

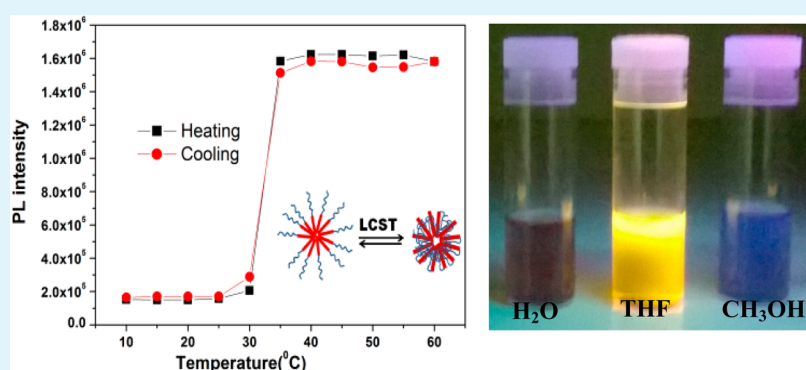
Amphiphilic and Thermoresponsive Conjugated Block Copolymer with Its Solvent Dependent Optical and Photoluminescence Properties: Toward Sensing Applications

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Supporting Information



ABSTRACT: Herein, we present a new class of amphiphilic, thermoresponsive rod–coil conjugated block copolymer having regioregular poly(3-hexyl thiophene) and poly(*N*-isopropylacrylamide). Optical and luminescence properties of these polymers significantly depend on the self-assembled nanostructures formed in different solvent and are easily tailored by changing the solvent composition or external stimuli like heat. Unique optical and electronic properties of this block copolymer are believed to make it promising for applications like sensor, fluorescence thermometer, optoelectronic, and bioelectronics devices.

KEYWORDS: conjugated polymer, amphiphilic, thermoresponsive, block copolymer, polythiophene, poly(*N*-isopropylacrylamide)

INTRODUCTION

Design and synthesis of new conjugated polymeric materials with novel functionality and wide processability has generated tremendous research attention because of their enormous potential applications in sensors, energy storages, corrosion inhibitors, optoelectronic devices, etc.^{1–5} Particularly, there is a significant demand of water-soluble conjugated polymeric materials related to their applications achieved from environmentally friendly steps and applications centered on their use in biological environments.⁶ Block copolymers where the functionality of the individual blocks are varied independently, self-assemble into fascinating set of periodic nanostructures and are very attractive targets to device materials where precise control over nanoscale organization is crucial.^{7–11} Synthesizing new conjugated block copolymer with varying functionality is one of the most convenient ways to manipulate the optical and electronic properties of a conjugated polymer in the rapid optimization manner.^{12,13} Poly(3-hexyl thiophene) (P3HT) is one of the widely studied conjugated polymers and workhorse for polymeric transistors and photovoltaics.¹⁴ P3HT has been incorporated into different types of block copolymers such as P3HT-*b*-polylactide, P3HT-*b*-poly(4-vinylpyridine), P3HT-*b*-polystyrene, P3HT-*b*-fullerene, P3HT-*b*-poly(acrylic acid) and

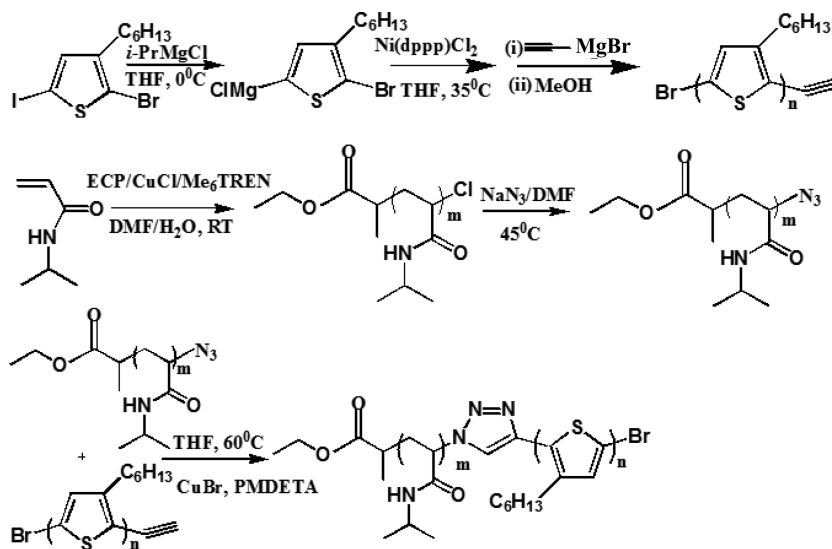
others.^{13,15–26} Within these block copolymers, some are amphiphilic in nature where the P3HT is combined with hydrophilic polymers like poly(ethylene oxide)¹³, poly(acrylic acid)²⁵ and poly(4-vinylpyridine).²⁶ These copolymers are generally synthesized using a grafting-from approach, where an end-functionalized polythiophene is acted as a macroinitiator for the chain extension polymerization of a second block. A major drawback to this strategy is the requirement of multiple post polymerization modifications as the requisite initiator must be attached to the end of the P3HT chain. A convenient alternative approach is to use a grafting-to technique, where the individual constituent homopolymers are independently prepared and subsequently connected together by Cu-catalyzed “click” azide–alkyne cycloaddition²⁷ which is both high yielding and functional group tolerant.²¹ Earlier efforts were made to develop thermally responsive polythiophene based copolymer by grafting thermoresponsive polymer on the

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Scheme 1. Reaction Scheme for the Synthesis of P3HT-*b*-PNIPAM

backbone of regioregular polythiophene,^{28,29} which is not a proper semiconducting material and restricts its applications.

Here, a novel class of amphiphilic, thermosensitive rod-coil conjugated block copolymer (P3HT-*b*-PNIPAM) composed of regioregular P3HT and a thermoresponsive polymer poly(*N*-isopropylacrylamide) (PNIPAM) has been synthesized in order to manipulate the properties of P3HT. The optical and luminescence property of P3HT-*b*-PNIPAM is different from P3HT and deeply depends on the nature of the solvent or composition in a mixed solvent. P3HT-*b*-PNIPAM shows lower critical solution temperature (LCST), which is detected from both UV-vis and luminescence studies.

EXPERIMENTAL SECTION

Materials. All chemicals including magnesium, 1-bromohexane, 3-bromothiophene, Na₂SO₄, *N*-bromosuccinimide, Na₂S₂O₃, KOH, Iodine, iodobenzene diacetate, 1,3-bis(diphenylphosphino)propanenickel(II) chloride [Ni(dppp)Cl₂], *t*-BuMgCl, ethynylmagnesium bromide, *N*-isopropylacrylamide, tris(2-aminoethyl)amine, formaldehyde, formic acid, CuCl, ethyl-2-chloro-propionate, and DMF NaN₃ were purchased from Sigma-Aldrich Pvt. Ltd. and used as received. Other solvents like THF, Ether, Methanol, Chloroform etc. were obtained from Rankem. THF was dried over Na under inert condition and used immediately for reactions. Copper(I) chloride (CuCl) was purified by washing with glacial acetic acid three times and twice with diethyl ether. *N*-Isopropylacrylamide was recrystallized twice from benzene/hexane (65:35 v/v) prior to use. All glass apparatus needed for polymerization were heated, cooled down under argon atmosphere and all reactions were performed in Schlenk line.

Characterization. Fourier transform infrared (FTIR) spectra in the region of 4000–500 cm⁻¹ were recorded at room temperature using KBr pallet of the samples in a PerkinElmer FTIR spectrometer [Spectrum two]. Nuclear magnetic resonance (NMR) spectra were obtained on a 500 MHz Bruker instrument. Chemical shifts were expressed in parts per million (*d* scale) relative to the internal standard tetramethylsilane (*d*_{1/4} 0.00 ppm) for ¹H NMR spectra. The number-average molecular weight (*M*_n) and polydispersity index (*M*_w/*M*_n) of P3HT samples were determined by Shimadzu prominence Gel Permeation Chromatography system in THF as solvent. The columns were calibrated against polystyrene standard samples. For PNIPAM and PNIPAM-*b*-P3HT, DMF was used as solvent and the columns are calibrated against PMMA standard.

Matrix assisted laser desorption ionizations spectroscopy with time-of-flight detection mass spectroscopy (MALDI-TOF MS) measurements were done on a Bruker Reflex III using dithranol as matrix and a

mixture of 1000:1 (Matrix: Polymer). The laser intensity was set to around 70%. UV-vis absorption studies were carried out at room temperature on a UV-vis spectrophotometer (Hewlett-Packard, model 8453) from 300 to 1000 nm using a quartz cell (10 mm path length). The spectra were subtracted by the background UV-vis spectra of the same solvent. The UV-vis spectra in the solid state were recorded from the thin film prepared by spin-casting of the chloroform solution on a quartz substrate. Emission experiments of the above spin-casted thin films were performed in a Horiba Jobin Yvon (Fluoromax-3) luminescence spectrometer with an excitation wavelength 490 nm at a 45° angle of the thin film plane with the excitation beam. PL spectra of the solutions were performed taking the solution 1 mg/mL in a quartz cell of path length 10.00 mm and the excitation wavelength is 430 nm. Thin films were prepared from P3HT-*b*-PNIPAM solution (5 mg/mL) by spin-coating on thoroughly cleaned patterned ITO-coated glass substrate at the speed 2000 rpm. The samples were dried at 60 °C for an additional 3 h in a vacuum oven for complete removal of the solvent. A thin layer of Al acting as the top electrode was deposited on the thin film. *I*-*V* characteristics of thin film were measured using a dc source electrometer (Keithley model 617) by interfacing with a computer. Atomic force microscopy (AFM) topography was carried out in a Dimension 3100 scanning force microscope (Digital Instruments, Inc., Santa Barbara, CA) in the tapping mode. The tip characteristics were spring constant 1.5–3.7 N m⁻¹, resonant frequency 45–65 Hz, and tip radius about 10 nm. Dynamic light scattering (DLS) experiments were done in a Malvern instrument. For temperature-dependent study, the solution (1 mg/mL) was heated from 25 to 45 °C at a rate of 5 °C/min. Before each measurement, the solution was allowed to stand for 5 min at the particular temperature.

Synthesis of Azide End-Functionalized Poly(*N*-isopropyl) Acrylamide (PNIPAM-N₃). In a typical polymerization method,³⁰ 1g (8.84 mmol) of NIPAM was taken in Schlenk tube and then added to DMF/H₂O in 1:1 ratio. The mixture was degassed by bubbling with nitrogen for 30 min under magnetic stirring. Required amounts of CuCl (0.0302 mmol, 2.98 mg) and degassed Me₆TREN (0.0302 mmol, 8.5 μL) were added into the reaction mixture under nitrogen atmosphere. After that, degassed ECP (Ethyl-2-chloro-propionate) (0.0302 mmol, 3.847 μL) was added to the reaction mixture by a microsyringe. The polymerization was initiated at room temperature and the reaction mixture was kept for 4 h. After that, the reaction was ceased using liquid nitrogen and left for defreezing. The polymerization was stopped by exposing the mixture to air and added 1 to 2 mL H₂O. The solvent was removed by using liquid nitrogen trap under vacuum and the reaction mixture was dissolved in THF. Copper salt from the reaction mixture was removed by passing the THF solution through

basic alumina column. The polymer was purified by precipitation with excess amount of hexane for 3 times. Then polymer was kept inside a vacuum oven for drying 24 to 48 h at 50 °C (yield 85%). The molecular weight of the polymer was calculated by GPC, $M_n = 33\,000$ g/mol, PDI = 1.20. After synthesizing chloro-end functionalized PNIPAM, it was further converted to PNIPAM- N_3 by the following procedure. In a 25 mL round-bottom flask, PNIPAM-Cl (0.850 mg), DMF (7 mL), and NaN_3 (14 mg, 0.215 mmol) were added. The reaction mixture was stirred at 45 °C for 48 h. After removing DMF at reduced pressure, the remaining portion was diluted with THF, and it was precipitated into an excess of anhydrous diethyl ether. Obtained precipitate were redissolved in THF, passed through a neutral alumina column to remove residual sodium salts and was dried overnight in a vacuum oven for 24 h (yield: 90%). The polymer was characterized by NMR and the end functionalization was checked by FTIR (see Figure S7 in the Supporting Information).

Synthesis of P3HT-Alkyne Terminated. The detailed synthesis and characterization of monomer 2-bromo-3-hexyl-5-iodothiophene is given in the Supporting Information. The typical synthesis procedure³¹ of P3HT-alkyne terminated is as follows. In a Schlenk flask, 1.865 g (5 mmol) of 2-bromo-5-iodo-3-hexylthiophene monomer was taken into highly pure argon atmosphere and evacuated under reduced pressure to remove moisture and oxygen inside the flask. Fifty milliliters of THF was added and the solution was stirred at 0 °C under Argon. Isopropylmagnesium chloride in THF (2.5 mL, 5 mmol) was added dropwise and allowed to react for 30 min at 0 °C. Next, the solution was heated to 35 °C followed by the addition of Ni(dppp)Cl₂ (54.2 mg, 0.1 mmol). The resulting mixture was stirred for 30 min, cooled to 0 °C and further reacted with 0.5 M ethynylmagnesium bromide (5 mL, 2.5 mmol) for an additional 10 min. The reaction mixture was quenched in methanol to receive a dark-purple solid, which was filtered and washed with excess methanol. The oligomer or low molecular weight fraction was removed by successive washing of the product with hexane and dried under vacuum to yield 0.40 g of P3HT-alk (50% yield). GPC: $M_n = 13\,100$ g/mol, PDI = 1.47. ¹H NMR (CDCl₃) 6.98 (1H, s, CH_{aro}), 3.52 (s, 1 H, ≡C-H), 2.8 (2H, t, CH₂-(CH₂)₄-CH₃), 1.70 (2H, m, CH₂-CH₂-(CH₂)₃-CH₃), 1.44–1.35 (6 H, m, CH₂-CH₂-(CH₂)₃-CH₃), 0.91 (3H, t, CH₂-(CH₂)₄-CH₃).

Synthesis of P3HT-*b*-PNIPAM. The typical synthesis procedure of the P3HT-*b*-PNIPAM is as follows (Scheme-1). Into a 25 mL Schlenk flask were added 221.06 mg (16.87 μmol) of alkyne-terminated P3HT, 3.873 mg (27 μmol) of CuBr, 500 mg (13.5 μmol) of PNIPAM- N_3 and 30 mL of dry THF. The tube was degassed by three freeze-thaw cycles in liquid N₂ and then 5.629 μL (27 μmol) degassed PMDETA was added to the reaction mixture and refluxed at 60 °C for 24 h. After opening the reaction mixture in air, it was further diluted with THF and passed through neutral alumina column to remove Cu catalyst. After that THF was removed by rotary evaporator and the polymer was further dissolved in DMF. The unreacted P3HT was removed by filtering the DMF solution. Finally, the purple color polymer was obtained by removing DMF in rotary evaporator and drying the sample in a vacuum oven for 48 h at 60 °C (60% yield). The resulting block copolymer was further characterized by GPC and NMR. ¹H (see Figure S5 in the Supporting Information) (CDCl₃) 6.98 (1H, s), 2.80 (t, 2H), 2.8–0.89 (m, aliphatic H of PNIPAM and P3HT), 7.78 (s, 1H, triazole -CH-), 4.0(m, 1H, (CH₃)₂CHNH, PNIPAM).

RESULTS AND DISCUSSION

Scheme 1 depicts the straightforward route for the synthesis of copolymer P3HT-*b*-PNIPAM. From the monomer 2-bromo-5-iodo-3-hexylthiophene,^{31,26} P3HT-alkyne terminated (P3HT-alk) has been successfully prepared by quenching the polymerization with ethynylmagnesium bromide. The incorporation of ethynyl terminal group has been checked by ¹H NMR spectrum (Figure 1, singlet at 3.52 ppm).²⁶ MALDI-TOF MS measurements further (see Figure S6 in the Supporting

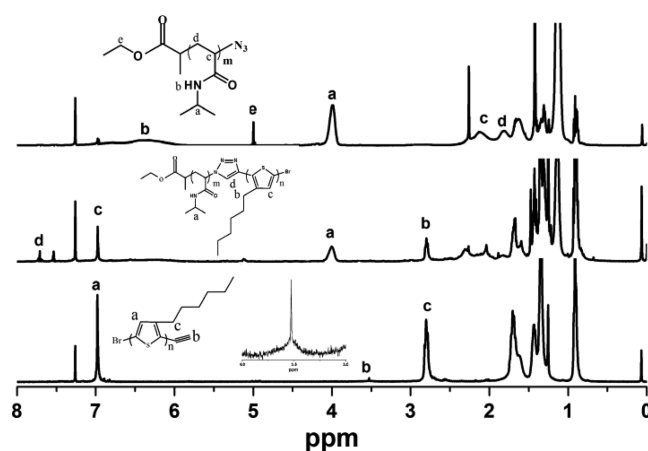


Figure 1. ¹H NMR spectra of P3HT-alk, P3HT-*b*-PNIPAM, PNIPAM- N_3 in CDCl₃.

Information) confirm the successful synthesis of P3HT with sufficient end (~85%) termination by ethyne group and the termination occurs at one side of P3HT.²⁶ The number-average molecular weight (M_n) and polydispersity index (PDI) were estimated to be 13,000 and 1.47 by GPC. The other block, azide-end functionalized PNIPAM, was synthesized by standard atom transfer radical polymerization (ATRP) using ECP (Ethyl-2-chloro-propionate) as initiator and CuCl/Me₆TREN system as catalyst.³⁰ Conversion of end chloro group to azide was performed by reaction with NaN_3 and characterized by FTIR (see Figure S7 in the Supporting Information). P3HT-*b*-PNIPAM was prepared successfully by connecting two homopolymers through Cu-catalyzed click reaction (for details, see the Supporting Information). The presence of the triazole proton at $\delta = 7.78$ ppm,^{26,32} as well as the disappearance of both ethynyl proton at ($\delta = 3.52$ ppm) in ¹H NMR (Figure 1) and the azide stretching frequency ~ 2110 cm⁻¹ in FTIR spectra³³ (see Figure S7 in the Supporting Information) confirm the successful synthesis of P3HT-*b*-PNIPAM. The M_n and PDI of P3HT-*b*-PNIPAM are around 44,000 and 1.4 respectively. At room temperature, the synthesized P3HT-*b*-PNIPAM is soluble/dispersible in several solvents such as chloroform, THF (good solvent for both the block), and water, methanol, DMF (poor solvent for P3HT) (Figure 2a and Figure S9 in the Supporting Information). This wide range solubility is due to the amphiphilic nature of the block copolymer and solutions display different colors typically orange in good solvent and purple color in poor solvent for P3HT. Nature of salvation is clearly manifested in AFM topology (Figure 2c, d). In THF, good solvent for both the blocks, P3HT-*b*-PNIPAM forms phase separated nanostructure characteristics of block copolymers, which is due to the immiscibility of P3HT and PNIPAM segments.¹³ In non-selective polar solvent like water, P3HT-*b*-PNIPAM forms self-assembled into core/shell-type nanostructure with hydrophobic P3HT in the core and hydrophilic PNIPAM in the shell. The Z-average particle size of P3HT-*b*-PNIPAM in water and methanol are 129 and 167 nm, respectively (see Figure S17 in the Supporting Information). The higher Z-average particle size of P3HT-*b*-PNIPAM in methanol compared to water may be explained from the higher solubility of the PNIPAM in methanol resulting more extended chains and formation of larger aggregates.

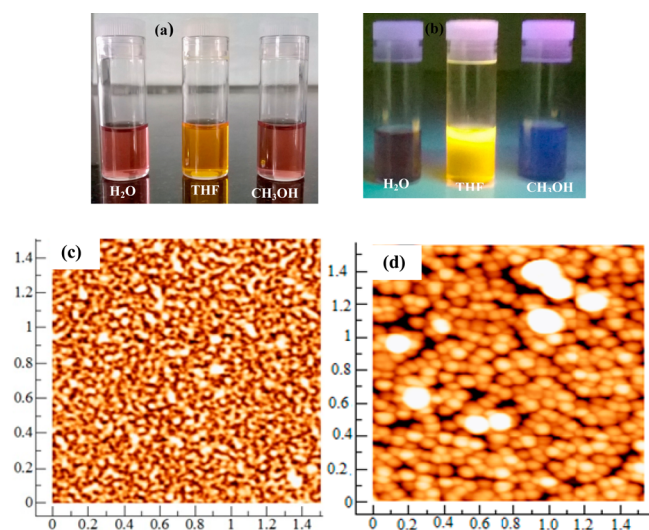


Figure 2. (a) color of the P3HT-*b*-PNIPAM in various solvent, (b) distinct color emission under UV illumination, (c, d) AFM phase images of P3HT-*b*-PNIPAM thin films deposited from (c) THF and (d) water.

UV-vis spectra of P3HT and P3HT-*b*-PNIPAM in various solvent are presented in Figure 3a. As it can be seen in

chloroform, P3HT exhibits a single peak with λ_{max} at 449 nm assigned as the $\pi-\pi^*$ transition which is blue-shifted to 429 nm upon grafting with PNIPAM. The spectral shift is the result of change in the effective conjugation length as the P3HT chains adopt more coil conformation due to the steric interaction with the PNIPAM chain as well as change in the solvophobic environment near the polythiophene main chain.²⁸ In THF, the UV absorption peak of block copolymer are trifurcated into three different peaks at 374, 396, and 425 nm having almost equal intensity with additional shoulders at 357 and 457 nm. In solvent like methanol and water where P3HT is not hydrated, two absorption peaks at 429 and 510 nm are observed. The peak at 429 is assigned to $\pi-\pi^*$ transition of P3HT and 510 nm is possibly originated from the aggregation of P3HT-*b*-PNIPAM. But in case of solvent like chloroform or THF where the P3HT is fully hydrated shows no additional peak around 500 nm originated from aggregation of P3HT-*b*-PNIPAM. The different λ_{max} for different solvent is result of the different conformation adopted by P3HT-*b*-PNIPAM causing change in the effective conjugation length as evidenced by AFM study. Interestingly, it is observed that all the UV-vis spectra of the block copolymer shows additional vibronic peaks (which is absent in P3HT) arising from strong interchain $\pi-\pi$ interaction induced by PNIPAM. As it is expected, the P3HT thin film (Figure 3b) shows the $\pi-\pi^*$ absorption peak at 514 nm with a

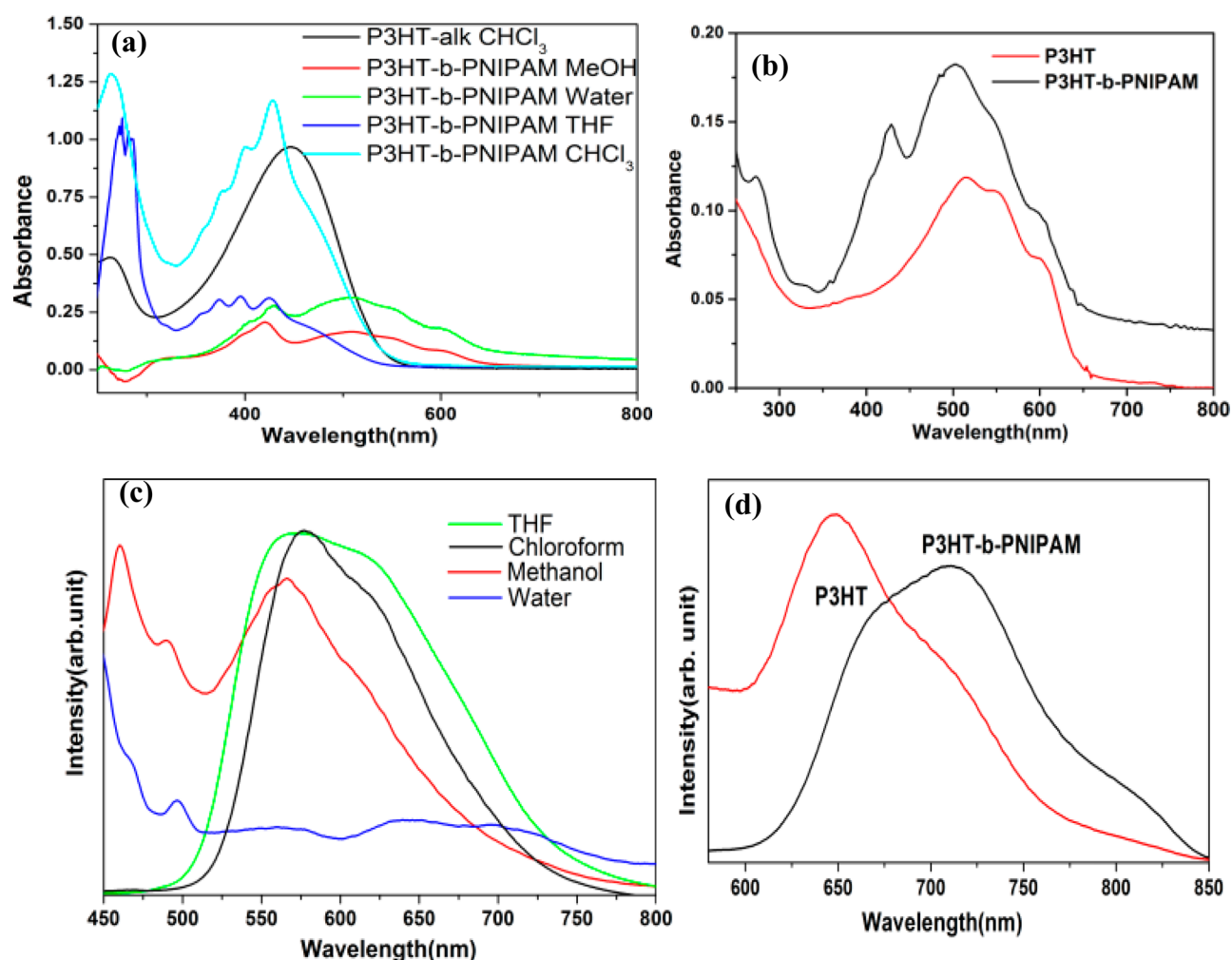


Figure 3. (a, b) UV-vis and (c, d) PL spectra of P3HT and P3HT-*b*-PNIPAM in solution and thin film state.

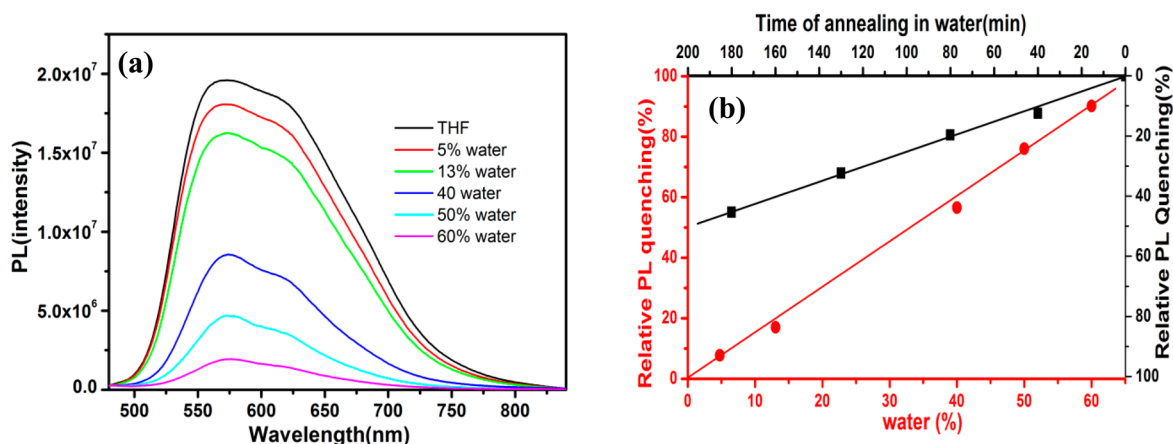


Figure 4. (a) PL quenching after addition of water in different proportion in THF solution of P3HT-*b*-PNIPAM (b) Relative PL quenching (%) vs % of water in a THF water mixture (red) and relative PL quenching (%) vs annealing time in water of a thin film of the block copolymer (black).

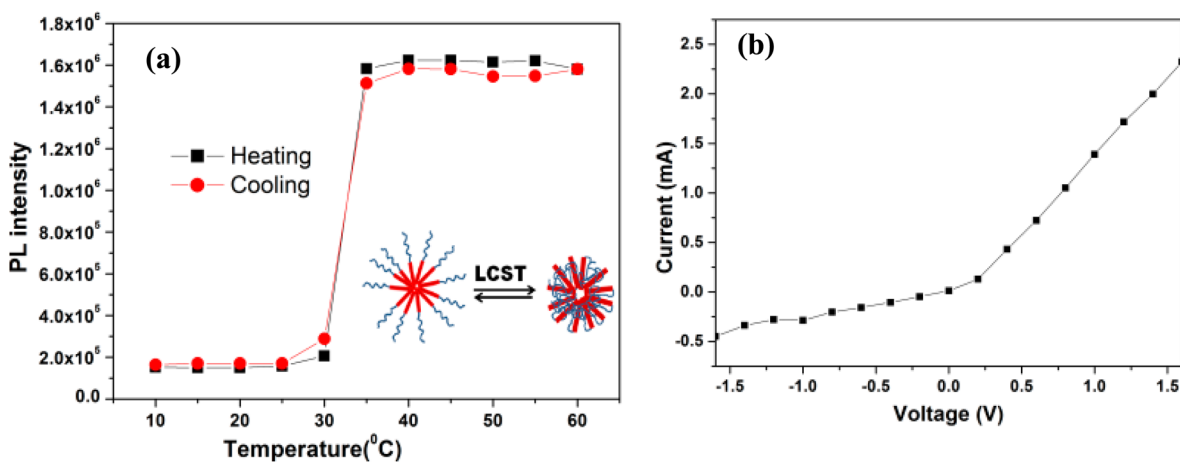


Figure 5. (a) Variation in PL intensity at different temperatures of P3HT-*b*-PNIPAM solution in water. (b) *I*–*V* characteristics curve of P3HT-*b*-PNIPAM.

red shift from the corresponding solution absorption at 449 nm because of the strong interchain interaction in thin film. The main absorption peak of the P3HT-*b*-PNIPAM film centered at 503 nm (with an additional peak at 429 nm), 13 nm below that of the P3HT thin film, though it is also red-shifted from the corresponding solution absorption at 429 nm. The spectral shift in block copolymer to the lower wavelength is due to the decrease of effective conjugation length caused by different type of assembly in thin film compared to P3HT. The block copolymer shows solvent dependent color emission, orange in THF, purple in water and blue in methanol (Figure 2b). Figure 3c demonstrates the PL spectra of the block copolymer in four different solvents. The PL emission peaks are 577, 574, and 566 nm (with additional intense peaks at 460 and 491 nm) for chloroform, THF and methanol, respectively. In the case of water, the PL intensity substantially decreases and the peak becomes broader and red-shifted. The different color emission originates from different type of nanostructures attributed to the different conjugation length formed in different solvents.^{28,34} For methanol, the additional emission peaks at 460 and 491 nm contribute to the blue color emission. The dramatic decrease of PL intensity in water is due to the increased interchain Förster energy transfer from more close proximity of the P3HT chains in micelles. In thin film state P3HT generates a peak at 648 nm, whereas the peak shifted to

711 nm in case of P3HT-*b*-PNIPAM (Figure 3d). The red shift in PL spectra is due to the energy transfer to low energy sites³⁴ in the packed P3HT chains induced by PNIPAM. Figure 4a shows the PL quenching (Figure 4b, relative PL quenching) with % of water in the THF water mixture for varying composition. As expected, the PL intensity of the THF solution reduces with increase of the amount of water without any significant change in the emission peak. Figure 4b also demonstrates the relative PL quenching of the block copolymer thin film vs annealing time in water up to 3 h. From both the cases, it is clear that the plots are almost linear. It is a very interesting observation that predicts the potentiality of this material for detecting analytes. Figure 5a displays the temperature dependence PL intensity for P3HT-*b*-PNIPAM in water upon heating. A sharp reversible change in the PL intensity between 30 to 35 °C has been observed. The sudden increase of the PL intensity is due to reversible conformational change of the PNIPAM from an extended hydrated coil to a collapsed hydrophobic globule³⁵ (as shown in the inset of Figure 5a) at LCST. In collapse conformation, the PL intensity will be high as the intercalated PNIPAM chain will separate the P3HT chains from each other and prevent PL quenching through interchain mechanism. The reversible change of conformation from an extended hydrated coil to a collapsed hydrophobic globule³⁵ near LCST is also supported by

temperature dependent DLS study (Figure S18 and S19 in the Supporting Information). There is a sharp decrease in the average particle size from 126 to 101 nm on heating from 30 to 35 °C. On further heating the average particle size again increases (at 40 °C, 153 nm) as these collapse chain conformation is unstable and forms larger aggregation. The water solution of the polymer also shows sudden increase of absorption intensity at 510 nm between 30 to 35 °C upon heating (see Figures S10 and 11 in the Supporting Information). Both the observations clearly demonstrate the potentiality of P3HT-*b*-PNIPAM for fabrication of delicate temperature sensor. *I*–*V* characteristics of the thin film device formed into block copolymer is presented in Figure Sb. The nonlinear *I*–*V* characteristics curve shows semiconducting behavior and confirms its applications for electronic and optoelectronic devices.³⁶

CONCLUSION

In summary, an amphiphilic, thermoresponsive rod–coil conjugated block copolymer P3HT-*b*-PNIPAM has been successfully synthesized by a Cu-catalyzed click reaction which couples ethynyl-terminated regioregular poly(3-hexylthiophene) and azide-terminated PNIPAM. In nonselective solvent, the block copolymer is self-assembled into phase separated nanostructure whereas in polar solvent like water aggregated into core/shell–type nanostructure. The optical and luminescence property of the block copolymer is different from its pure analogue and highly depends on the nature of the solvent or composition in a mixed solvent. Temperature dependent photoluminescence and UV–vis study clearly indicate that between 30 and 35 °C in water P3HT-*b*-PNIPAM undergoes a reversible phase transition from a collided structure to collapsed globule. By varying the composition of the P3HT block in the block copolymer one can further tune the solubility, nanostructured morphology and thereby can tune its optical and electronic properties in a controlled manner. We believe that the unique optical and electronic properties will make it promising for many applications like sensor, fluorescence thermometer, optoelectronic, and bioelectronics devices.

ASSOCIATED CONTENT

Supporting Information

Detailed synthesis, characterization like NMR, UV–vis, FTIR, GPC, IV, etc. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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