scaling factor: 1.2−2.3) due to their rigid characteristics. To verify the molecular weight, matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) studies were conducted to determine the molecular weight of a P3BS homopolymer. In Figure S3, the P3BS sample with the molecular weight of 8700 g/mol determined by GPC showed the molecular weight between 3000 and 4000 g/mol measured by MALDI-TOF, indicating that GPC-derived molecular weights are a factor of ~2 times higher than that of MALDI-TOF.

It has been widely recognized that self-assembly of CPs in the marginal or mixed solvents enables the organization of CPs into intriguing nanostructures. Thus, we used toluene as the marginal solvent to tailor the crystallization-driven self-assembly of P3HS-b-P3BS DBCPs into nanostructures. When the introduced CdSe NPs are at low concentration, they predominantly attach to the nanostructures in an end-to-end mode. At high concentration of CdSe, these NPs are assembled in a coexisted side-by-side (majority) and layer-by-layer (minority) mode to the fibril axes.

![Figure 1](image-url). (a) Representative dark-field scanning TEM (DF-STEM) and (b) AFM image of HS31BS69 nanofibers yielded from the nanofiber toluene solution. (c) TEM image of HS31BS69−CdSe NR nanocomposites over a large area with the CdSe NRs concentration of 1 mg/mL. (d) Stepwise representation of the formation of HS31BS69−CdSe NR nanocomposites via two consecutive self-assembly processes. First, P3BS chains self-assemble into nanofibers via interchain π−π stacking in an edge-on orientation manner (first self-assembly), while P3HS chains situate in an amorphous state. Subsequently, the addition of CdSe NPs leads to the formation of HS31BS69−CdSe NR nanocomposites driven by the favorable affinity between aliphatic ligands on the surface of CdSe and the hexyl side chains of the P3HS block in HS31BS69 as well as the coordination interaction between the Se of P3HS and the surface of CdSe. When the introduced CdSe NPs are at low concentration, they predominantly attach to the nanostructures in a coexisted side-by-side (majority) and layer-by-layer (minority) mode to the fibril axes.
solvent for P3BS block. In a typical procedure, P3HS-b-P3BS was dissolved in toluene (1 mg/mL) by heating and cooling to room temperature to self-assemble into P3HS-b-P3BS nanofibers. It was found that the block ratios of P3HS to P3BS greatly influenced the copolymer morphology and crystalline structures in solution. For the HS70BS30 DBCP (P3HS:P3BS = 70:30), the short disordered and relatively unstructured nanofibers were observed in the TEM image due to weak π−π interaction as it contains long P3HS chains which dissolve well in toluene (Figure S4). While in the HS31BS69 system, compared with HS70BS30, much longer 1D nanofibers formed as a result of stronger π−π interaction due to the reduced solubility of HS31BS69 containing a large content of poorly soluble P3BS chains (Figure 1a). The selected area electron diffraction (SAED) pattern is shown as an inset in Figure 1a, where the diffraction ring can be assigned to the crystallographic (020) plane with a d_{020}-spacing of 4.3 Å. This suggests that the polyselenophene chains adopt an edge-on orientation with the direction of π−π stacking (i.e., the (010) direction; b-axis in Figure 1d) and the layers of alkyl side chains (i.e., the (100) direction; a-axis in Figure 1d) parallel and perpendicular to the substrate, respectively. The strong resemblance of nanofiber morphology measured by TEM (Figure 1a) and AFM (Figure 1b) signifies that the dry sample represents the case in the solution since the solvent evaporation during their sample preparation was fast, which did not influence the morphology of samples in the solution. The nanofibers are homogeneously distributed on the substrates (i.e., TEM grid), indicating they are uniformly, stably dispersed in the solution. The TEM image analysis shows that the HS31BS69 nanofibers have an average width of ~13 nm, approximately the contour length of the major P3BS block in the DBCP (see detailed calculations in the Supporting Information). The height of HS31BS69 nanofibers is ~8 nm as measured by AFM (Figure S5). On the basis of the results described above, it is plausible that the HS31BS69 nanofibers may be produced from the self-assembly (i.e., crystallization) of the major blocks (i.e., P3BS blocks), while the minor blocks (i.e., P3HS blocks) exist in the amorphous phase that renders the solubility in toluene.

To identify the crystalline structures in the DBCP nanofibers, 2D synchrotron grazing incidence X-ray diffraction (2D GIXRD) measurements on the P3HS, P3BS, and P3HS-b-P3BS thin films were performed (Figure 2). P3HS and P3BS homopolymers show a family of (h00) diffraction patterns along the out-of-plane (q_z) direction, which are characteristic of the edge-on orientation. The intense (100) diffractions of P3HS and P3BS homopolymers are at a scattering vector (q_z) of 3.95 and 6.32 nm⁻¹, corresponding to an interlayer spacing (d_{100}) of 15.9 and 9.9 Å, respectively. It has been reported that P3HS has two polymorphs, i.e., forms I and II with the d_{100} of 15.5 and 12.1 Å, respectively.35 P3BS also has similar form I and II polymorphs. As shown in Figure S6, the as-cast P3BS sample showed a single diffraction peak at 2θ = 9.39° measured by X-ray diffraction (XRD), corresponding to the (100) reflection of form II (d_{100} = 9.4 Å). After thermal annealing, the initial form II crystals change to form I with the diffraction peak at 2θ = 7.29° (d_{100} = 12.1 Å). Because of the interdigitation of side chains, the interlayer spacing in form II is shorter than that in form I. Thus, the 15.9 and 9.9 Å diffraction peaks can be assigned to the P3HS form I and the P3BS form II, respectively. For the DBCPs, HS70BS30 and HS31BS69 exhibit the (100) diffraction pattern at 4.10 and 6.38 nm⁻¹, respectively, which are close to the respective q_z of P3HS and P3BS homopolymers noted above and can thus be attributed to the crystallization of P3HS in HS70BS30 and P3BS in HS31BS69. This clearly indicates that the major blocks in P3HS-b-P3BS DBCPs dominate the crystallization while the crystallization of the minor blocks is greatly inhibited.36 As a result, 1D nanofibers of HS31BS69 are produced from the crystallization (i.e., self-assembly) of the major P3BS blocks while the covalently linked P3HS blocks remain amorphous, which is consistent with the TEM study and the contour length calculation discussed above.

As inorganic nanocrystals, CdSe NRs passivated with n-tetradecylphosphonic acid (TDPA) ligands were synthesized.32 TEM measurements revealed the synthesized TDPA-capped CdSe NRs are of high quality, possessing clear lattice fringes as evidenced by high-resolution TEM (HRTEM) imaging (Figure S7). These NRs are 21.3 ± 2.4 nm in length and 5.5 ± 1.2 nm in diameter. Self-assembly of TDPA-capped CdSe NRs and P3HS-b-P3BS BCPS to yield P3HS-b-P3BS−CdSe NR nanocomposites was accomplished by simply introducing TDPA-capped CdSe in toluene into the P3HS-b-P3BS nanofiber toluene solution and stirring overnight. Nanocomposites resulted from the self-assembly of HS70BS30 nanofibers and CdSe NRs were first investigated, where CdSe NRs randomly dispersed and intercalated into HS70BS30 nanofibers can be seen (Figure S8). In contrast, nanocomposites produced from the self-assembly of HS31BS69 nanofibers and CdSe NRs over a large area were observed (Figure 1c). There are very few, if any, isolated NRs, indicating that the CdSe NRs may have some specific interaction with the HS31BS69 nanofibers, which will be discussed later. Additionally, cryo-TEM of the P3HS-b-P3BS−CdSe NR nanocomposites in toluene solution was performed, revealing that hierarchically assembled P3HS-b-P3BS−CdSe NR nanocomposites, that is, self-assembled P3HS-b-P3BS nanofibers decorated by semiconducting CdSe NRs self-assembled on nanofibers, are formed in the original solution instead of during the solvent evaporation process (Figure 3). When comparing HS70BS30−CdSe NR (Figure S8) with HS31BS69−CdSe NR...
nanocomposites (Figures 1c), it is not surprising that HS70BS30 contains more amorphous portions than HS31BS69 as the former dissolves better in toluene and is less crystalline, thereby resulting in the mixing and intercalation of CdSe NRs into the amorphous domains of HS70BS30 more randomly. Thus, we center our study of 1D HS31BS69–CdSe NR nanocomposites in the following. Figure 1d depicts the stepwise crafting of 1D hierarchically assembled HS31BS69–CdSe NR nanocomposites, where the CdSe NR concentration-dependent placement and distribution will be discussed in the following.

The amount of CdSe NRs decorating on the HS31BS69 nanofibers can be readily controlled by varying the concentration of CdSe NRs (Figures 1d and 4). Furthermore, it is interesting to note that the CdSe concentration greatly influences their arrangement on nanofibers. At low CdSe NRs concentration (0.5 mg/mL), they predominantly attach to the HS31BS69 nanofibers with the long axes of NRs oriented parallel to the fibril axis, displaying a string-like end-to-end self-assembly (lower right panel in Figure 1d and Figure 4a–d). After analyzing nearly 400 NRs from TEM images, ~79% of CdSe NRs are parallelly oriented within 10° to the nanofiber axis (Figure 5a,b). Tomographic elemental mapping and line scan of nanocomposites revealed the presence of Se in both the nanofiber and NR regions, while Cd can only be detected in the NR region (Figure 4b,c), which agrees well with the elemental compositions of HS31BS69 and CdSe NRs. As the CdSe concentration increases to 1 mg/mL, the NRs are more tightly assembled in two modes, that is, a majority of side-by-side placement at a certain angle to the fibril axes (lower right panel in Figure 1d and Figure 4e–h) and a minority of layer-by-layer arrangement (i.e., multiple layers of NRs oriented parallel to the nanofiber axis; lower left panel in Figure 1d and Figure 5c,d). 3D tomography reconstruction was also performed to explore the assembly of nanocomposites (Figure 6). For the side-by-side orientation mode, the orientation angle, θ, between the NR and the fibril axes was found to vary over a large range, among which nearly 60% NRs are aligned at

![Figure 3. Cryo-TEM image of HS31BS69–CdSe NR nanocomposites, demonstrating that nanocomposites are formed from the initial toluene solution instead of during the solvent evaporation process. The concentration of CdSe NRs toluene solution is 0.5 mg/mL.](image1)

![Figure 4. Representative dark-field scanning TEM (DF-STEM) images of HS31BS69–CdSe NR nanocomposites produced at different concentrations of CdSe NRs. The concentrations of CdSe NRs are (a–d) 0.5 mg/mL and (e–h) 1.0 mg/mL, respectively. (b, f) Elemental mapping and (c, g) elemental line scans of HS31BS69–CdSe NR nanocomposites, corresponding to the TEM images shown in (a) and (e), respectively. (d, h) Close-ups of HS31BS69–CdSe NR nanocomposites, where the crystalline lattices of CdSe are clearly evident.](image2)
CdSe NRs are (a, b) 0.5 mg/mL and (c, d) 1.0 mg/mL in toluene.

Figure 6. 3D reconstruction of HS31BS69—CdSe nano-composites obtained by the TEM tomography. The concentration of CdSe is 1 mg/mL in toluene. The slices show the sections in the three directions in space.

θ = 50°–90° (Figure 5c,d). It is notable that further increase of the concentration of CdSe (2 mg/mL) did not obviously change the coexistence of side-by-side and layer-by-layer alignments of CdSe NRs (Figure S9).

Typically, inorganic NCs tend to aggregate intrinsically. In addition, they phase separate from most of polymer matrix within composites to reduce the interfacial area. Therefore, the association of CdSe NRs to the DBCP nano-fibers signifies certain specific interaction between them. Notably, the reports have shown that the main driving forces for the formation of hybrid structures of P3HT and nanocrystals (NCs) are assumed to be the attractive van der Waals interaction between the aliphatic chains on the surface of PbS and the hexyl side chains of P3HT or the coordination interaction between the sulfur atom of P3HT and the surface of CdS or CdSe. To better elucidate the interaction between the copolymer P3HS-b-P3BS and CdSe in our system, control experiments by capitalizing on Au-tipped CdSe NRs mixed with HS31BS69 nanofibers were performed. The Au-tipped CdSe NRs were synthesized according to the literature with the Au tip capped by dodecylamine (Figure S10a). Upon the addition of Au-tipped CdSe NRs, there is no distinct selectivity between Au tip and CdSe NR body attaching to the nanofibers (Figure S10b,c). The NRs can attach to the polymer nanofibers via either Au tip (i.e., capped by dodecylamine; without the cadmium (Cd) component) or CdSe body (i.e., capped by n-tetradecyolphosphonic acid). From the two nanocomposite systems (HS31BS69 loaded with CdSe NRs or Au-tipped CdSe NRs), it supports that van der Waals interaction between the aliphatic chains of CdSe and the hexyl side chains of the copolymer can drive the formation of such nanocomposites.

On the other hand, the coordination interaction between the Se atom of P3HS and the surface of CdSe nanocrystals may also contribute to the formation of such nanocomposites. To investigate the potential coordination interaction, X-ray photoelectron spectroscopy (XPS) spectra of HS31BS69, CdSe NRs, and their nanocomposites were studied (Figure S11). From the XPS analysis, the constituting elements in HS31BS69 and HS31BS69—CdSe nanocomposites are clearly identified (Figure S11a,b). The Se (3d) XPS spectra were decomposed with a Voigt curve fitting function within a Shirley background. For the CdSe NRs, the decomposition ensured a perfect fit for two peaks at 53.86 and 54.87 eV, corresponding to the Se (3d_{5/2}) and Se (3d_{3/2}) core levels of Se^{2-} anions, respectively, of the CdSe crystal (Figure S11c). HS31BS69 exhibited two peaks at 55.88 and 56.81 eV (Figure S11d). Compared to the respective constituents, two new peaks at 54.85 and 55.84 eV were observed in the HS31BS69—CdSe nanocomposites, which reveals a new intermediate bonding energy and can be assigned to the C—Se—Cd bond connecting the copolymer and CdSe NRs (Figure S11e). This observation supports the formation of close contact between the copolymer and CdSe due to the coordination interaction between the Se atom of polyselenophene and the surface of CdSe NRs. Therefore, the driving forces to yield P3HS-b-P3BS—CdSe nanocomposites in our system are likely two interactions, that is, attractive van der Waals interactions between the aliphatic chains of CdSe and the hexyl side chain of P3HS and the coordination interaction between the Se of P3HS and the surface of CdSe.

It is well-known that for a polymer/NR mixture the distribution of NRs depends on a complex interplay among the enthalpy change originating from the ligand on the NR surface and the polymer interaction (ΔH_{ligand—polymer}), the enthalpy change resulting from the NR—NR interaction (ΔH_{rod—rod}), the entropy change owing to the polymer chain deformation upon the incorporation of NRs (ΔS_{polymer}), and the entropy change due to the assembly of NRs (ΔS_{rod}). The overall change of Gibbs free energy can be described as follows:

\[ ΔG = ΔH_{ligand—polymer} + ΔH_{rod—rod} = T(ΔS_{polymer} + ΔS_{rod}) \]

When CdSe NRs are associated with P3HS-b-P3BS DBCPs, the amorphous or less crystalline regions of DBCPs are more energetically favorable to localize NRs than the crystalline
concentrations was carried out. The diagram of two-dimensional Monte Carlo (MC) simulation with a series of NR nanocomposites, two-dimensional lattice assembly of conjugated DBCPs and CdSe NRs into one-dimensional simple lattice mode used in the simulation is shown in Figure S12. It is interesting to note that the MC simulation results with the increased NR concentration (Figure 7d–f) agree very well the experimental observations (Figure 7a–c). The concentrations of CdSe NRs in the MC simulation are \( c_{\text{MC}} = 0.023 \) (Figure 7d), 0.067 (Figure 7e), and 0.111 (Figure 7f), and the simulation results at these three concentrations qualitatively reproduce the morphologies of nanocomposites observed by TEM at \( c = 0.5 \) mg/mL (Figure 7a), 1 mg/mL (Figure 7b), and 2 mg/mL (Figure 7c), respectively. At \( c_{\text{MC}} = 0.023 \), almost all NRs are attached to the DBCP nanofiber in a string-like end-to-end mode. At \( c_{\text{MC}} = 0.067 \), both side-by-side and layer-by-layer arrays of NRs are emerged. Intriguingly, at \( c_{\text{MC}} = 0.111 \), the population of side-by-side arrangement of NRs increases. We note that in the MC simulation the orientation angles, \( \theta \), between the NR and the fibril axis are set to be \( \theta = 0^\circ \) in the end-to-end and layer-by-layer modes and \( \theta = 45^\circ \) and \( 90^\circ \) in the side-by-side mode. This is because the movement of NRs is restricted by the lattice mode. We only count the range of three beads (i.e., the length of one NR) around the two sides of nanofiber in the two-dimensional MC lattice to determine the fraction of the NR self-assembly modes (see the Experimental Section). Figure 7g shows the fraction of end-to-end and layer-by-layer arrays gradually decreases from 97% at \( c_{\text{MC}} = 0.023 \) to 50% at \( c_{\text{MC}} = 0.067 \), and from 3% at \( c_{\text{MC}} = 0.023 \) to 50% at \( c_{\text{MC}} = 0.105 \) and remains relatively steady (~54%) after \( c_{\text{MC}} \) exceeds 0.133. The simulation results also indicate the self-assembly of nano-

In contrast, at high concentrations (\( c = 1 \) or 2 mg/mL) of CdSe NRs, an increased number of NRs prefer to assemble in a majority of side-by-side mode coexisting with some layer-by-layer arrays (lower left and central panels in Figure 1d). Clearly, upon the addition of more CdSe NRs, an increasing number of NRs adopt a side-by-side assembly as it is more energetically favorable due to more contact area between the NRs and the nano-fiber (i.e., both \( \Delta H_{\text{ligand-polymer}} \) and \( \Delta H_{\text{rod-rod}} \) are minimized) compared to the end-to-end assembly. The coexistence of side-by-side and layer-by-layer assemblies can be ascribed to the fact that both the energy reduction from the ligand–polymer interaction (i.e., \( \Delta H_{\text{ligand-polymer}} \)) and the NR–NR interaction (i.e., \( \Delta H_{\text{rod-rod}} \)) are the same in these two kinds of arrangements of CdSe NRs. This is because almost all the contact areas of the DBCP nano-fiber surface is occupied by CdSe NRs at high NR concentrations, and the contact areas between NRs in these two arrangements remain the same. Therefore, both side-by-side and layer-by-layer CdSe NRs are energetically favored at high concentration of CdSe NRs. Instead of some dominated angles, the diversity of the orientation angle, \( \theta \), between the NR and the fibril axes (Figure 5d and Figure S9) suggests a delicate balance of various energetic contributions in the P3HS-6-P3BS–CdSe nanocomposites.

To better understand the mechanism of hierarchical self-assembly of conjugated DBCPs and CdSe NRs into one-dimensional hybrid nanocomposites, two-dimensional lattice Monte Carlo (MC) simulation with a series of NR concentrations was carried out. The diagram of two-dimensional simple lattice mode used in the simulation is shown in Figure S12. It is interesting to note that the MC simulation results with the increased NR concentration (Figure 7d–f) agree very well the experimental observations (Figure 7a–c). The concentrations of CdSe NRs in the MC simulation are \( c_{\text{MC}} = 0.023 \) (Figure 7d), 0.067 (Figure 7e), and 0.111 (Figure 7f), and the simulation results at these three concentrations qualitatively reproduce the morphologies of nanocomposites observed by TEM at \( c = 0.5 \) mg/mL (Figure 7a), 1 mg/mL (Figure 7b), and 2 mg/mL (Figure 7c), respectively. At \( c_{\text{MC}} = 0.023 \), almost all NRs are attached to the DBCP nanofiber in a string-like end-to-end mode. At \( c_{\text{MC}} = 0.067 \), both side-by-side and layer-by-layer arrays of NRs are emerged. Intriguingly, at \( c_{\text{MC}} = 0.111 \), the population of side-by-side arrangement of NRs increases. We note that in the MC simulation the orientation angles, \( \theta \), between the NR and the fibril axis are set to be \( \theta = 0^\circ \) in the end-to-end and layer-by-layer modes and \( \theta = 45^\circ \) and \( 90^\circ \) in the side-by-side mode. This is because the movement of NRs is restricted by the lattice mode. We only count the range of three beads (i.e., the length of one NR) around the two sides of nanofiber in the two-dimensional MC lattice to determine the fraction of the NR self-assembly modes (see the Experimental Section). Figure 7g shows the fraction of end-to-end and layer-by-layer arrays gradually decreases from 97% at \( c_{\text{MC}} = 0.023 \) to 50% at \( c_{\text{MC}} = 0.067 \), and from 3% at \( c_{\text{MC}} = 0.023 \) to 50% at \( c_{\text{MC}} = 0.105 \) and remains relatively steady (~54%) after \( c_{\text{MC}} \) exceeds 0.133. The simulation results also indicate the self-assembly of nano-
composites ceases to evolve with a further introduction of NRs once the fraction of the side-by-side self-assembly reaches 54%, signifying the structure may reach a stable state. It is noteworthy that the key to successfully crafting 1D HS31BS69–CdSe NR nanocomposites is the use of self-assembled DBCP nanoﬁbers formed via strong interchain π–π stacking of the HS31BS69 chains (i.e., first self-assembly). For comparison, instead of adding CdSe NRs into the preformed nanofiber solution to yield nanocomposites (i.e., formed by two consecutive self-assembly processes, that is, a two-step self-assembly) as noted above, when CdSe NRs are introduced during the solvent-driven nanofiber formation process (i.e., one-step self-assembly), the resulting nanocomposites show CdSe NRs randomly decorating the nanofibers without any predominant arrangement (Figure S13).

To explore optoelectronic properties of the resulting nanocomposites, UV–vis and photoluminescence (PL) measurements were first performed (Figure 8). For the simply blended composite of HS31BS69/CdSe NRs, indicating more intimate contact between the donor and acceptor species in the former system. The charge transfer dynamics in nanocomposites was supported by the subsequent time-resolved PL measurements (Figure 8c), revealing a fluorescence lifetimes of 17.01 ns for HS31BS69–CdSe NR nanocomposites and 27.09 ns for CdSe NRs. The shorter lifetime of nanocomposites compared to that of CdSe NRs suggests an improved interfacial contact between HS31BS69 and CdSe NR, thereby facilitating the exciton dissociation and thus a rapid charge transfer between CdSe NRs and HS31BS69. This result correlates well with the static PL study (Figure 8b), in which charge transfer results in the quenched PL of nanocomposites due to the dissociation of photogenerated exciton.

In general, the lower electronegativity of Se than S atom greatly decreases the lowest unoccupied molecular orbital (LUMO) level, leading to a narrower bandgap of the Se-based CPs. To better understand the electronic properties of P3HS-b-P3BS DBCPs, their highest occupied molecular orbital (HOMO) and LUMO energy levels were investigated by cyclic voltammetry (CV) (Figure 9) and optical bandgap measurements. The results are summarized in Table S2 and Figure 8d where the energy level of CdSe is also included. The HOMO levels of CP films can be estimated by the equation $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ eV, where $E_{\text{ox}}$ is the onset oxidation potential relative to the ferrocene standard material. HS70BS30 and HS31BS69 show the HOMO levels of 5.21 and 5.17 eV, respectively, which are positioned between the HOMO levels of P3HS (5.39 eV) and P3BS (5.08 eV) and well above the valence band of CdSe (6.10 eV). We note that all the HOMO levels are lower than that of P3HT (4.9 eV), suggesting the higher stability of P3HS-b-P3BS DBCPs against air oxidation. The LUMO levels are calculated by estimating the optical bandgaps derived from the absorption onset, yielding the LUMO levels of P3HS, HS70BS30, HS31BS69, and P3BS of 3.78, 3.57, 3.50, and 3.40 eV, respectively. It is notable that as the P3BS content increases, both the HOMO and LUMO levels are raised; however, the degree of the LUMO level rising is relatively larger, resulting in slightly increased bandgap.

Figure 8. (a) UV–vis absorption, (b) photoluminescence (PL), and (c) normalized time-resolved PL decays of HS31BS69, CdSe NRs, and HS31BS69–CdSe NR nanocomposites at different CdSe NR concentrations. The concentrations of CdSe NRs are 0.5 and 1.0 mg/mL in HS31BS69–CdSe (1:0.5) and (1:1) nanocomposites, respectively. In (b), a simply blended composite of HS31BS69/CdSe was also included for comparison. The fittings in (c) yield the average lifetimes of 27.09 ns for CdSe NRs and 17.01 ns for nanocomposites. (d) Schematic illustration of the energy levels of both HS31BS69 and HS31BS69–CdSe NR nanocomposites. The shorter lifetime of nanocomposites compared to that of CdSe NRs suggests an improved interfacial contact between HS31BS69 and CdSe NR, thereby facilitating the exciton dissociation and thus a rapid charge transfer between CdSe NRs and HS31BS69. This result correlates well with the static PL study (Figure 8b), in which charge transfer results in the quenched PL of nanocomposites due to the dissociation of photogenerated exciton.

In general, the lower electronegativity of Se than S atom greatly decreases the lowest unoccupied molecular orbital (LUMO) level, leading to a narrower bandgap of the Se-based CPs. To better understand the electronic properties of P3HS-b-P3BS DBCPs, their highest occupied molecular orbital (HOMO) and LUMO energy levels were investigated by cyclic voltammetry (CV) (Figure 9) and optical bandgap measurements. The results are summarized in Table S2 and Figure 8d where the energy level of CdSe is also included. The HOMO levels of CP films can be estimated by the equation $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ eV, where $E_{\text{ox}}$ is the onset oxidation potential relative to the ferrocene standard material. HS70BS30 and HS31BS69 show the HOMO levels of 5.21 and 5.17 eV, respectively, which are positioned between the HOMO levels of P3HS (5.39 eV) and P3BS (5.08 eV) and well above the valence band of CdSe (6.10 eV). We note that all the HOMO levels are lower than that of P3HT (4.9 eV), suggesting the higher stability of P3HS-b-P3BS DBCPs against air oxidation. The LUMO levels are calculated by estimating the optical bandgaps derived from the absorption onset, yielding the LUMO levels of P3HS, HS70BS30, HS31BS69, and P3BS of 3.78, 3.57, 3.50, and 3.40 eV, respectively. It is notable that as the P3BS content increases, both the HOMO and LUMO levels are raised; however, the degree of the LUMO level rising is relatively larger, resulting in slightly increased bandgap. Clearly, the higher HOMO and LUMO levels of DBCPs than
the valence (6.10 eV) and conduction bands (4.30 eV) of CdSe NRs, respectively, suggests an energetically favorable exciton dissociation and charge transfer at the P3HS-b-P3BS/CdSe interfaces (i.e., charge transfer between P3HS-b-P3BS and CdSe NRs).

**CONCLUSION**

In summary, we have developed a facile bottom-up, consecutive self-assembly strategy for crafting 1D semiconducting hybrid organic–inorganic nanocomposites composed of P3HS-b-P3BS DBCPs and CdSe NRs. First, P3HS-b-P3BS DBCPs are self-assembled into nanofibers. Subsequently, depending on the CdSe NR concentration, they self-assemble in either a string-like end-to-end fashion or side-by-side coexisted with layer-by-layer fashion along the long axis of P3HS-b-P3BS nanofibers, as revealed by a combined MC simulation and experimental study. The quenching of CdSe PL in nanocomposites is seen, which can be ascribed to charge transfer between CdSe NRs and P3HS-b-P3BS DBCPs. The strategy for hierarchical self-assembly of conjugated poly-selenophene-based DBCPs and semiconducting NRs into 1D hybrid nanocomposites demonstrated in this study is simple and effective. It can be readily extended to produce hierarchical nanocomposites comprising preassembled conjugated polymers decorated by other functional NRs with unique sensing, optical, electronic, and optoelectronic properties.

**ASSOCIATED CONTENT**

1. Supporting Information
   The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01744.
   
   Detail characterization of P3HS-b-P3BS, MALDI-TOF mass spectra of P3BS, AFM image of HS31BS69 nanofibers, XRD patterns of P3BS films, TEM images of HS70BS30 in toluene, HS70BS30–CdSe NR nanocomposites, CdSe NRs, Au-tipped CdSe NRs and HS31BS69–Au-tipped CdSe NR nanocomposites, XPS spectrum, diagram of two-dimensional simple square lattice mode used in the Monte Carlo (MC) simulation (PDF)

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Notes
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