

Tuning the Optoelectronic Features of Poly(3-hexylthiophene-2,5-diyl) with Oligoplatinaynes-Functionalized Gold Nanoparticles

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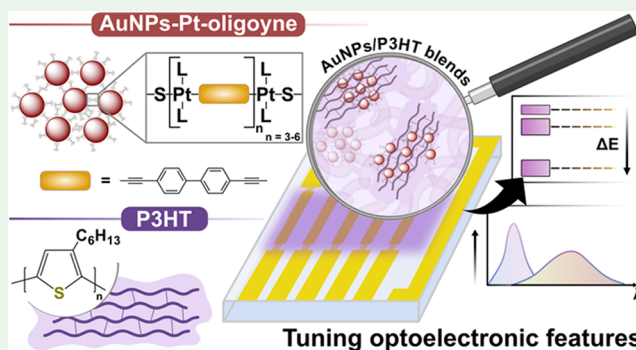
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ABSTRACT: Hydrophobic gold nanoparticles (AuNPs) covalently functionalized with organometallic platinum-containing oligomers (Pt–DEBP_n, DEBP = 4,4'-diethynylbiphenyl) with different chain lengths were synthesized and incorporated into a poly(3-hexylthiophene-2,5-diyl) (P3HT) matrix to obtain inorganic/organic AuNPs/P3HT blends with tuned optoelectronic properties. The Pt–DEBP_n ($n = 3, 4, 6$) chain length was modulated by carefully controlling reaction conditions in a catalyst-free polycondensation reaction and monitored using UV–visible spectroscopy. Spherical AuNPs with a (3.3 ± 1.1) nm diameter from solid-state microscopies and narrow size distributions, evaluated in colloidal suspension by dynamic light scattering (DLS), were obtained by a two-phase wet chemical reduction in the presence of thiolate organometallic ligands. Structural analyses by FTIR and SR-XPS confirmed the functionalization via Au–S bonds. Platinum-containing ligand introduced additional emissive pathways, including long-wavelength emission, attributed to increased rigidity and reduced nonradiative decay in AuNPs. AuNPs/P3HT blends were obtained with different compositions (from 10 to 90 wt % AuNPs content) by a simple room-temperature mixing approach in organic solvents and spin-coated onto an interdigitated ITO substrate. Homogeneous films with a mean thickness of about 3 nm were revealed by atomic force microscopy (AFM). Electrical I/V measurements (range ± 10 V) carried out on AuNPs/P3HT blends demonstrated a composition-dependent response. The blend containing 10 wt % AuNPs showed a ~ 30 -fold increase in the relative electrical response compared to pristine P3HT and a reduced optical band gap ($2.13 \rightarrow 2.06$ eV). Photoluminescence studies revealed red-shifted and broadened P3HT emission with increasing AuNP content, highlighting strong AuNP plasmon–polymer interactions. Further grazing-incidence wide-angle X-ray scattering (GIWAXS) and nanofocused X-ray scattering measurements (nano-GIWAXS) revealed composition-dependent structural and thermal stability. It is noteworthy that low AuNPs wt % promoted a more effective interconnectivity with P3HT chains, responsible for enhanced electronic coupling in blends compared with pristine counterparts. Results showed that this nanoscale arrangement offers tunable properties for optoelectronic applications.

KEYWORDS: gold nanoparticles (AuNPs), organometallic ligands, oligoplatinaynes, poly(3-hexylthiophene-2,5-diyl) (P3HT), polymer blends, nanocomposites, electrical response, thermal behavior



1. INTRODUCTION

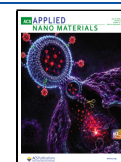
The applicative need for flexible functional materials has boosted interest in inorganic/organic blends, in which metal nanoparticles are mixed with different polymer matrices. In this context, gold nanoparticle–polymer nanostructures are promising as passive or active layers in optoelectronic devices.^{1,2} Their great structural stability³ and optical properties, originating from the localized surface plasmon resonance (LSPR) in the visible range (500–600 nm), offer new perspectives in advanced applications.^{4,5} The LSPR shows great sensitivity to the chemical surroundings, with variation in

optical response of a single particle compared with the assembled or interconnected counterpart,⁶ and it is easily tunable according to the AuNP size, shape, and surface functionalization.⁷ AuNPs-based inorganic/organic blends

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allow for enhancing preexisting properties, providing novel multifunctional features through a synergistic combination of the components. Indeed, polymer blends with nanoscale fillers yield significant properties at much lower loadings compared to undoped polymer composites.^{8,9} It has been shown that the electronic and optical properties of conjugated polymers can be enhanced by tailoring the stacking and ordering in the form of thin films, which increases the power conversion efficiency (PCE), electrical conductivity, and photoluminescence.^{10,11} Owing to its thermal stability, low cost, environmental friendliness, and easy solution processability, poly(3-hexylthiophene-2,5-diyl) (P3HT) has been identified as one of the most promising semiconducting p-type polymers in organic thin-film transistors (OTFTs)¹² and organic solar cells.¹³ The charge carrier mobility of P3HT is crucial to obtain good electrical performance with reasonable light absorption.¹⁴ It strongly depends on P3HT crystallinity and structural order, which in turn is heavily influenced by the regioregularity and the interchain interactions between crystalline and amorphous regions of the polymer (especially near the film–substrate interface).

Pristine P3HT possesses a high HOMO energy level (estimated to be in the range of 5.1–5.2 eV)¹⁵ and a wide energy band gap (2.1 eV),¹⁵ which limits the absorption of red and infrared wavelengths (the most intense parts of solar radiation).¹³ The light absorption of P3HT is also impeded by its low charge carrier mobility (generally less than 10^{-4} – 10^{-1} cm²/(V s))¹⁶ that restricts the acceptable thickness of the organic active layer to <100 nm.¹³ Another drawback that limits P3HT technological applications is due to polymer photodegradation by the simultaneous action of incident light, oxygen, and humidity.¹⁷ To enhance polymer charge transport properties and device performance, the development of functional hybrid materials using a blending strategy with the dispersion of metal NPs into the P3HT matrix was studied.¹⁸ It was assessed that the incorporation of AuNPs into the P3HT films can minimize photodegradation,¹⁹ enhance light absorption,²⁰ and enhance solar cell efficiency,²¹ also improving the structural stability of the conducting polymer. Notably, it has been observed that AuNPs often tend to separate out from the polymer to minimize the free energy of the system,¹⁸ depending on the dispersion, affinity, and in turn, on the AuNPs surface chemistry, i.e., the type of functionalizing/stabilizing agent, which is used to prevent irreversible aggregation of colloidal AuNPs.²¹

In this framework, interest in bifunctional thiol ligands (containing two sulfur-end groups) as AuNPs capping agents has increased, since they allow (i) the covalent functionalization of gold nanostructures via Au–S bonds, and (ii) the formation of interconnected AuNPs with fixed interparticle distances, tuning both physicochemical and electronic properties, compared with single thiol ligands.²² AuNPs functionalized with bifunctional organic ligands were already used as fillers in a regioregular P3HT matrix with a strong improvement of the electrical conductivity.^{23,24} Among others, organoplatinum rigid-rod conjugated polyynes show peculiar electronic and optical properties^{25,26} due to the presence of direct platinum–carbon σ -bonds in the main chain, which allows the delocalization of the π -system from the organic moiety through the Pt orbitals.^{27,28} The addition of thiolate ending groups (–SH or –SCOCH₃) makes oligoplatinaynes suitable as ligands in the design of AuNPs.²⁹ Compared with conventional thiol ligands or purely organic π -conjugated

ligands, the incorporation of Pt heteroatoms within a π -conjugated system in a square-planar Pt(II) in *trans* configuration enables (i) metal-to-ligand or ligand-to-metal charge transfer (MLCT or LMCT) phenomena, (ii) long-lived excited-state lifetimes (in the ns to ms regime), and (iii) tuned photophysical properties, as a consequence of strong spin–orbit coupling (SOC) and strong π -back bonding between the organic chain and the metal center, thus behaving as an active interface.^{30,31} Fine-tuning of their functional properties can be achieved using different auxiliary coligands or bridging spacer groups.^{27,32,33}

Starting from these results, we report here a detailed study on the synthesis and characterization of AuNPs stabilized with the synthetic dithioacetate organometallic ligands *trans,trans*-[CH₃CO–S–(Pt(PBu₃)₂)–(C $\equiv$ C–C₆H₄–C₆H₄–C $\equiv$ C–)]_nPt(PBu₃)₂–S–COCH₃] (with $n = 3, 4, 6$, i.e., L3, L4, and L6, respectively) and their related blends with regioregular P3HT polymer (from 10 to 90 wt % AuNPs content). L3, L4, and L6 oligomers having dithioacetate ending moieties were employed as capping agents during AuNPs synthesis.

Compared to a previous study on AuNPs/P3HT composites functionalized with purely organic π -conjugated ligand,²³ the integration of Pt(II) centers within the spacer backbone opens perspectives in the modulation of the interparticle distance via the variable oligoplatinaynes chain lengths and enabled charge transfer (MLCT, LMCT) processes, enhancing the electronic coupling between the NPs and the polymer matrix. The chain length dependence of the optical, morphological, and structural properties of the AuNPs was investigated in suspension and on dry thin films. Complementary techniques, namely, spectroscopic UV–visible extinction and photoluminescence, Fourier transform infrared (FT-IR) absorption, dynamic light scattering (DLS), ¹H- and ³¹P-NMR, synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS), and microscopic (atomic force microscopy (AFM), high-resolution transmission electron microscopy (HR-TEM), and field emission scanning electron microscopy (FESEM)) techniques were used for a comprehensive characterization of gold colloids and AuNPs/P3HT blends. Advanced structural studies on pristine AuNPs and the blends before and after annealing were carried out by grazing-incidence wide-angle X-ray scattering (GI-WAXS). The influence of different chain lengths on the electrical response of nanocomposite blends was also examined.

2. EXPERIMENTAL SECTION

2.1. Materials

Reagents were purchased from Merck and used without further purification: potassium tetrachloroplatinate(II) (K₂PtCl₄ 99.99%, M.W. 415.09 g/mol), tri-*n*-butylphosphine (PBu₃, C₁₂H₂₇P 99%, M.W. 202.32 g/mol), potassium thioacetate (CH₃CO₂K 98.0%, M.W. 114.21 g/mol), tetrachloroauric acid(III) trihydrate (HAuCl₄·3H₂O 99.0%, M.W. 393.83 g/mol), sodium borohydride (NaBH₄ ≥ 96%, M.W. 37.83 g/mol), tetraoctylammonium bromide (TOAB, [CH₃(CH₂)₇]₄N(Br) 98%, M.W. 546.79 g/mol), 4,4′-Diethynylbiphenyl (H–C $\equiv$ C–C₆H₄–C₆H₄–C $\equiv$ C–H, DEBP, M.W. 202.26 g/mol) was prepared as previously reported.³⁴ Poly(3-hexylthiophene-2,5-diyl) (P3HT, M.W. 60,000 g/mol, PDI 2.1, and the regioregularity higher than 96.8%) was purchased from Rieke RMI-001EE.

Anhydrous solvents were purchased from Merck: toluene (C₇H₈), absolute ethanol (EtOH, C₂H₆O), dichloromethane (DCM, CH₂Cl₂), chloroform (CHCl₃), tetrahydrofuran (THF, C₄H₈O), diethylamine ((CH₃CH₂)₂NH), petroleum ether 40–60, chloroform-*d* (CDCl₃).

All solvents were stored over activated molecular sieves (3 Å, 4–8 mesh) prior to use to ensure anhydrous conditions. Ultrapure water ($\text{H}_2\text{O}_{\text{up}}$) with conductivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ (Zener Power Scholar-UV, Full-Tech instruments) was used in the preparation of all aqueous solutions. Thin-layer chromatography (TLC) separation was performed with silica gel on TLC-PET foils with fluorescent indicator 254 nm (Merck Sigma-Aldrich). For thin-film deposition, an Electron mec PRS 5 V Spinner (Electron mec, Milan, Italy) was used (speed 600 rpm, 1 min).

2.2. Characterization Techniques

2.2.1. UV–Visible Extinction Spectroscopy (UV–Vis). All UV–vis extinction spectra were measured on a Varian Cary 100 spectrophotometer equipped with a 1 cm path length quartz cuvette. Each sample was scanned between the wavelengths 200–900 nm, using CH_2Cl_2 or CHCl_3 as a solvent. Resolution: 1 nm.

2.2.2. Photoluminescence Spectroscopy (PL). Steady-state emission spectra were recorded on a PerkinElmer LS50 luminescence spectrometer using a quartz cuvette with a 1 mm optical path for excitation. The monochromator slit resolution was set at 5 or 15 nm for both excitation and emission, and a 25 nm/min scan speed was used to acquire the spectra. The excitation wavelength was set according to the UV–vis absorption maxima for each sample in CH_2Cl_2 (for AuNPs) or CHCl_3 (for nanocomposites) as solvents.

2.2.3. Fourier Transform Infrared Spectroscopy (FT-IR). Fourier transform infrared (FT-IR) and far-infrared (Far-IR) spectroscopy analyses were carried out with a Bruker Vertex 70 spectrophotometer. Spectra in the 4000 to 400 cm^{-1} wavenumber range were acquired in transmittance mode on samples deposited by drop-casting from CH_2Cl_2 or CHCl_3 onto KRS-5 (TlBr-TlI) cells. Far-IR analyses were performed on drop-casted iPr–OH films or from oily suspensions onto a polyethylene disk (transparency range from 500 to $>100\text{ cm}^{-1}$)³⁵ under dry N_2 flux. The resolution was set at 4 cm^{-1} with a minimum of 32 scans.

2.2.4. Nuclear Magnetic Resonance (NMR). ^1H NMR and ^{31}P NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400.13 MHz for the proton in CDCl_3 (reference ^1H NMR CDCl_3 : 7.26 ppm), and the chemical shift values were given in parts per million (δ , ppm) and coupling constants (J) in Hz. ^1H NMR spectra were acquired at 295 K with 64 k data points, a spectral width of 15 ppm, 32 scans, and a relaxation delay of 6.55 s in order to achieve full relaxation for all resonances. Proton-decoupled ^{31}P NMR spectra were acquired at 295 K with 64 k data points, a spectral width of 120 ppm, 16 scans, and a relaxation delay of 2.00 s.

2.2.5. Dynamic Light Scattering (DLS). DLS measurements were carried out using a glass cuvette and CHCl_3 as solvent on a Zetasizer Nano ZS90 instrument (Malvern Instruments) with a 10 mW 633 nm He/Ne laser source in backscattering mode (detection angle = 173°). All measurements were performed in triplicate at room temperature, and the results were expressed as the mean value $\pm$ standard deviation of the data.

2.2.6. Synchrotron Radiation X-ray Photoelectron Spectroscopy Experiments (SR-XPS). SR-XPS experiments were performed on cast-deposited films on titania substrates at the BACH (Beamline for Advanced DiChroism) line of IOM-CNR at the Elettra synchrotron facility in Trieste (Italy).³⁶ XPS data were collected in fixed analyzer angular mode (pass energy = 50 eV) with a Scienta R3000 hemispherical analyzer at an angle of 60° with respect to the X-ray incidence direction. The spectra were recorded in a normal emission geometry, with the light linearly polarized in the horizontal plane. The monochromator entrance and exit slits were optimized at 30 and 20 μm , respectively, and a photon energy of 360 eV was used for the C 1s, Au 4f, S 2p, Pt 4f, and P 2p spectral regions with an overall energy resolution $\text{NE} = 0.22\text{ eV}$. Calibration of the energy scale was made referencing the spectra to the C 1s core level signal of aliphatic/aromatic C atoms, found at 285.00 eV, for all samples. Curve-fitting analysis of the C 1s, Au 4f, S 2p, Pt 4f, and P 2p spectra was done with Gaussian curves as fitting functions. The S $2p_{3/2,1/2}$ and the P $2p_{3/2,1/2}$ doublets were fitted using the same full width at half-maximum (fwhm) for both components, a spin–orbit

splitting of 1.2 and 0.9 eV, respectively, and a branching ratio ($2p_{3/2}/2p_{1/2}$) of 2. For the Au $4f_{7/2,5/2}$ and the Pt $4f_{7/2,5/2}$ doublets, a splitting of 3.6 and 3.3 eV, respectively, a branch ratio $4f_{7/2}/4f_{5/2}$ of 4/3, and the same fwhm values for both spin–orbit components were used. When different species were identified in a spectrum, the same fwhm value was set for all individual photoemission bands.

2.2.7. Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) and Nanofocused X-ray Scattering Measurements (nano-GIWAXS). Structural studies of the pure AuNPs and the blends were carried out using GIWAXS at beamline BL9 of the DELTA synchrotron radiation facility in Dortmund, Germany. The films were measured at a shallow incident angle of $\alpha_i = 0.007^\circ$. The X-ray energy used in this experiment was 13 keV, corresponding to a wavelength of 0.95 Å. This beamline is dedicated to small-angle X-ray scattering and GIXD experiments, using an image plate 2D detector (MAR345, 3450×3450 pixels, 100 μm per pixel resolution). The angular scale was calibrated by measuring the diffraction pattern of silver behenate. *In situ* annealing studies were conducted using a Linkam HFSX350 heating stage. The samples were measured at room temperature. All diffraction patterns were collected under the same GIWAXS conditions, with the samples being exposed for 300 s.

Synchrotron-based nanofocused X-ray measurements were performed at the Nanofocus Endstation of the P03 beamline at the PETRA III synchrotron (DESY, Hamburg, Germany).³⁷ A monochromatic X-ray beam with a photon energy of 19.8 keV was focused to a spot size of approximately $310 \times 340\text{ nm}^2$ (horizontal $\times$ vertical) using Kirkpatrick–Baez (KB) mirrors. The samples were investigated in a nano-GIWAXS geometry, enabling high lateral spatial resolution while scanning the sample relative to the focused beam. Measurements were carried out at an incidence angle of $\alpha_i = 0.04^\circ$. The scattered intensity was collected using a two-dimensional large-area Eiger 9 M detector with a pixel size of $75 \times 75\text{ }\mu\text{m}^2$, positioned at a sample-to-detector distance of 192 mm. Sample prealignment was achieved using an optical microscope. Samples were measured after annealing at 100°C , keeping them for 5 min at each temperature. The acquired data were processed, analyzed, and visualized using the PyFAI software package in combination with custom-developed MATLAB scripts.

2.2.8. Field Emission Scanning Electron Microscopy (FESEM-EDX). Field emission scanning electron microscopy (FESEM) images were recorded with an FESEM Auriga Zeiss model (Carl Zeiss) equipped with an energy dispersive X-ray (EDX) detector. Resolution: 1 nm and 6–20 kV applied voltage. Samples were deposited by drop-casting onto a silicon substrate and air-dried before being observed.

2.2.9. Atomic Force Microscopy (AFM). AFM analyses were carried out with an AFM Multimode model (Veeco Instruments) equipped with a Nanoscope IIIa controller and RTESP-300 probe (Bruker) (nominal parameters $r = 8\text{ nm}$, $f = 300\text{ kHz}$, $k = 40\text{ N m}^{-1}$) with a 512×512 pixels resolution. Postcapture correction by polynomial background filters and analysis were performed using the software Gwyddion 2.56. Prior to measurement, the Si/SiO₂ substrate was washed twice with acetone and chloroform to remove any traces of pollutants. For the sample preparation, AuNPs colloids and AuNPs/P3HT blends were spin-coated (speed 600 rpm, 1 min) onto the Si/SiO₂ substrate from their chloroform or dichloromethane suspension.

2.2.10. High-Resolution Transmission Electron Microscopy (HR-TEM). HRTEM imaging of AuNPs dispersed by drop-casting onto carbon films (thickness: 28–30 nm) on TEM copper grids was performed using an aberration-corrected FEI Titan 80–300 microscope operating at 300 keV. The spherical aberration coefficient C_s was adjusted to a slightly negative value of $-0.8\text{ }\mu\text{m}$ to minimize spatial delocalization and enable precise particle size measurements.

2.2.11. Electrical Characterization. The electrical characterization was carried out on a Keithley 595 quasi-static CV meter in the 0–20 V range equipped with an Ossila Low Density OFET Test Board, at room temperature and constant relative humidity ($\pm 20\text{ V}$ voltage range, V step 0.5 V). 100 μL of samples were deposited by spin-coating (Electron MEC PRS 5 V Spinner. Parameters: speed 600

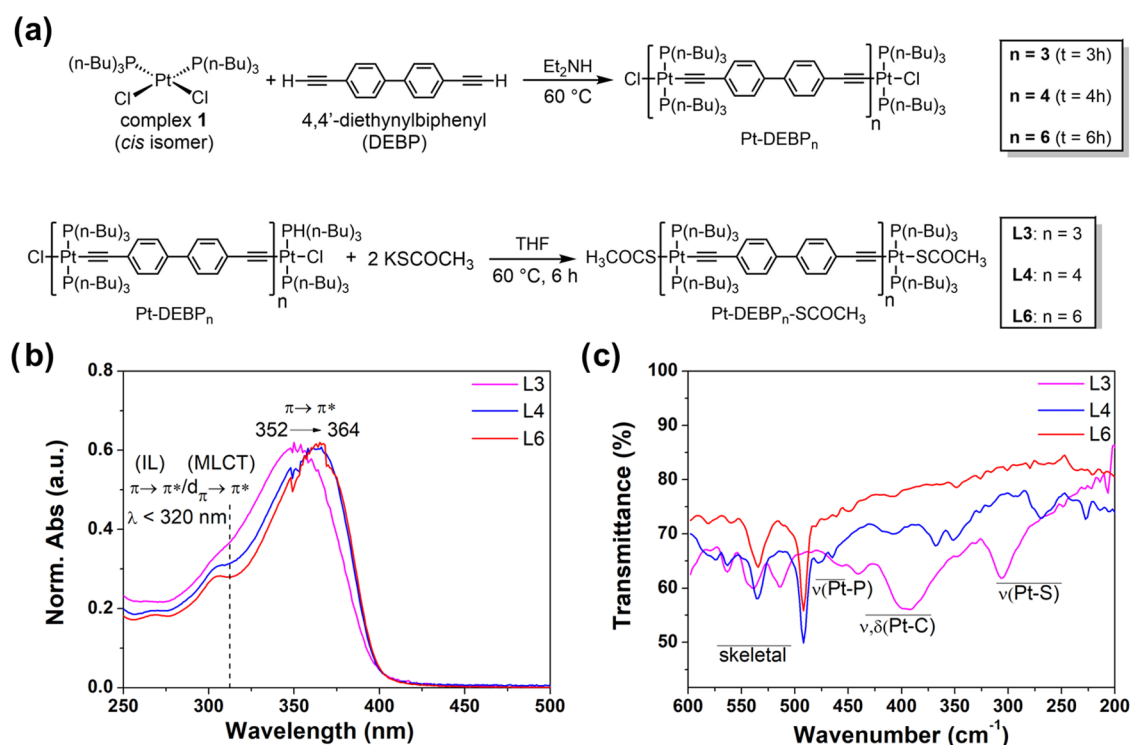


Figure 1. Pt-DEBP oligomers synthesis and characterization. (a) Schematic synthesis pathway to obtain Pt-DEBP_n-SCoCH₃ ligands with different chain lengths (L3, L4, L6). (b) UV-vis spectra of oligomers recorded in CH₂Cl₂. IL = intraligand, MLCT = metal-to-ligand charge transfer transitions. (c) Superimposed Far-IR spectra of L3, L4, and L6. Samples were deposited as a thin film from iPr-OH on a PE plate and air-dried. Assignments: ν = stretching vibrations, δ = bending vibrations.

rpm, 1 min) from their chloroform or dichloromethane suspension onto the Ossila prepatterned fully oxidized ITO OFET (20 × 15 mm) with interdigitated finger electrodes having channel dimensions of 30 mm (W) × 50 μm (L). Substrates were cleaned with isopropyl alcohol, acetone, and chloroform prior to use. The electrical conductivity was calculated using eq 1:³⁸

$$\sigma(S/m) = \frac{G(S) \cdot L(m)}{t(m) \cdot W(m)} \quad (1)$$

where G = conductance ($1/R$ in $1/\Omega = S$) derived from the slope of I/V measurements, t = thickness of each film from AFM, L = length between electrodes, and W = electrode length (in m), both depending on electrode design. Measurements were carried out in triplicate, and the values were reported as mean ± standard deviation.

2.3. Synthesis Procedures

2.3.1. Synthesis of Oligoplatinaynes Ligands. A series of platinum-based dithioacetate oligomers, *trans,trans*-[CH₃CO-S-(Pt(PBu₃)₂-(C≡C-C₆H₄-C₆H₄-C≡C))_nPt(PBu₃)₂-S-COCH₃] with $n = 3$ (L3), 4 (L4), and 6 (L6) were synthesized and purified via a general dehydrohalogenation procedure followed by ligand substitution reaction, optimized from the literature.²⁹ Complete synthesis procedures of *cis*-[Pt(PBu₃)₂Cl₂] complex (1) and Pt-DEBP_n oligomers are reported in the Supporting Information section with full optical and structural characterizations.

2.3.2. Synthesis of Thiol-Functionalized AuNPs. AuNPs functionalized with the organometallic ligands L3, L4, and L6 were synthesized according to a previously reported procedure.²⁹ The AuNPs synthesis in the presence of the L3 thioacetate is reported as a typical procedure: an aqueous solution of HAuCl₄·3H₂O (0.100 g, 2.54 × 10⁻⁴ mol) in H₂O_{up} (10 mL) was mixed with a solution of tetraoctylammonium bromide (TOAB) (0.1388 g, 2.54 × 10⁻⁴ mol, HAuCl₄/TOAB 1/1 molar ratio) in toluene (20 mL). The two-phase mixture was vigorously stirred until all the metal ion precursor was transferred into the toluene layer, giving an orange solution. Subsequently, a solution of L3 (0.2981 g, 1.269 × 10⁻⁴ mol, Au/S

1/1 molar ratio) dissolved in 20 mL of toluene was added. The mixture was kept under an Ar atmosphere for 15 min; then, an aqueous solution of sodium borohydride (0.0961 g, 2.54 × 10⁻³ mol, HAuCl₄/NaBH₄ 1/10 molar ratio) in ultrapure water (10 mL) was added under vigorous stirring. After further stirring for 3 h at room temperature, the aqueous phase was discarded, and the organic phase was separated and washed repeatedly with fresh water. The organic phase was reduced to 2 mL in a rotary evaporator, and 40 mL of ethanol was added. The mixture was kept overnight at -18 °C and then centrifuged at 10,000 rpm for 15 min to remove the solvent, after which the precipitate was repeatedly washed with ethanol by centrifugation at 13,400 rpm (17,063g) for 10 min. After purification, the colloidal precipitate was redispersed in dichloromethane, obtaining a ruby red suspension of -S-Pt-DEBP-capped AuNPs.

Control samples based on AuNPs stabilized with 4-bromobenzenethiol (4BBT) and 1-dodecanethiol (DDT) were synthesized for comparison according to a previously published protocol,²⁴ employing HAuCl₄/ligand molar ratios of 1:4 and 1:2 for AuNPs-4BBT and AuNPs-DDT, respectively. Characterizations of AuNPs-4BBT and AuNPs-DDT are reported in Figures S1 and S2.

2.3.3. Preparation of AuNPs/P3HT Blends. AuNPs functionalized with L3, L4, and L6 ligands were blended with P3HT polymer through a one-step blending approach at room temperature. 0.0040 g of P3HT was dissolved in CHCl₃ at a concentration of 2 mg/mL. Similarly, a 2 mg/mL CHCl₃ suspension of AuNPs was prepared by redispersing 0.0040 g of AuNPs in 2 mL of organic solvent. Then, P3HT and AuNPs suspensions were mixed in a total volume of 1 mL, exploring different AuNPs/P3HT weight ratios: 10:90, 30:70, 50:50, 70:30, 90:10 (i.e., 10, 30, 50, 70, and 90 wt %, respectively). The mixture was gently stirred for 3 h at room temperature and in the dark. Each blend suspension was dried using a rotary evaporator and stored in the dark at +4 °C for further use. Suspensions maintained their colloidal stability up to 12 months in these conditions.

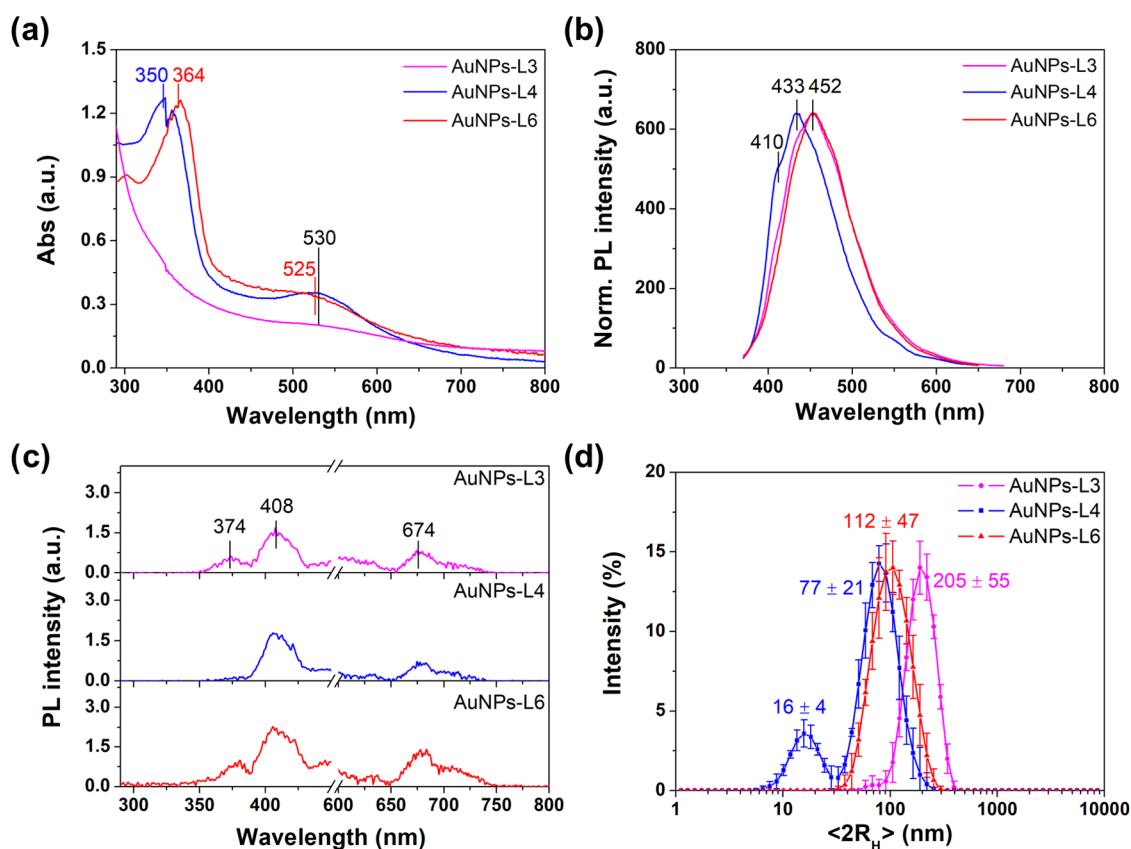


Figure 2. (a) UV-vis extinction spectra of AuNPs-L3 ($\lambda_{\text{LSPR}} = 530$ nm); AuNPs-L4 ($\lambda_{\text{LSPR}} = 530$ nm); AuNPs-L6 ($\lambda_{\text{LSPR}} = 525$ nm). (b) Emission spectra of functionalized AuNPs at ($\lambda_{\text{exc}} = 350$ nm). (c) Emission spectra of functionalized AuNPs at $\lambda_{\text{exc}} = 530$ nm. (d) DLS size distributions of AuNPs. All measurements were carried out in CH_2Cl_2 .

3. RESULTS AND DISCUSSION

3.1. Organometallic Oligoplatinaynes Synthesis and Characterization

Rod-like organometallic platinum(II) oligomers were synthesized starting from *cis*-[Pt(PBu₃)₂Cl₂] complex (**1**), and the π -conjugated dialkyne 4,4'-diethynylbiphenyl ($\text{H}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{H}$, DEBP) as precursors, following a well-established procedure.²⁹ Synthesis procedure and characterization of complex (**1**) are given in the Supporting Information and Figure S3. Chlorinated organometallic oligomers (Pt-DEBP_{*n*}) with a different chain length, from one Pt center (2 h, *n* = 1, monoacetylide complex)³⁹ up to 6 Pt centers (6 h, *n* = 6), were obtained by controlling the condensation in a typical dehydrohalogenation reaction. Subsequent modification via ligand substitution reaction in the presence of potassium thioacetate yielded the corresponding *trans,trans*-[dithiodibis(tributylphosphine)diplatinum(II)-4,4'-diethynylbiphenyl] (with *n* = 3, 4, 6) oligomers, i.e., ligands L3, L4, and L6, respectively, following the reaction pathways summarized in Figure 1a.²⁹ Based on a theoretical calculated S-to-S^{40,41} distance of 2.03 nm for the dinuclear model compound [CH₃CO-S-Pt(PBu₃)₂-C≡C-C₆H₄-C₆H₄-C≡C-Pt(PBu₃)₂-S-COCH₃] (experimental value: 2.1 nm²⁹), the corresponding oligomer length were calculated to be L3 = 5.17 nm, L4 = 6.74 nm, and L6 = 9.87 nm, with little or no variation with respect to the corresponding chlorinated Pt-DEBP_{*n*}. Complete synthesis protocol and characterization of Pt-DEBP_{*n*} oligomers, along with that of platinum precursor, are given in the Supporting Information,

listed in Table S1 and Figure S4. The chemical structures of products were readily identified by FT-IR, Far-IR spectroscopy, and ¹H, ³¹P-NMR based on their frequencies, chemical shifts, and splitting patterns. In particular, the increase in the chain length of oligomers determined a red shift of the UV-Vis extinction maxima following the trend L6 (364 nm) > L4 (362 nm) > L3 (352 nm) (Figure 1b). These UV-Vis absorption bands are due to $\pi-\pi^*$ transitions of the alkynyl ligands. As reported for similar Pt(II) acetylide complexes, the absorption tails $\lambda < 320$ nm, red-shifted compared to those of the free alkynes and complex (**1**), can be assigned to the intraligand (IL) transition of DEBP ligands and to the Pt → C≡CR metal-to-ligand charge transfer (MLCT) transition from a filled metal d orbital to vacant π^* DEBP orbitals, thus being best described as a mixture of $\pi \rightarrow \pi^*(\text{C}\equiv\text{CR})$ IL/ $d_\pi(\text{Pt}(\text{II})) \rightarrow \pi^*(\text{C}\equiv\text{CR})$ MLCT.^{42,43} Structural assessment was carried out via FT-IR spectroscopy in the mid- and far-infrared regions. A comparison between the FT-IR spectrum of the halogenated Pt-DEBP₆ oligomer and its thioacetate L6 derivative is shown in Figure 1c. In both compounds, the presence of the aromatic DEBP moiety and PBu₃ ligand was assessed (for complete assignments, see Figure S5).^{44–46} Vibrations involving L3, L4, and L6 were investigated by Far-IR in the 600–200 cm^{−1} wavenumber range. Far-IR spectra of related Pt-DEBP_{*n*} oligomers can be found in Figure S4. As can be seen from Figure 1c, the three higher-frequency bands were assigned to skeletal vibrations at ca. 580 cm^{−1} (very weak, *in-plane* and *out-of-plane* aromatic ring deformations, two bands), 560 and 535 cm^{−1} due to a combination of $\nu(\text{Pt}-\text{C})$ and C_{*n*}H_{2*n*+1} and C–C–C alkyl chain deformation modes,

consistent with literature values for bis-phosphine Pt(II) alkynyl complexes.^{47,48} The vibrations at ca. 490 cm⁻¹, and 410 cm⁻¹ were further assigned to $\nu(\text{Pt}-\text{C})$ of the bridging alkynyl ligands ($\text{Pt}-\text{C}\equiv\text{C}$).⁴⁹ The bands of medium intensity centered at 450 cm⁻¹ were due to $\nu(\text{Pt}-\text{P})$, whereas the signals at 390 cm⁻¹ can be assigned to the $\delta(\text{C}-\text{C}-\text{P})$.⁵⁰ Metal–sulfur stretching frequencies $\nu(\text{M}-\text{S})$ lie in the range 298–205 cm⁻¹ for the transition-metal complexes,⁵¹ allowing to assign the band at about 300 cm⁻¹ to the $\nu(\text{Pt}-\text{S})$, which is shifted to a lower frequency with respect to simple thiolate complexes owing to the strong *trans* influence of the alkynyl ligand. The same band was absent in the Pt-DEBP_n spectrum. Conversely, in the halogenated oligomer, a band was present at 305 cm⁻¹, typically assigned to terminal $\nu_s(\text{Pt}-\text{Cl})$ in *trans* configuration (see Figure S4).^{49,52}

The structure of the as-obtained oligomers showed: (1) a rod-like structure based on rigid linearity of the carbon–carbon triple bond and the square-planar *trans* configuration of the metal, (2) a regular arrangement of the metal in the backbone,²⁹ and (3) –SR (R = –COCH₃) ending functionalities that allow their use as functionalizing agents for the subsequent AuNPs synthesis.

3.2. Organometallic Oligomers as AuNPs Stabilizers

3.2.1. UV–Vis Extinction Spectroscopy Characterization. AuNPs functionalized with the bifunctional *trans*–[CH₃CO–S–(Pt(PBu₃)₂)₂–(C≡C–C₆H₄–C₆H₄–C≡C–)]_nPt(PBu₃)₂–S–COCH₃] ligands (L3, L4, and L6) were obtained through reduction of Au³⁺ precursor adapting a two-phase Brust-Schiffrin procedure.²⁹ The acidic conditions of [AuCl₄][–] aqueous solution (pH < 2 at a concentration of 25 mM) allowed a convenient *in situ* deprotection of the thiol groups of L3, L4, and L6 oligomers by removal of the acyl ending moiety, which rapidly reacts with the gold precursor to form the organometallic functionalized AuNPs colloids after the addition of [BH₄][–] reducing agent.²⁹ The UV–vis extinction spectra of the as-obtained functionalized AuNPs are shown in Figure 2a. All the spectra clearly showed a single LSPR band in the 525–530 nm region, typical of spherical AuNPs with a diameter <10 nm, and the absorption of the organometallic –S–Pt–DEBP_n ligands functionalizing the AuNPs surface at $\lambda < 400$ nm.

Upon covalent binding of Pt(II) oligomers to the surface of AuNPs involving the sulfur donor atoms, the absorption related to the Pt-based ligand was found in the 300–400 nm wavelength region. Notably, for AuNPs capped with the six-residue oligomer (AuNPs–L6, red line in Figure 2a), the LSPR maximum value is at a lower wavelength ($\lambda_{\text{LSPR}} = 525$ nm) compared to AuNPs–L3 and AuNPs–L4. This could be ascribed to a different interparticle coupling effect among AuNPs. Indeed, the two S-ending groups can covalently bind different AuNPs in an interconnected system. The extinction spectra of NPs are very sensitive to the separation distance between AuNPs and are strongly influenced by the interparticle coupling; a blue-shift in the LSPR band typically occurs with increasing nanoparticle spacing.⁵³ In this case, considering the Pt-DEBP oligomers of different chain length used during AuNPs synthesis, it was possible to qualitatively hypothesize the formation of interconnected AuNPs with different NP–NP distances. The three samples showed different full width at half-maximum (fwhm) values of the LSPR band, with AuNPs–L4 having the smallest fwhm compared with AuNPs–L3 and AuNPs–L6. Normally, the different band-

width accounts for different polydispersity of the samples; the narrower the fwhm, the lower the polydispersity.⁵⁴ However, the extinction spectra of very close AuNPs also comprise interband absorptions of AuNPs and coupled LSPR bands (via near-field interaction, resulting in coupled plasmon modes) of interacting AuNPs, which contribute to LSPR band broadening.⁵⁵ Thus, based on the UV–Vis results, it is possible to hypothesize the formation of Pt-DEBP_n-capped AuNPs arranged into interconnected systems, also assuming the formation of isolated nanoparticles to some extent.

3.2.2. Photoluminescence Properties of Pristine Oligomers and AuNPs. The luminescence spectra of the chlorinated platinum complexes, *n* = 3, 4, 6, and pristine AuNPs were recorded at room temperature. The optical properties of both chlorinated complexes and functionalized AuNPs are summarized in Figure S4 and Table S2. The PL properties of functionalized AuNPs were studied by exciting both within the absorption region of the organometallic ligand and at the LSPR centered at 530 nm. Excitation spectra of all AuNPs types were also collected and reported in Figures S6–S8. Emission spectra of functionalized AuNPs in the ligand excitation range are reported in Figure 2b. The optimal AuNPs excitation at 350 nm resulted in a structureless emission in the violet/blue region, centered at 433 for AuNPs–L4, and at 452 nm for AuNPs–L3 and AuNPs–L6. These results support the presence of Pt(II) functional groups interacting with the AuNP surface. The spectral shift for Pt–DEBP oligomers after AuNPs synthesis reflected changes in the local environment, consistent with the known sensitivity of square-planar Pt(II) complexes to their immediate surroundings.^{29,32} PL excitation at the AuNPs LSPR band revealed multiple emissive pathways (Figure 2c). Excitation at 530 nm yielded unexpectedly high-energy bands at about 374, 408, and 675 nm, with no significant spectral shifts among samples. In this case, the emission reasonably comes from the Pt(II) complexes functionalizing the surface, since only small-sized Au clusters (<2 nm) are known to exhibit intrinsic luminescence.^{38,56} The long-wavelength emission, close to that of the free Pt–DEBP_n ($\lambda_{\text{em}} \approx 547$, 595 nm), can be attributed to Pt–DEBP_n MLCT transitions, slightly affected by the covalent interaction with AuNPs. The increased rigidity of the system suppresses nonradiative decay, intermolecular quenching, and weak interactions (e.g., hydrogen-bonding/ π -stacking interactions), featuring the red-shifted emission band at ~ 670 nm.⁵⁷

3.2.3. DLS Hydrodynamic Size Evaluation. In order to confirm previous assumptions about different sample polydispersity (see Section 3.2.1), hydrodynamic diameter ($\langle 2R_{\text{H}} \rangle$, nm) evaluation was carried out by DLS analysis (Figure 2d, intensity-weighted distributions). The first population was found at (72 ± 11) nm, with the biggest at (205 ± 55) nm (PDI = 0.32 ± 0.05) indicating the coexistence of aggregates of AuNPs with different sizes with intensity percentages (4 and 96%, respectively); for AuNPs–L4 the first population was centered at (16 ± 11) nm and the second one at (77 ± 21) nm (PDI = 0.4 ± 0.2), which agreed with the presence of smaller, isolated AuNPs, at least in a higher percentage than in the previous sample (18%), as also demonstrated by the different PDI values. Conversely, the AuNPs–L6 showed a single distribution at (112 ± 47) nm (PDI = 0.29 ± 0.04), consistent with more uniform interconnected AuNPs.

3.2.4. Morphological Studies. To evaluate the morphology and size of the as-synthesized functionalized AuNPs (Figure 3a), solid-state microscopies were employed. FESEM

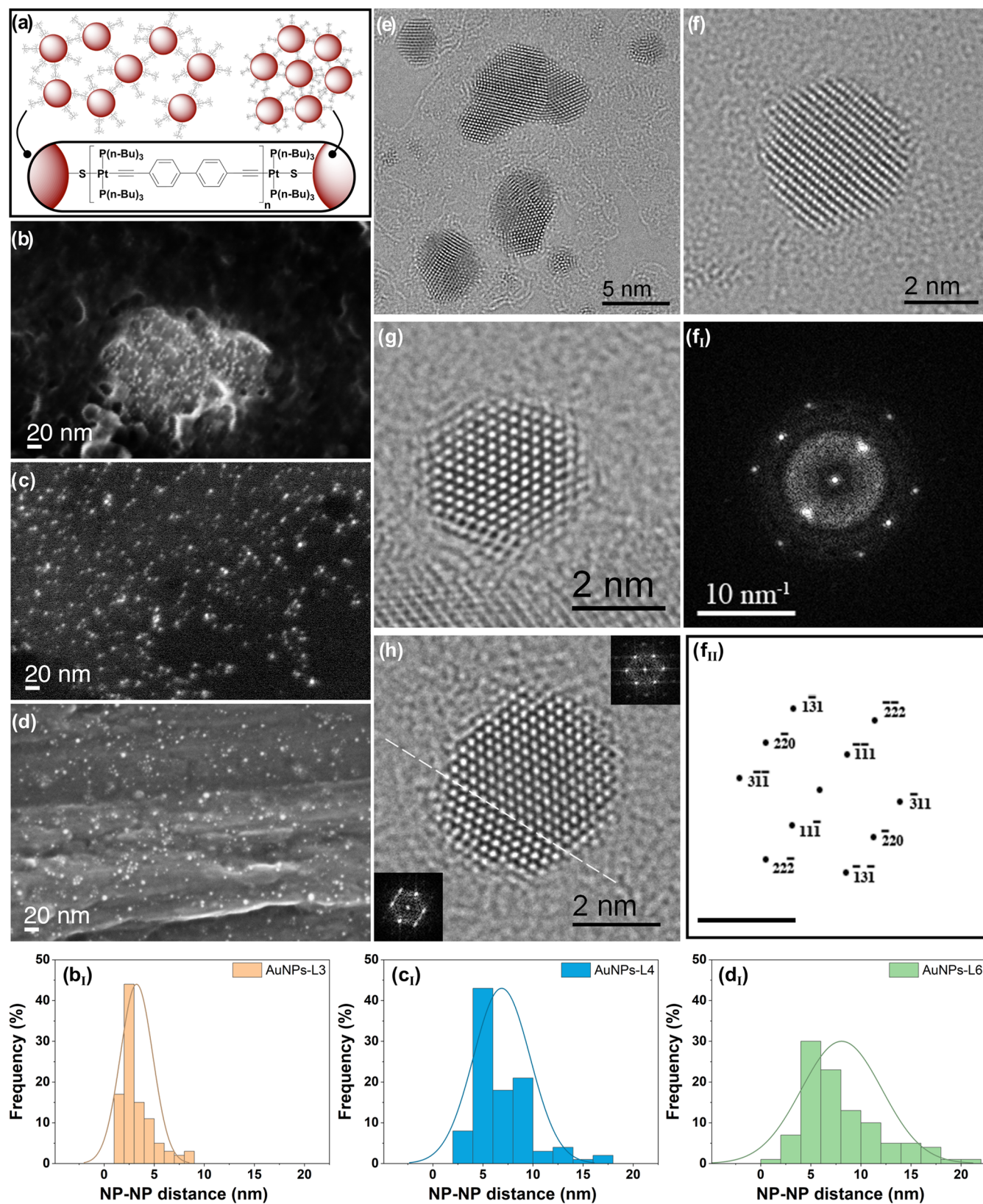


Figure 3. Morphological analyses carried out on AuNPs-Pt-DEBP. (a) Generic structure of AuNPs. (b) FESEM image of AuNPs-L3. (b_i) NP-NP distance histogram distribution. (c) FESEM image of AuNPs-L4. (c_i) NP-NP distance histogram distribution. (d) FESEM image of AuNPs-L6. (d_i) NP-NP distance histogram distribution. All FESEM samples were deposited on Al stub from their CHCl₃ dispersion and air-dried. (e) HRTEM imaging of AuNPs-L6 dispersed onto a carbon membrane. (f) HRTEM image of a spherical NP observed along a <112> crystallographic axis. (f_i) Corresponding fast Fourier transform (FFT) of the HRTEM image. (f_{ii}) Simulated diffraction pattern of the fcc structure along the <112> zone axis. (g) HRTEM image of a faceted AuNP. (h) HRTEM image of a twinned AuNP. As shown by the FFTs in the opposite corners of the

Figure 3. continued

image, the two parts on both sides of the twin boundary (dashed line) are rotated around the $\langle 110 \rangle$ axis with respect to each other. Data fitted by Gaussian convolution functions with $p < 0.01$ statistically significant difference between experimental and theoretical data fitting.⁵⁸

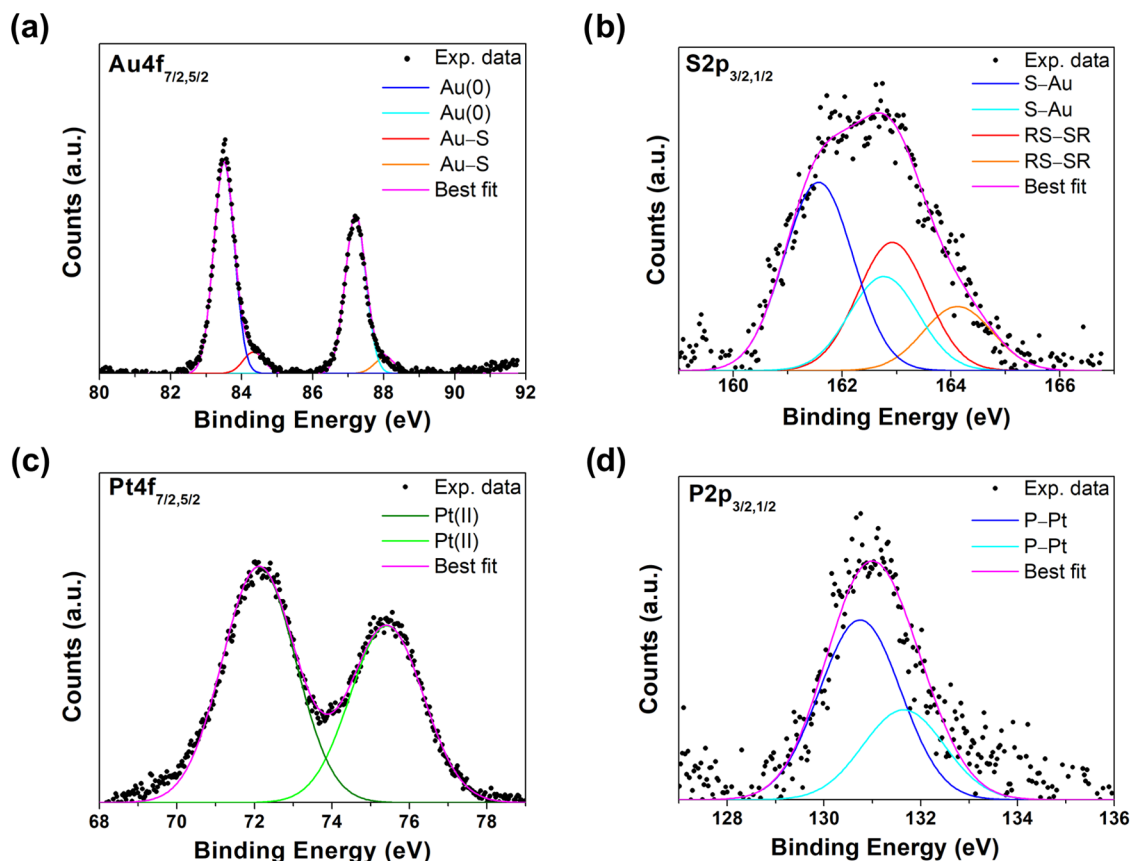


Figure 4. SR-XPS spectra of (a) Au 4f, (b) S 2p, (c) Pt 4f, and (d) P 2p core levels in AuNPs-L6.

images in Figure 3b–d showed the presence of NPs assemblies, likely due to the formation of interconnected AuNPs mediated by the bifunctional Pt-based ligands, leading to superaggregated structures.³² In all samples, spherical AuNPs with diameters below 10 nm were observed, with AuNPs-L3 showing a more compact arrangement (Figure 3b). The mean NP-NP distances calculated from FESEM images were: AuNPs-L3 = (3 ± 1) nm (Figure 3b_I), AuNPs-L4 = (6 ± 2) nm (Figure 3c_I), and AuNPs-L6 = (8 ± 4) nm (Figure 3d_I), consistent with the expected ligand length. From the detailed compositional analysis via EDX, signals from the Au and Pt atoms in the nanoparticle structure were found (Figure S9).

To further investigate the size, morphology, and crystalline quality of AuNPs, detailed HRTEM analysis was carried out on AuNPs-L6 as a representative sample. The images obtained on the AuNPs deposited on carbon films showed that they appeared either as isolated particles or aggregated in packets (Figure 3e), depending on the region observed. Detailed analysis demonstrated the formation of mostly rounded AuNPs (Figure 3f), with a mean diameter of (3.3 ± 1.1) nm, only a minority being faceted (Figure 3g) or irregularly shaped. Detailed Fourier analysis of the acquired HRTEM images confirmed that the NPs adopt the typical face-centered cubic (fcc) structure of bulk Au (Figure 3f_{II}). However, extended defects, such as twin boundaries parallel to the $\{111\}$ planes,

are frequently observed in the NPs (Figure 3h). It is worth noting that the TEM observations cannot provide insight into the chemical interactions between neighboring NPs, as it cannot be excluded that the observed configurations (e.g., Figure 3e) result from the dispersion method itself.

3.2.5. FTIR Spectroscopy Characterization. The occurred surface functionalization was assessed by FTIR spectroscopy. Infrared spectra of AuNPs are reported in Figure S10 with full assignment. As first evidence, the spectrum recorded on AuNPs did not show the 1730 cm^{-1} stretching band of $>\text{C}=\text{O}$ functional groups, due to the occurrence of the deacetylation reaction of terminal $-\text{SCOCH}_3$ in acidic conditions, followed by the formation of a metal–sulfur bond.²⁹ In the far-infrared spectra of the AuNPs (Figure S10), bands in the $580\text{--}530\text{ cm}^{-1}$ and $490\text{--}380\text{ cm}^{-1}$ regions are assigned to skeletal and Pt–C stretching and bending vibrations arising from both the tributylphosphine ligands and the DEBP moiety, in line with reported ranges for pristine complexes (see paragraph 3.1). Most notably, all three samples displayed a strong absorption centered at $\sim 250\text{ cm}^{-1}$, characteristic of the $\nu(\text{Au-S})$ vibration.³⁸ This band occurs at substantially lower frequency than the corresponding $\nu(\text{Pt-S})$ in Pt(II) complexes (typically in the range $298\text{--}205\text{ cm}^{-1}$).⁵¹ Its presence provides evidence for the covalent anchoring of the oligomer to the AuNPs surface through thiolate bonds, while the higher-frequency bands confirmed

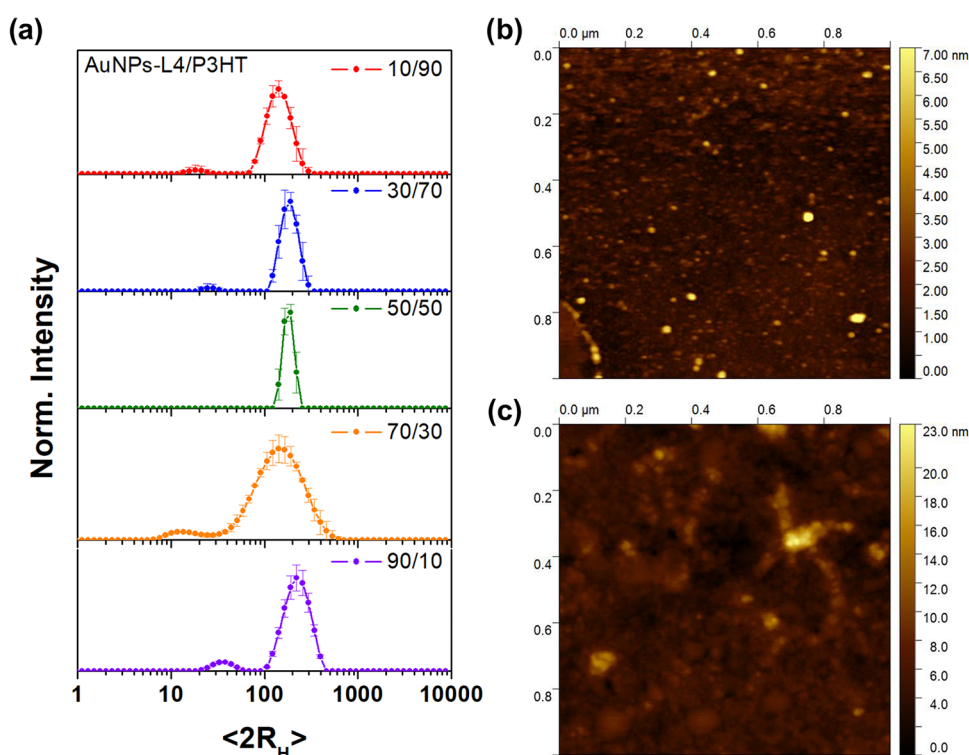


Figure 5. (a) Normalized DLS intensity-weighted size distributions of AuNPs-L4/P3HT blends: wt % 10/90 ($\langle 2R_H \rangle = 19 \pm 4$ nm and 140 ± 34 nm), 30/70 ($\langle 2R_H \rangle = 26 \pm 4$ nm and 196 ± 41 nm), 50/50 ($\langle 2R_H \rangle = 176 \pm 22$ nm), 70/30 ($\langle 2R_H \rangle = 14 \pm 5$ nm and 170 ± 105 nm), 90/10 ($\langle 2R_H \rangle = 36 \pm 8$ and 229 ± 66 nm) recorded in CHCl_3 . (b) AFM image of AuNPs-L4 spin-coated onto Si/SiO₂ substrate from their CHCl_3 suspension and air-dried. (c) AFM profile of AuNPs-L4/P3HT 50/50 blend spin-coated onto Si/SiO₂ substrate from their CHCl_3 suspension and air-dried.

that the alkynyl and phosphine coordination motifs were preserved.

3.2.6. SR-XPS Analysis. For AuNPs-L3 and AuNPs-L6, SR-XPS measurements were carried out at the C 1s, Au 4f, S 2p, Pt 4f, and P 2p core levels in order to study the effect of the longer and shorter ligands. XPS spectra and the parameters extracted from their analysis (BE, fwhm, atomic ratios) are reported in Figure 4a,b and Table S3. As the SR-XPS spectra of the two samples are essentially superimposable, only the data of AuNPs-L6 are herein presented, whereas full spectra of AuNPs-L3 can be found in Figure S11. C 1s spectrum (Figure S12) was deconvoluted into two components. The peak at 285.0 eV was associated with aliphatic (C–C), alkyne (C≡C), aromatic, and C–P carbons, while the right peak at around 286.5 eV was ascribed to C–O carbons of contamination. Au 4f spectrum (Figure 4a) showed two spin–orbit (Au 4f_{7/2}, Au 4f_{5/2}) doublets, with the Au 4f_{7/2} component considered as the reference. The Au 4f_{7/2} signal around 83.5 eV was assigned to metallic Au(0) atoms, while the component around 84.5 eV was assigned to substrate–thiol interface atoms.⁵⁹ Similarly, the S 2p spectrum (Figure 4b) showed two pairs of spin–orbit (S 2p_{3/2}, S 2p_{1/2}) peaks. The BE position of the S 2p_{3/2} signals was taken as a reference for the S 2p_{3/2–1/2} spin–orbit pair and used as an indicator of whether the sulfur atom was covalently bonded to the gold surface. In the S 2p spectrum, thiols chemisorbed on gold and thiols covalently bonded to metal nanoparticle surfaces exhibited a S 2p_{3/2} BE of approximately 161.7 eV. Conversely, the S 2p_{3/2} signal centered around 163.0 eV was assigned to physisorbed thiols or thiolates.⁶⁰ Pt 4f core level spectrum was reported in Figure 4c. The spectrum, as expected, was composed of a single pair of spin–orbit

components (Pt 4f_{7/2}, Pt 4f_{5/2}). The main Pt 4f_{7/2} component at nearly 72.0 eV was consistent with oxidized Pt, most likely Pt(II). However, the unusually large fwhm (2.38 eV) indicates that the signal cannot be attributed to a single Pt chemical state, suggesting the presence of multiple Pt components, such as a mixture of different Pt(II) coordination environments.^{29,32} Finally, the P 2p core level spectrum in Figure 4d showed one spin–orbit doublet (P 2p_{3/2}, P 2p_{1/2}). The main P 2p_{3/2} component around 130.8 eV was attributed to the P–C of phosphine ligands.

3.3. Integration of Gold Nanoparticles into P3HT Blends

3.3.1. Hydrodynamic Size and Morphology of the Blends. The AuNPs/P3HT nanocomposites were obtained by blending the AuNPs and regioregular P3HT suspensions in CHCl_3 at different weight percentages (wt %) under air atmosphere and at room temperature (for experimental details, refer to Section 2.3.3). The presence of gold colloids inside the P3HT was investigated in suspension via DLS. As can be seen from Figure 5a, the presence of larger aggregates of $\langle 2R_H \rangle = (140\text{--}230)$ nm prevailed over a small population centered at about 20 nm. After polymer blending, a bimodal size distribution was observed. In all cases, the main population showed a slight increase in hydrodynamic size, likely due to the formation of a solvated corona generated by interactions between the P3HT matrix and the nanoparticle surface, particularly for AuNPs-L4.

A detailed morphological analysis was carried out on pristine AuNPs-L4, and AuNPs-L4/P3HT 50/50 (as a representative sample) using tapping mode AFM. Pristine AuNPs-L4 (Figure 5b) resulted in homogeneous, spherical-shaped small-sized NPs (<10 nm, in agreement with FESEM images).

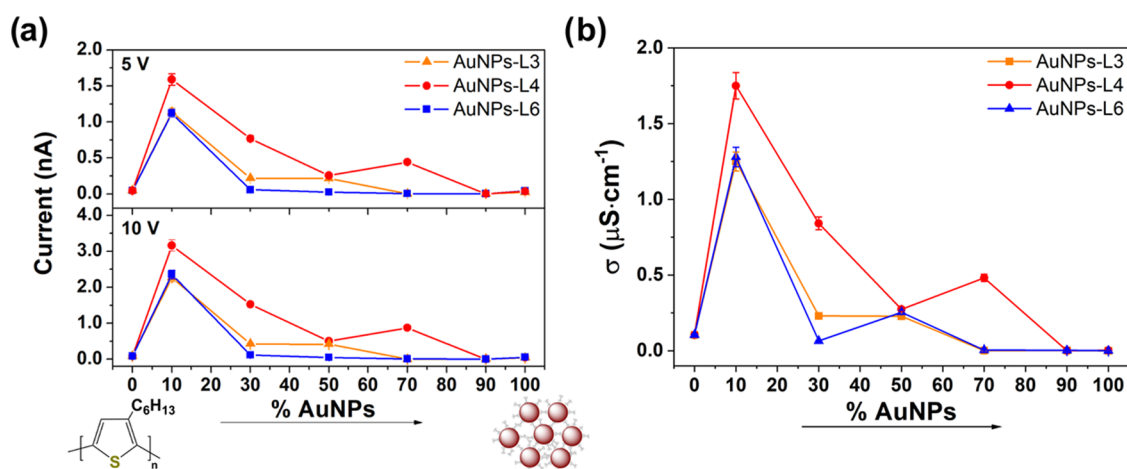


Figure 6. (a) Comparison of the electrical response at 5 and 10 V of each AuNPs/P3HT sample. 0% means P3HT only. (b) Electrical conductivity calculated for AuNPs/P3HT blends at room temperature.

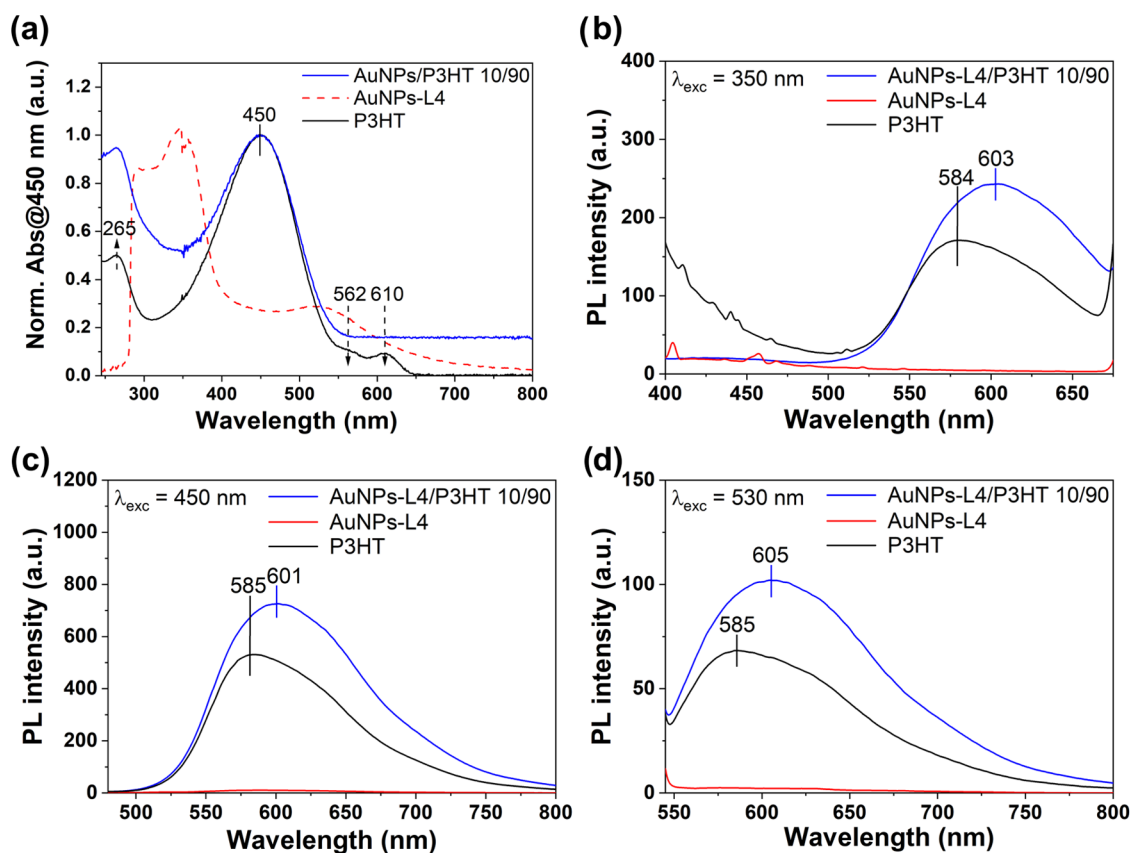


Figure 7. Optical characterizations (UV-vis, PL) recorded in CHCl_3 . (a) Overlapped UV-vis spectra of pristine AuNPs-L4, AuNPs-L4/P3HT 10/90, and pure regioregular P3HT. (b) PL spectra of AuNPs-L4/P3HT 10/90, pure P3HT-at 90% conc, and AuNPs-L4 at 10% conc with $\lambda_{\text{exc}} = 350$ nm. (c) PL spectra of AuNPs-L4/P3HT 10/90, pure P3HT at 90% conc, and AuNPs-L4 at 10% conc with $\lambda_{\text{exc}} = 450$ nm. (d) PL spectra of AuNPs-L4/P3HT 10/90, pure P3HT at 90% conc, and AuNPs-L4 at 10% conc with $\lambda_{\text{exc}} = 530$ nm.

In the AuNPs-L4/P3HT blend (Figure 5c), the bright aggregates were due to the presence of AuNPs uniformly distributed within the polymer matrix with no apparent clustering of NPs at the P3HT/air interface (3D profile can be found in Figure S13). These observations were consistent with good miscibility between the AuNPs functionalized with rigid π -conjugated organometallic polymer and the P3HT chains. Indeed, the interactions between the AuNPs surface ligand and mixed polymer chains largely determine the

thermodynamics/miscibility and hence the morphology of films.⁶⁰

3.3.2. Electrical Properties. A direct comparison of the electrical behavior was done based on the current–voltage response in the interval of -10 to $+10$ V (Figure S14). The P3HT and control samples I/V measurements are reported in Figure S15 for comparison. Concerning the AuNPs/P3HT blends with AuNPs-L3, AuNPs-L4 and AuNPs-L6 all exhibited a fully linear I/V dependence, indicative of ohmic

transport. These trends can be explained based on (1) the absence of a contact energy barrier between the AuNPs and the P3HT matrix, i.e., a good Ohmic contact, owing to the favorable alignment between HOMO level of P3HT (in the 5.1–5.2 eV range) and the work function of gold in the 5.0–5.1 eV range, and (2) a high concentration of free charges at the thermal equilibrium.⁶¹ The AuNPs–L4/P3HT blends showed the highest variation among the different formulations (Figure S14), probably owing to a more efficient dispersion and distribution within the P3HT matrix, which reduced the resistance and boosted the current response to different biases. A comparison of the electrical properties of blends at specific DC (Direct Current) voltage levels used in electronic devices and systems, i.e., 5 and 10 V, is presented in Figure 6a. The AuNPs/P3HT samples showed the same electrical trend for both applied voltages and, in all cases, the AuNPs/P3HT 10/90 composition represented the optimized weight ratio. The best results were obtained for the AuNPs–L4/P3HT 10/90, with an increase in the current intensity of more than 30 times the pristine P3HT. A similar concentration-dependent behavior was already reported for analogous nanocomposite blends.^{23,38} Figure 6b shows the electrical conductivity of blends, calculated considering a mean film thickness of (3 ± 1) nm (measured by AFM). The conductivity achieved with 10% loading of AuNPs was higher than all other compositions and pristine AuNPs. For AuNPs–L4/P3HT 10/90, the calculated value ($1.75 \mu\text{S}\cdot\text{cm}^{-1}$) was nearly 16.5-fold higher than that of pristine P3HT at 0.5 mg/mL ($0.105 \mu\text{S}\cdot\text{cm}^{-1}$). A dramatic improvement was also found when compared to $4.23 \times 10^{-4} \mu\text{S}\cdot\text{cm}^{-1}$ of the same blend with 90% AuNPs loading. This trend was observed in all the blends, although confirming superior properties of AuNPs–L4/P3HT type. The observed conductivity enhancement can be primarily attributed to improved P3HT ordering, with a secondary contribution from ligand-mediated hopping.⁶²

3.3.3. Optical Properties of the Blends. UV–vis measurements normalized to the peak intensity at 450 nm were carried out on pristine P3HT (given as a reference) and AuNPs–L4/P3HT blends in CHCl_3 and are reported in Figure 7a. The presence of AuNPs can be evidenced by the appearance of a scattering effect at higher wavelengths, although the extinction spectrum was mainly dominated by the P3HT profile, which is present in the system at 90 wt %. The polymer itself exhibited an absorption band at 450 nm arising from the π – π^* transitions in a coiled (disordered, flexible) conformation.²³ This band did not show any significant changes after AuNPs addition, providing initial evidence of little to no perturbation by the NPs of the disordered regions of the polymer. Conversely, the additional bands at 562 nm (0–1 transition of the intrachain excitons) and 610 nm (0–0 transition of interchain-delocalized excitation resulting from the strong π -stacking of the polymer chains) underwent a significant reduction upon loading with AuNPs. In particular, the band at 610 nm is commonly used to monitor the *in situ* crystallization and the presence of crystalline P3HT aggregates in solution.²³ This attenuation can be attributed to perturbation of the π – π stacking and effective conjugation length of P3HT chains due to electronic interactions with the AuNPs–L4 interface. Similar effects, where incorporation of metallic or functionalized nanostructures alters the aggregation and optical response of P3HT, have been reported in the literature.^{9,18,23,63} The band centered at 265 nm showed an increased intensity, attributable to the

overlapping of this band with the organometallic ligands functionalizing the AuNPs surface, thus confirming the presence of gold colloids dispersed in the polymer matrix. Remarkably, the optical (direct) band gap (responsible for generating electron–hole pairs) of the AuNPs–L4/P3HT 10/90 nanocomposite, estimated using the Tauc's plot method from the UV–Vis absorption edge,³⁸ was reduced by the AuNPs addition from 2.13 eV¹⁵ of pure P3HT to 2.06 eV. Tauc's plots with band gap estimation method are reported in Figure S16. This direct gap is crucial for its function as a light-absorbing material in organic electronic devices, since its slight reduction to ~ 2.0 eV is beneficial as it modestly enhances the absorption of red and near-infrared wavelengths (the most intense part of the solar spectrum).⁶⁴

3.3.4. Photoluminescence Behavior of the Blends. PL properties were investigated at the excitation wavelengths corresponding to the maximum absorption peak of Pt–DEBP ligand on AuNPs (350 nm), LSPR band (530 nm), and pure P3HT (450 nm). Spectra were acquired under nonsaturating conditions, ensuring a linear response regime suitable for extracting reliable quantitative information (Figure 7b–d) at a blend concentration of 7.5×10^{-4} mg/mL. Full spectra are reported in Figure S17.

For pristine P3HT (Figure 7b–d), the excitation at 350, 450, and 530 nm resulted in an emission peak centered at 583.5, 584.5, and 585.0 nm, respectively (Stokes shift of ~ 0.63 eV), as typical.⁶⁵ Upon 10% AuNPs–L4 addition, P3HT emission was red-shifted to the 603–605 nm range (Stokes shift of ~ 0.70 eV) with a featureless and broader profile. Negligible emission was found for pristine AuNPs–L4 in this spectral region. Qualitatively, this effect is more pronounced by increasing the AuNPs content in the P3HT matrix, i.e., AuNPs/P3HT 70/30 blend (Figure S18). In the latter, a small contribution at 450 nm ($\lambda_{\text{exc}} = 350$ nm) due to the organometallic oligomer functionalizing the AuNPs surface was found. Interestingly, the excitation on the LSPR maximum resulted in a broad emission centered at ~ 600 nm for both blends. Such behavior can be ascribed to a more amorphous arrangement of the polymer inside blends compared with pristine P3HT. Therefore, a larger Stokes shift would be expected as a result of enhanced structural relaxation after photoexcitation, with the structural disorder being the main driver of observed PL red-shifts and broadening.⁶³ In addition to spectral changes, a quantitative analysis of the emission behavior of P3HT was carried out at 10% AuNPs loading by evaluating the quenching factor (Q) at $\lambda_{\text{exc}} = 450$ nm through normalization of the photoluminescence intensity to the concentration of the emitting species, according to eq 2:⁶⁶

$$Q = \frac{(I_{\text{PL}}/C)_{\text{free P3HT}}}{(I_{\text{PL}}/C)_{\text{P3HT with AuNPs-L4}}} \quad (2)$$

where I_{PL} corresponds to the photoluminescence intensity and C represents the nominal concentration (mg/mL) within the blend. This approach relies on the proportionality between emission intensity and photoluminescence quantum yield under identical experimental conditions. The resulting value of $Q = 0.81$ indicated the absence of significant quenching; instead, a clear enhancement of the emission efficiency is observed in the presence of 10% AuNPs–L4. Since AuNPs with size >4 nm are not fluorescent,³⁸ FRET effect is unlikely to occur. The observed emission enhancement suggested that nonradiative energy transfer or charge separation processes are

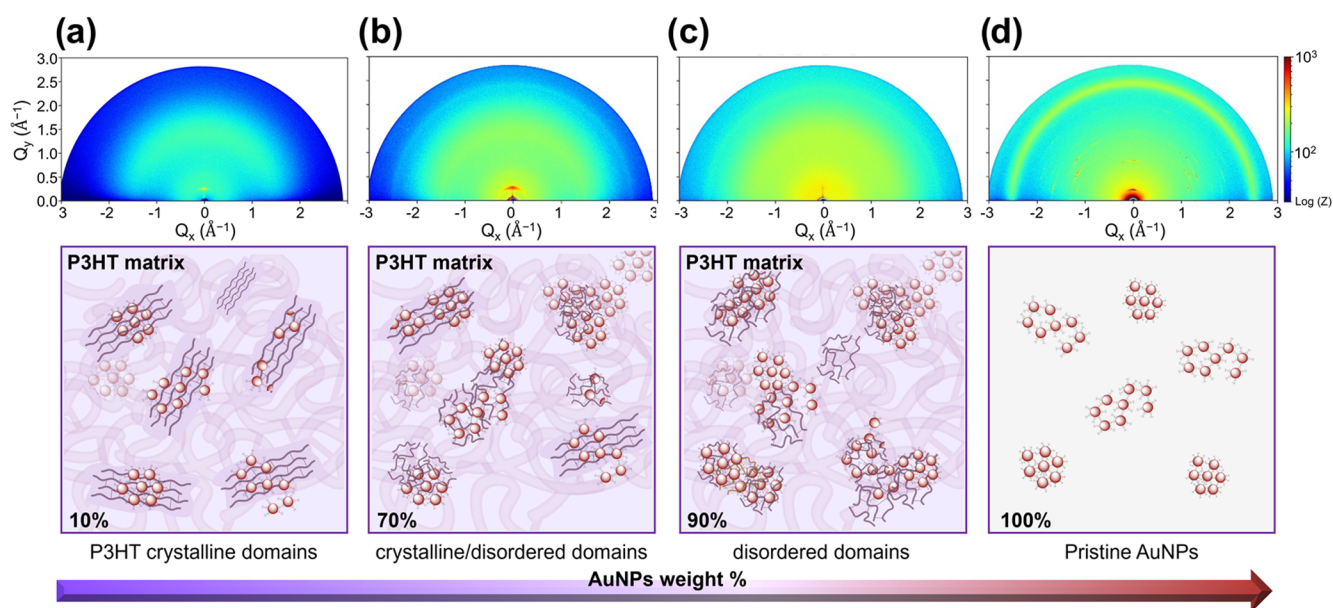


Figure 8. (a–d) Experimental GISAXS pattern of the AuNPs assembly at increasing nanoparticle concentration and schematic representation of the resulting nanoparticle organization (schematics below).

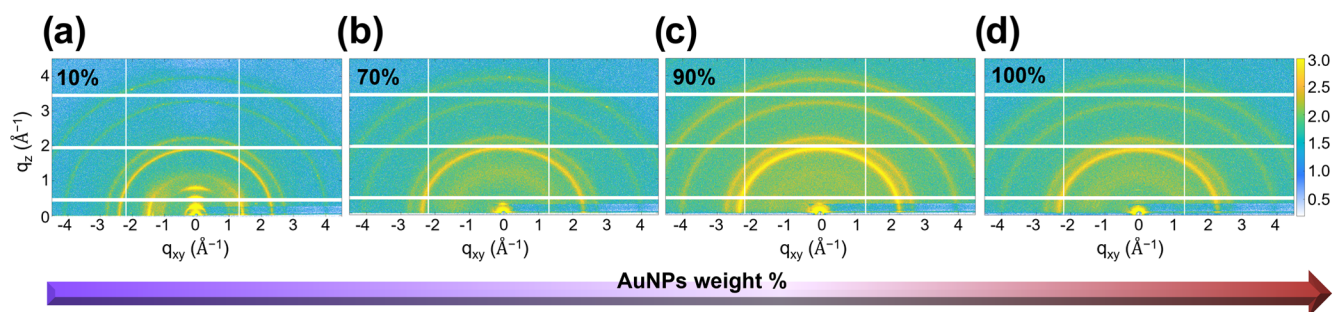


Figure 9. Nano-GIWAXS scattering profiles after annealing at 100 °C of AuNPs/P3HT at (a) 10/90%, (b) 70/30%, (c) 90/10% loading, and (d) pristine AuNPs.

not dominant under these conditions. Rather, the observed increase in radiative decay of P3HT in the presence of AuNPs in the blend (metal-enhanced fluorescence) can be explained based on the coupling between photogenerated excitons of P3HT and surface plasmon of noble metal nanoparticles, as already reported for similar systems.^{67,68} This coupling interaction depends on the overlap between the emission frequency of the semiconducting polymer and the LSPR field of the AuNPs, leading to stronger fluorescence enhancement. Such behavior has been reported as a valuable property for organic-based displays and nanometer-scale optoelectronics.⁶⁹

3.3.5. GISAXS/GIWAXS Structural Studies. Focusing on the AuNPs–L4/P3HT sample, chosen for detailed analysis based on the electrical measurements, the structural features of the pristine AuNPs–L4 and related blends in the solid state were investigated via GISAXS/GIWAXS (Figure 8) and nano-GIWAXS studies (Figure 9). In the AuNPs–L4/P3HT 10/90 wt % sample (Figure 8a), the diffraction pattern revealed only the characteristic reflections of P3HT, while no Au-related diffraction rings were detected. This absence can be ascribed to the low Au content within the polymer matrix. For AuNPs–L4/P3HT 70/30 wt % blend (Figure 8b), both the typical AuNPs ring feature and the strong 111 peak of P3HT were observed. In the AuNPs–L4/P3HT 90/10 wt % blend (Figure 8c), there was an improvement in both the AuNPs 111 ring

and the P3HT 100. Pristine AuNPs–L4 film (Figure 8d) showed Au 111 ring at higher q values, with multiple peaks at lower q values related to linker-induced strong ordering. In freshly prepared blends, a general evolution from P3HT crystalline domains in the lower AuNPs-containing blend to a disordered arrangement at higher AuNPs content was observed. The latter disordering effect on the P3HT matrix could be ascribed to the formation of AuNPs aggregates, with structural defects and grain boundaries playing a crucial role in modulating the interconnectivity between counterparts. These findings strongly support the electrical results in which the balance between P3HT crystallinity, charge mobility, and P3HT/AuNPs interconnectivity resulted in the best electrical performances at 10% of AuNPs rather than 90% loading.

3.3.6. Nano-GISAXS/GIWAXS Thermal Behavior. Nanofocused X-ray measurements were carried out on samples after annealing at 100 °C (Figure 9). A substantial improvement of the microstructure of the AuNPs/P3HT 10/90 wt % sample was found (Figure 9a), possibly linked with its superior electrical performance, as well as local heating during device performance.⁷⁰ At 70 and 90% AuNPs loading (Figure 9b,c), both the AuNPs 111 ring and the P3HT 100 structures were clearly visible, resulting in higher stability, with only minor changes upon annealing. Pristine AuNPs–L4 annealed up to 100 °C (Figure 9d) showed that interparticle order was

maintained, with little or no variation with temperature. Thus, also in the case of thermally treated samples, the 2D pattern of AuNPs/P3HT 10/90 wt % strongly supported the electrical measurement results: the more homogeneous distribution of AuNPs in the P3HT matrix resulted in enhanced signals from both the P3HT and the AuNPs, indicating the formation of improved interconnectivity and ordered arrangement.

4. CONCLUSIONS

Colloidal, hydrophobic gold nanoparticles (AuNPs) in the (3.3 ± 1.1) nm size range were synthesized in the presence of platinum-containing polyyne with different chain lengths and incorporated into a poly(3-hexylthiophene-2,5-diyl) (P3HT) matrix for potential optoelectronics and storage device uses. Organometallic dithioacetate *trans* square-planar Pt(II) complexes containing 4,4'-diethynylbiphenyl (DEBP) as π -conjugated rigid spacer with different numbers of Pt centers (Pt-DEBP_{*n*}, *n* = 3, 4, 6) were chosen for covalent stabilization of gold colloids via Au-S bond, as detected by infrared and SR-XPS studies. Each of them allowed the formation of interconnected AuNPs with different NP-NP distances. Upon covalent attachment to AuNPs, excitation either at the ligand absorption maxima or at the LSPR band (530 nm) revealed additional emissive pathways, compared to the pristine ligand and AuNP systems, including long-wavelength emission (~ 670 nm) attributed to enhanced rigidity and suppressed non-radiative decay in the AuNPs. Blending AuNPs-Pt-DEBP_{*n*} with regioregular P3HT produced nanocomposites with a mean thickness of (3 ± 1) nm and uniform distribution of AuNPs within the polymer matrix, as evidenced by DLS and AFM, indicating a good miscibility between counterparts. Quantitative photoluminescence analyses demonstrated that the incorporation of AuNPs-L4 did not induce significant PL quenching in P3HT, promoting instead an enhancement of the radiative emission, consistent with plasmon-assisted fluorescence enhancement rather than nonradiative energy transfer processes.

At room temperature, electrical I vs V measurements (± 10 V range) were carried out on AuNPs/P3HT blends with different compositions (10/90 to 90/10 wt %). AuNPs-L4/P3HT 10/90 wt % represented the best composition, showing an improvement of the electrical conductivity with respect to the pristine polymer of about 30 times, and a reduced optical band gap ($2.13 \rightarrow 2.06$ eV). GIWAXS and nanofocused GIWAXS studies further supported the electrical results, revealing a composition-dependent structural and thermal stability, with the AuNPs-L4/P3HT 90/10 wt % blend with an enhanced electronic coupling due to a homogeneous distribution and interconnectivity of AuNPs within P3HT, and improved microstructure ordering upon mild annealing.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.6c02966>.

Characterizations of AuNPs-4BBT; characterizations of AuNPs-DDT; synthesis and characterizations of *cis*-, *trans*-[Pt(PBu₃)₂Cl₂]; synthesis and characterizations of chlorinated Pt-DEBP_{*n*} oligomers and free DEBP; synthesis of thioacetate S-Pt-DEBP_{*n*} ligands; FTIR spectra of Pt-DEBP₆ and L6 free ligand; excitation spectra of AuNPs-L3, AuNPs-L4, and AuNPs-L6;

EDX spectrum of AuNPs-L4; FTIR and Far-IR spectra of AuNPs; SR-XPS spectra of AuNPs-L3; C 1s SR-XPS spectra of AuNPs-L6; AFM 3D topography of AuNPs-L4/P3HT 50/50; I/V measurements of AuNPs/P3HT blends; electrical measurements of regioregular pristine P3HT, free Pt-DEBP₄, AuNPs-4BBT, and AuNPs-DDT; Tauc's plot of P3HT and AuNPs-L4/P3HT; full photoluminescence spectra of AuNPs-L4, P3HT, and AuNPs-L4/P3HT 10/90 blend; qualitative photoluminescence spectra of pure P3HT, AuNPs-L4/P3HT 10/90, and AuNPs-L4/P3HT 70/30; spectral data of [Pt(PBu₃)₂Cl₂], Pt-DEBP_{*n*} and S-Pt-DEBP oligomers (Table S1); summary of the optical properties of Pt-DEBP_{*n*} and AuNPs (Table S2); and SR-XPS data of AuNPs-L3 and AuNPs-L6 (Table S3) (PDF)

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Notes

The authors declare no competing financial interest.

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