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Multiresponsive of highly water-soluble poly(3-hexylthiophene)-*block*-poly(phenylisocyanide) block copolymers†

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ABSTRACT. Design and synthesis of highly water-soluble conjugated block copolymers with multi-responsive properties are of great interesting due to their potentials as solution processable semiconductor materials. Herein, we report on one-pot synthesis of well-defined block copolymers containing conjugated poly(3-hexylthiophene) (P3HT) and poly(phenyl isocyanide) (PPI) bearing hydrophilic tri(ethylene glycol) monomethyl ether chains. These block copolymers have good solubility in water and exhibit excellent thermoresponsive behavior. The lower critical solution temperature (LCST) in water can be facilely tuned through the variation on the concentration or polymer composition. Moreover, optical properties of the block copolymer were dependent on the solvents used owing to the distinct self-assembled structures. In $CHCl_3$, the P3HT-*b*-PPI block copolymer exhibit pH-responsive with the emission color shuttled between orange and blue upon alternate additions of trifluoroacetic acid and trimethylamine. In addition, such block copolymers were revealed to be good materials for living cell imaging.

Introduction

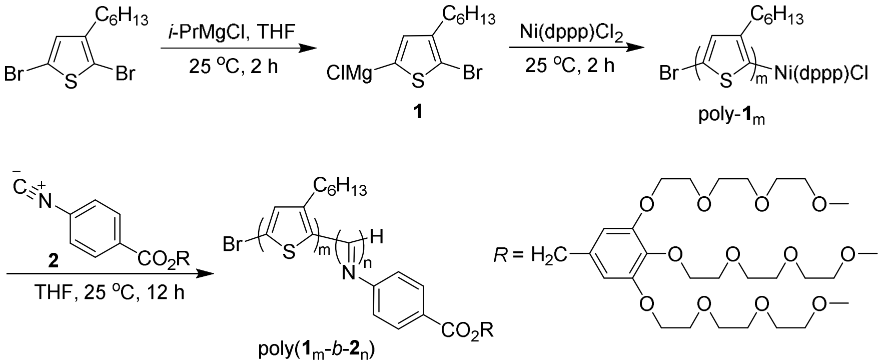
Solution-processable conjugated polymers have received considerable attentions in recent years due to their applications in optoelectronics and biosensory.[1] Highly water-soluble conjugated polymers are of great interesting, particularly in the applications that can benefit from environmentally friendly processing steps or those applications that focus on the use of conducting polymers in biological environments.[2] In this context, conjugated polymers with a wide variety of solubilizing groups are needed, including those made soluble in aqueous media without the use of ionic solubilizing groups.[3] Introduction of an environmental-stimulus coils onto a conjugated polymer to form a block copolymer not only improve the solubility but also provide additional interesting features because their nanostructures and photophysical properties can be significantly tuned by external stimuli, such as pH, temperature, light, etc.[4] Among the reported conjugated polymers, polythiophene (PT) and its derivatives have received considerable research attentions due to its excellent optoelectronic properties, environmental stability, and synthetic accessibility.[5] Regioregular PTs were usually prepared via a Ni-catalyzed Kumada catalyst-transfer polymerization (KCTP).[6] Taking advantage of the living nature of KCTP, a broad range of PT-containing block copolymers with PT covalently linked with a chemically different polymers was designed and synthesized.[7] However, most of these researches are focus on controlling the morphology to optimize the related optical and electronic properties.[8] Conjugated PT-based block copolymers with highly water-solubility and multiple responsive properties are rarely reported. Chen et al. developed a P3HT-*b*-poly(2-(dimethylamino)ethyl methacrylate) rod-coil block copolymers which exhibit both thermo- and pH-responsive properties.[9] Park and co-workers synthesized a poly(3-octylthiophene)-*b*-poly(ethylene oxide) copolymer which showed tunable emissions depending on solvent polarity and ionic additives.[10]

The PT-containing block copolymers were usually prepared through the coupling of a preformed homopolymer with appropriate end-functional group onto a PT bearing an complementary reactive terminus.[11] An efficient alternative is fabricating a specific initiator group on PT terminus that can further initiate a new polymerization of the second block.[12] However, such methodologies can be inefficient and usually require mass synthetic manipulations. Recently, we developed a novel synthetic approach for facile preparation of PT-containing block copolymers through the sequential block copolymerization of two different monomers in one-pot using a Ni(II) complex as a single catalyst. For example, Ni(II)-terminated poly(3-hexylthiophene) (P3HT) prepared by KCTP was directly chain-extended with phenyl isocyanide to give a well-defined P3HT-*b*-poly(phenyl isocyanide) block copolymer. Although the P3HT and poly(phenyl isocyanide) segments were polymerized via distinct mechanisms, the block copolymerization were revealed to proceed in living/controlled manners, afforded the block copolymer in high yields with controlled molecular weights (M_ns), narrow molecular weight distributions (M_w/M_ns) and tunable compositions.[13] Taking advantage of this synthetic method, a variety of P3HT-containing block copolymers was readily obtained including P3HT-*b*-poly(quinoxaline-2,3-diyl)[14] and P3HT-*b*-polyallene[15] copolymers. Among these block copolymers, the poly(phenyl isocyanide) segments have been the focus of intense research efforts due to theirs interesting rigid helical structure and applications in chiral recognition and supramolecular self-assembly.[16]

In this contribution, we report on one-pot synthesis of P3HT-*b*-poly(phenyl isocyanide) (P3HT-*b*-PPI) block copolymers containing regioregular conjugated P3HT and hydrophilic poly(phenyl isocyanide) bearing hydrophilic tri(ethylene glycol) monomethyl ether chains. The block copolymers have good solubility in most of organic solvents and importantly, highly-soluble in water. The concentration in water can be higher than 10.0 g/L. Very interestingly, the amphiphilic block copolymers behave multiple stimuli-responsive such as temperature, pH, and solvents. In addition, such block copolymer can be further utilized in living cell imaging.

Results and discussion

Polymer synthesis.



Scheme 1 One-pot synthesis of P3HT-*b*-PPI block copolymer

As illuminated in Scheme 1, amphiphilic P3HT-*b*-PPI block copolymers were prepared according the procedure we reported previously with slight modifications.[13] First, 2-bromo-3-hexyl-5-chloromagnesiothiophene (**1**) generated in situ from the reaction of 2,5-dibromo-3-hexylthiophene with *i*-PrMgCl in THF was polymerized using Ni(dppp)Cl_2 (dppp = 1,3-bis(diphenylphosphino)propane) as catalyst in THF at room temperature ($[\mathbf{1}]_0/[\mathrm{Ni}]_0 = 30$). When monomer **1** was complete consumed as indicated by size exclusion chromatography (SEC) analysis, the afforded Ni(II)-terminated P3HT ($M_n = 5.30 \times 10^3$ Da, $M_w/M_n = 1.36$) was treated with the phenyl isocyanide monomer (**2**) ($[\mathbf{2}]_0/[\mathrm{Ni}]_0 = 60$). The chain extended P3HT-*b*-PPI block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) was isolated in 86% yield over the two steps (the footnote indicates the initial feed ratio of monomer to catalyst). SEC traces of macroinitiator poly-$\mathbf{1}_{30}$ and the resulting poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) were displayed in Fig. 1, which indicate both polymers exhibit monomodal and symmetric elution peaks. Moreover, SEC chromatogram of the block copolymer was appeared at the higher molecular-weight region as comparing with its P3HT macroinitiator. The M_n of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) was estimated to be 2.40×10^4 Da, higher than that of the macroinitiator precursor ($M_n = 5.30 \times 10^3$ Da, $M_w/M_n = 1.36$) and kept the narrow M_w/M_n ($M_w/M_n = 1.22$). These studies suggest the one-pot block copolymerization of monomer **1** and **2** was succeed, afforded the expected P3HT-*b*-PPI block copolymer.

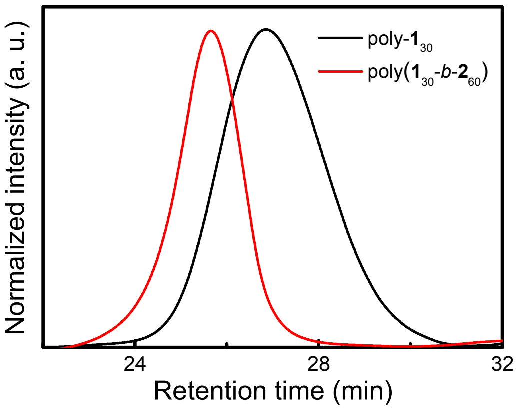


Fig. 1 Size exclusion chromatograms of the P3HT macroinitiator poly-$\mathbf{1}_{30}$ and the corresponding P3HT-*b*-PPI block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$). SEC condition: eluent = THF, temperature = 40 °C.

The chemical structure of the isolated block copolymer were further verified by ^{1}H NMR and FT-IR spectra. For comparison, homopolymer of **2**, poly-$\mathbf{2}_{30}$ was prepared according to a reported procedure.[17] ^{1}H NMR spectra of poly-$\mathbf{1}_{30}$, poly-$\mathbf{2}_{30}$ and poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) were shown in Fig. S1-S3 (see the ESI†). It was found that the ^{1}H NMR profile of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) is almost the superposition of that of the poly-$\mathbf{1}_{30}$ and poly-$\mathbf{2}_{30}$. The signals attributable to each segment could clearly be observed although the resonances of the PPI segment were relatively broad due its rigid helical conformation of the main chain. The block copolymer showed resonances at 6.97 ppm ascribe to the aryl proton of P3HT; and a series of resonances at 3.08−4.30 ppm come from tri(ethylene glycol) monomethyl ether chains of the PPI block. In addition, the block ratio of P3HT to PPI of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) copolymer determined by the integral analyses is about 1:2, which agree well with the initial feed ratio of the two monomers added to the reaction vessel. The FT-IR spectrum of the block copolymer shows intense absorptions at 1600 cm^{-1} corresponding to the vibration of C=N of the PPI backbone together with the vibrations come from P3HT segment (Fig. S4, see the ESI†). Collectively, these studies confirm the formation of expected P3HT-*b*-PPI block copolymer in one-pot via the sequential block copolymerization. Because such one-pot block copolymerization was proceed in a controlled chain-extension manner as we previously revealed, a series of P3HT-*b*-PPI block copolymers with different M_ns and narrow M_w/M_ns were readily synthesized under the same procedure just by varying the initial feed ratios of the two monomers and the catalyst (Table 1). The SEC chromatograms of the P3HT macroinitiators and the corresponding P3HT-*b*-PPI block copolymers were summarized in Fig. S5 (see the ESI†). Due to the amphiphilic nature, the synthetic block copolymers behave good solubility in most common organic solvents including $CHCl_3$, THF, acetonitrile, acetone, and methanol. Noted that the block copolymers have excellent solubility in water and the concentration can be as higher as 10.0 g/L. Probably this is one of the most highly water-soluble conjugated polymers that have been reported.

Table 1 Polymerization results for one-pot synthesis of P3HT-*b*-PPI block copolymers[a]

	poly-$\mathbf{1}_m$[b]		poly($\mathbf{1}_m$-*b*-$\mathbf{2}_n$)			Block ratio[e]
run	M_n[c]	M_w/M_n[c]	M_n[c]	M_w/M_n[c]	yield[d] (%)	m : n
1	5.30×10^3	1.36	2.40×10^4	1.22	84%	30 : 60
2	7.28×10^3	1.38	2.05×10^4	1.20	82%	40 : 40
3	9.20×10^3	1.35	2.62×10^4	1.19	86%	60 : 60
4	8.50×10^3	1.32	2.29×10^4	1.16	85%	50 : 40
5	1.12×10^4	1.30	2.17×10^4	1.18	83%	60 : 30
6	5.83×10^3	1.34	–	–	80%	30 : 0
7	–	–	1.45×10^4	1.25	85%	0 : 30

[a] The block copolymers were prepared according to Scheme 1 by first preparing macroinitiator poly-$\mathbf{1}_m$ of different M_ns, followed by the addition of **2** in one-pot. [b] The M_n and M_w/M_n of the macroinitiator were determined via SEC analysis of aliquots removed from the respective reaction mixture prior to the addition of **2**. [c] The M_n and M_w/M_n values were determined by SEC and are reported as their polystyrene equivalents. [d] Isolated yields over the two steps. [e] The block ratio of P3HT to PPI determined by ^{1}H NMR.

Thermoresponsive behavior of P3HT-*b*-PPI

With the aforementioned block copolymers in hand, efforts were then shifted toward the stimuli responsive behaviors. As shown in Fig. 2a, the synthetic block copolymers exhibit interesting heating induced phase transition. For example, a clear transparent aqueous solution of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) turned to turbid upon heating from room temperature to 65 °C. Transmittance (at 750 nm) versus temperature curves of this block copolymer in water was shown in Fig. 2a. The lower critical solution temperature (LCST) was estimated to be 57.8 °C. Note that the optical absorption edge of the P3HT-*b*-PPI block copolymer in water is around 650 nm and thus would not affect the observation of LCST by optical transmission at 750 nm. The optical transmittance curve of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) block copolymer upon heating and cooling cycle is reversible with some hysteresis, indicate the excellent thermoresponsive behavior of the synthetic block copolymer.

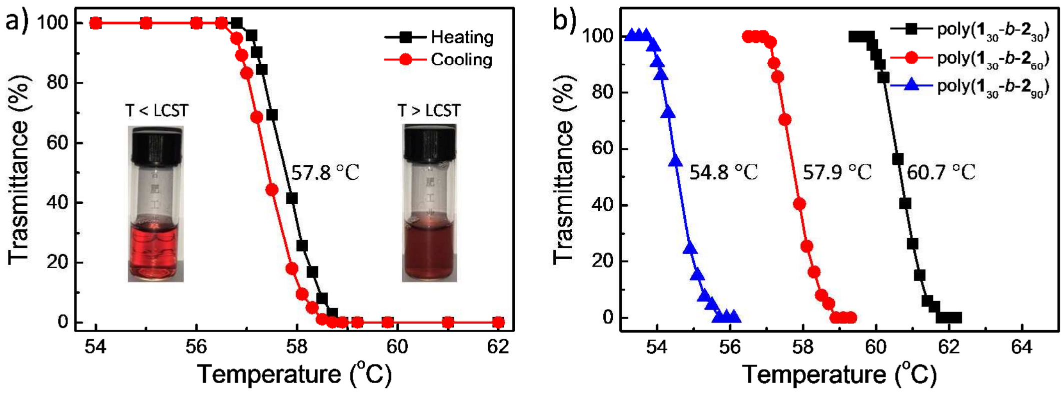


Fig. 2 (a) Photographs and transmittance versus temperature traces for poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in water (*c* = 0.5 g/L). (b) Transmittance versus temperature traces for solutions of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{30}$), poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$), and poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{90}$) in water (*c* = 0.50 g/L).

To get more details of the thermoresponsive property, three P3HT-*b*-PPI block copolymers poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{30}$), poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$), and poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{90}$) with the same chain length of P3HT but different in the chain length of PPI were prepared to disclose the influence of polymer composition on LSCT in water. The plots of transmittance versus of the temperature of those block copolymers in water at the same concentration were shown in Fig. 2b (*c* = 0.50 g/L). It was found that all these block copolymers exhibit excellent thermoresponsive properties in water upon heating from room temperature to 65 °C. The LCSTs for poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{30}$), poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$), and poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{90}$) in water were estimated to be 60.7, 57.9, and 54.8 °C, respectively. Thus, it can be concluded that the LCST of the P3HT-*b*-PPI block copolymer were dependent on the block composition, increase the chain length of the hydrophilic PPI segment will decrease the value of LCST. This result may be ascribed to that the longer hydrophilic segment, the easier interchain interaction and aggregation, which lead to the decrease of LCST value.

The dependence of the LCST on the concentration of the P3HT-*b*-PPI block copolymer in water was also investigated. As shown in Fig. 3a, the LCSTs of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in water was plotted against its concentrations. It was found that the LCST showed inversely correlation with the concentration, that is, increase the concentration of the block copolymer in water will decrease the LCST value of P3HT-*b*-PPI block copolymer. Probably, the higher concentration will facilitate polymer collapse and subsequent inter-chain aggregation of the PPI segment, which lead to the decrease of optical transmittance.

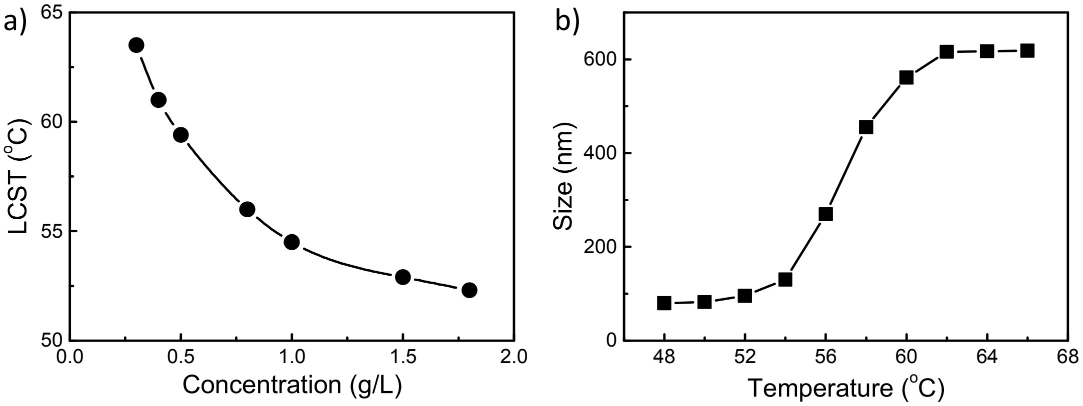


Fig. 3 (a) Plot of LCST values with the concentrations of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in water. (b) Plot of the sizes of the micelles of the temperature of the block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in water (c = 0.50 g/L).

The heating induced phase transition of the synthetic P3HT-*b*-PPI block copolymer in water was further confirmed by dynamic light scattering (DLS) analyses. Fig. 3b shows the hydrodynamic size of the aggregated formed from block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in water (c = 0.50 g/L) at temperature range of 48−66 °C. It was found that the hydrodynamic sizes of the block copolymer micelles are increase by elevated temperature, which is probably ascribe to the variation on the hydrophilic/hydrophobic balance of the tri(ethylene glycol) monomethyl ether chains on the PPI segment. The LCST for poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in water was estimated to be 57.7 °C by DLS, which agree well with that obtained from the plot of transmittance with temperature. At the temperature below LCST, the size of the block copolymer was estimated to be ca. 90 nm due to the formation of micelles in water (see below). When the temperature higher than LCST, the hydrodynamic size of the aggregates increased to ca. 600 nm due to formation of the interchain aggregations of the micelles.

Solvent effects.

Owing to the amphiphilic nature of the one-pot synthetic P3HT-*b*-PPI block copolymers, all the copolymers possessing good solvents in both polar and nonpolar solvents. However, the block copolymers exhibit interesting absorption and emission properties dependent on the solvents used. In the non-selective solvents, the solution color of the block copolymers is yellow, similar to that of the P3HT homopolymer. In solvents that selective to the hydrophilic PPI segment, the block copolymer gives purple colors (Fig. 4a). The absorption spectra of the block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in these solvents were shown in Fig. 4b. For example in THF and $CHCl_3$, the block copolymer showed an absorption maximum at 450 nm, mainly come from the P3HT segment (Fig. S6, see the ESI†). In CH_2Cl_2 solution, the absorption spectrum of the block copolymer showed new absorptions at 562 and 603 nm in addition to the absorption at 450 nm, indicative of the intermolecular π-π interactions of the P3HT block due the partially self-assembly of the block copolymer in this solvents. Interestingly, in the solvents of acetonitrile, methanol and water, the block copolymer showed strong absorptions at 523, 558, and 603 nm due the intense solvophobic and π-π interactions of the P3HT block.

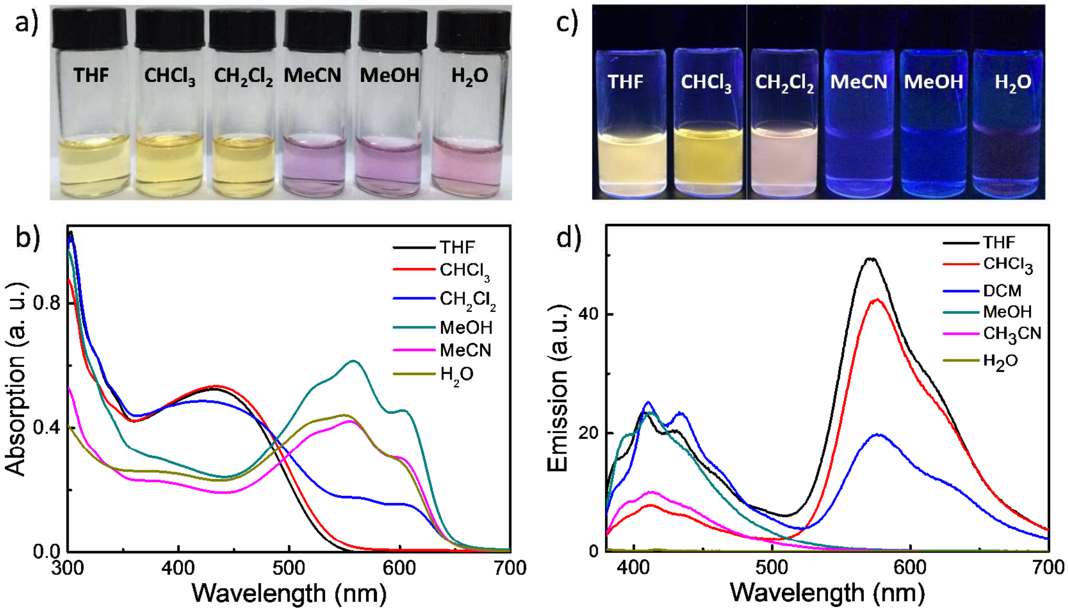


Fig. 4 Photographs of P3HT-*b*-PPI block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in different solvents at 25 °C under room light (a) and UV light at 365 nm (c) (c = 0.10 g/L). Absorption (b) and emission (d) spectra of the poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in different solvents at 25 °C (c = 0.10 g/L; λ_{exc} = 365 nm).

Remarkably, the emissions of the block copolymers were also depending on the solvents used. As shown in Fig. 4c, in non-selective solvents, the block copolymer exhibit orange emission under the illumination at 365 nm, similar to that of the P3HT homopolymer. However, it gives strong blue emission in the selective solvents such as acetonitrile and methanol. In water, the emission was almost completely quenched. The emission spectra of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in different solvents were shown in Fig. 4d. It was found that in non-selective solvents, the block copolymer exhibited strong emission at long-wavelength region with the maximum around 580 nm, accompanied by weak emissions at 392, 407, and 430 nm by excited at 365 nm. Thus it gives orange-red emission in these solvents. In CH_2Cl_2, the block copolymer showed emissions at both the short-wavelength region and long-wavelength, while the emission at 580 nm was substantially quenched, thus it showed a light orange emission. In the selective solvents such as acetonitrile and methanol, the block copolymer only exhibit emission at short-wavelength region (394, 413, and 435 nm), the emissions at the long wavelength region was completely quenched, and thus the block copolymer gives strong blue emissions. In water, the emissions of the block copolymer were completely quenched as revealed by the emission spectrum excited at 365 nm (Fig. 4d). Because the emission color of the P3HT-*b*-PPI block copolymer can be facilely tuned through the variation on solvent composition, a series of interesting light emissions can be readily achieved from poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in the mixture of THF and methanol under various volume ratios (Fig. S7-S9, see the ESI†).

The solvent-dependent absorption and emission properties of the one-pot synthetic P3HT-*b*-PPI block copolymer may be ascribed to the distinct self-assembled supramolecular structures in these solvents. To verify, the self-assembly morphologies of the poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in THF, methanol and water were investigated by DLS and transmission electron microscopy (TEM). As shown in Fig. 5a, DLS analyses revealed that the hydrodynamic diameters of the aggregates of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in THF is about 11 nm, suggesting the block copolymer was molecular dissolved in THF. However, the size was dependent on the concentration and can be increased to 20~30 nm at higher concentration due to the self-aggregation (Fig. S10, see the ESI†). In methanol and water, as shown in Fig. 5a, the diameters of the aggregates were respectively estimated to be ca. 120 and 90 nm. In these polar solvents, the block copolymer may self-assembled into micelles with the hydrophobic P3HT at the interior and the hydrophilic PPI at the exterior. The self-assembled morphologies of the block copolymer were further confirmed by TEM observations on the samples spin-casted from the solution of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in methanol and water at room temperature. The images were shown in Fig. 5b and 5c, which indicate the well-defined spherical nanoparticles were formed in both methanol and water. The diameters of the assembled supramolecular structures were estimated to be 123 nm in methanol and 91 nm in water with good homogeneity, which are consistent with those obtained from the DLS analyses. The interesting morphology of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) block copolymer in water was probably due to the formation of specific bilayered self-assembly structures (Fig. S11, see the ESI†).

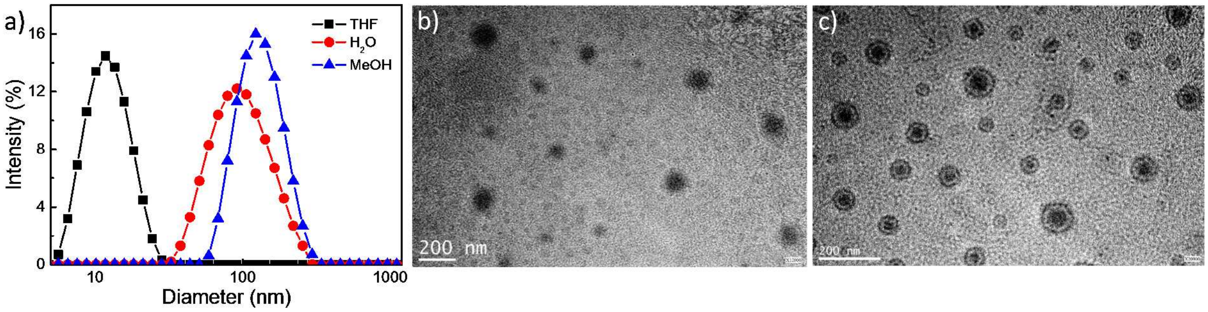


Fig. 5 (a) Dynamic light scattering curves of P3HT-*b*-PPI block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in THF, methanol, and water at 25 °C (*c* = 0.10 g/L). TEM images of the self-assembled structures of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in methanol (b) and water (c).

pH-Responsive.

Very interestingly, the one-pot synthetic P3HT-*b*-PPI block copolymers exhibit pH-responsive behavior in $CHCl_3$. For example, as shown in Fig. 6a, the orange color solution of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in $CHCl_3$ (*c* = 0.05 g/L) gradually turned to gray upon the addition of trifluoroacetic acid (TFA). The color was changed until the concentration of the TFA reach to 0.15 mM. Absorption spectra of the block copolymer in $CHCl_3$ also support this acid-induced color changes. The poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) exhibit strong absorption at 450 nm in $CHCl_3$, however, it gradually decreased upon the addition of TFA, accompanied by the new absorptions at 580 and 610 nm which were increased until the TFA was saturated (Fig. 6b). Interestingly, the acid-induced color and the absorption changes of the poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) block copolymer in $CHCl_3$ were reversible. As shown in Fig. 6a and 6b, neutralized the acidic solution of the block copolymer by trimethylamine (TEA), the color and absorption spectra can be recovered.

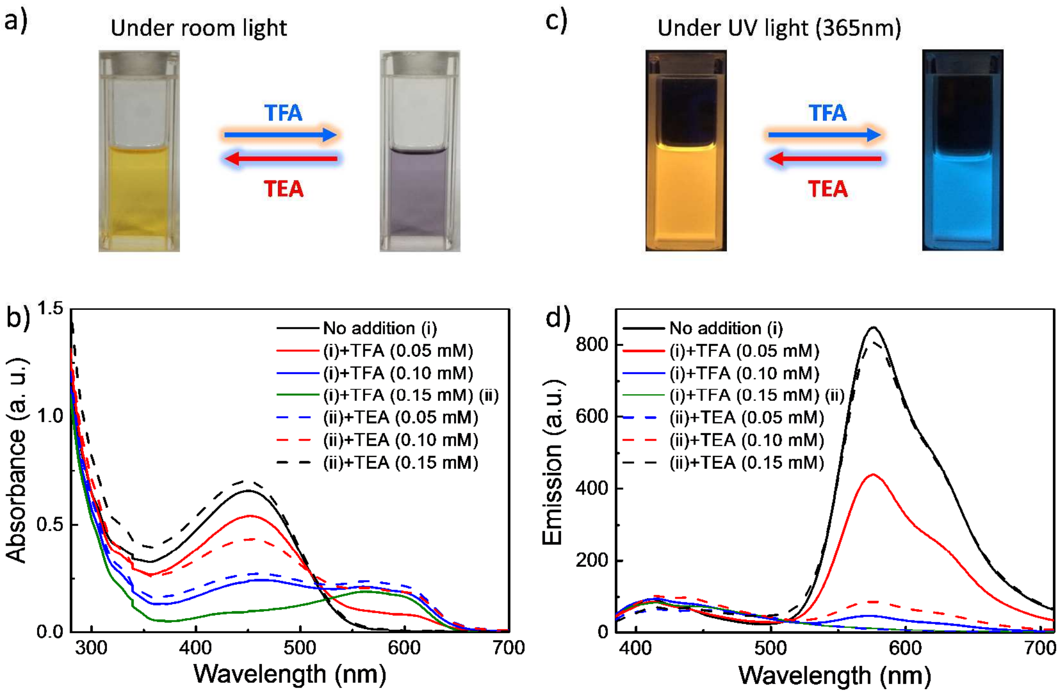


Fig. 6 Photographs of the P3HT-*b*-PPI block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in $CHCl_3$ (*c* = 0.05 g/L) upon alternate additions of TFA and TEA under room light (a) and UV light at 365 nm (c). Absorption (b) and emission (d) spectra of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in $CHCl_3$ upon alternate additions of TFA and TEA at 25 °C (*c* = 0.05 g/L).

The emissions of the poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) block copolymer also exhibit pH-responsive property in $CHCl_3$. As shown in Fig. 6c, under illuminated at 365 nm, poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) showed orange-light emission in $CHCl_3$. Upon addition of TFA, the orange emission gradually turned to blue. Neutralized the TFA in $CHCl_3$ solution by addition of TEA, the emission of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) can be gradually recovered, indicating the emission of the block copolymer is pH-responsive. The emission spectra of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in $CHCl_3$ upon additions of TFA and TEA also support the excellent pH-responsive behavior. As shown in Fig. 6d, the block copolymer showed intense emission at 580 and 640 nm, which were gradually quenched upon the addition of TFA. When the concentration of TFA is saturated, the emissions at the long-wavelength region were completely quenched, while the emission at the short-wavelength region were maintained. Thus, the block copolymer gives blue light emission by excited at 365 nm. When the acidic $CHCl_3$ solution was neutralized by TEA, the emission spectrum was recovered. Alternate additions of TFA and TEA to the $CHCl_3$ solution of the block copolymer, the emission color was shuttled between the orange and blue, and the cycle can be repeated more than 5 times (Fig. S12, see the ESI†). All these studies demonstrate the P3HT-*b*-PPI block copolymer possessing excellent pH-responsive property. However, similar pH-responsive behavior of P3HT-*b*-PPI block copolymer could not be observed in THF and methanol. To get more details, pH-responsive behaviors of both P3HT and PPI blocks were then investigated under the same experimental conditions to that of the P3HT-*b*-PPI block copolymer in $CHCl_3$. Adding TFA to the PPI solution of poly-$\mathbf{2}_{30}$ did not induced any changes on the absorption. However, the absorption of P3HT (poly-$\mathbf{1}_{30}$) at 450 nm in $CHCl_3$ was gradually quenched upon the addition of TFA (Fig. S13, see the ESI†). Neutralized the solution by TEA, the absorption can be completely recovered, suggesting the pH-responsive of P3HT-*b*-PPI block copolymer was ascribe to the interaction of P3HT with the added acid.[18]

Bio-imaging

Due to the highly water-solubility, the one-pot synthetic P3HT-*b*-PPI block copolymers may find applications in biochemistry such as in living cell imaging.[19] It had been established that nanoparticle with diameter smaller than ~200 nm would favor tumor accumulation *via* the enhanced permeation and retention effect within tumor tissues.[20] The dimension of the aggregates of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) in water was revealed to be ca. 90 nm, thus this block copolymer was selected for further investigation in bioimaging. Initially, the cytotoxic behavior of poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) micelles was studied on HepG2 cells with the concentration at 0.10 g/L. The cell viability assays revealed that the block copolymer is almost non-cytotoxic at current experimental conditions (data not shown). These studies suggest the poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) copolymer is suitable for intracellular imaging studies. Then, poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) was co-incubated with HepG2 cells and their imaging performance were checked by confocal laser scanning microscopy (Fig. 7). Typically, upon extending incubation time from 0 to 12 h, red emission can be gradually observed within HepG2 cells. These studies indicate the one-pot synthetic water-soluble P3HT-*b*-PPI block copolymers are good materilas for living cell imaging.

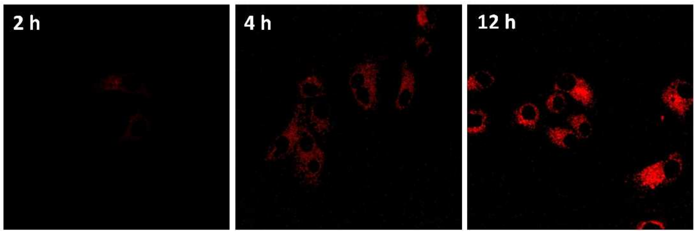


Fig. 7 Incubation duration-dependent confocal laser scanning microscopy images of live HepG2 cells culturing with poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) copolymer at 37 °C. The red channel was excited at 450 nm and collected between 555 and 600 nm.

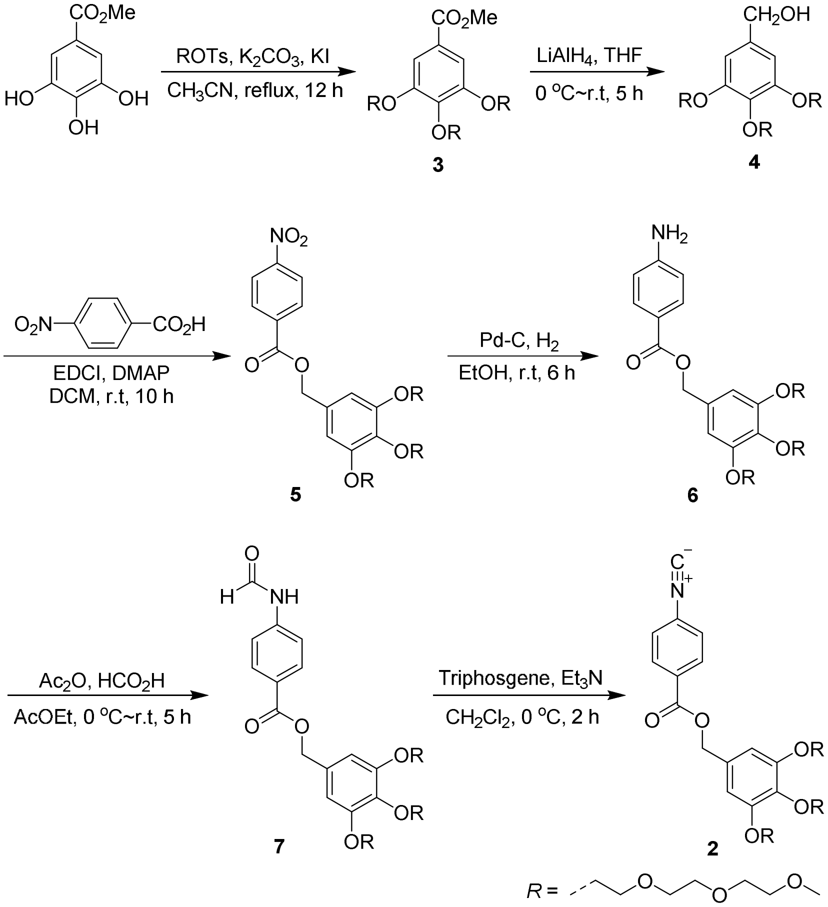
Conclusions

In summary, a series of well-defined highly water-soluble P3HT-*b*-PPI block copolymers with controlled M_ns and narrow M_w/M_ns were facilely prepared in one-pot using Ni(dppp)Cl_2 as a single catalyst through tandem polymerizations. The block copolymers exhibit multiple stimuli-responsives such as temperature, pH, and solvents. In water the block copolymer showed excellent thermoresponsive with the LCST dependent on concentration and the composition of the block copolymers. The block copolymers also showed solvatochromism property due to the different self-assembled structures in these solvents. In $CHCl_3$, the block copolymer exhibit interesting pH-responsive behavior by changing its color and emission upon alternate additions of TFA and TEA. Moreover, the water-soluble P3HT-*b*-PPI block copolymer was revealed to be a good material for living cell imaging. The conjugated block copolymers introduced here represent a new type of stimuli-responsive polymer that holds great potential as a smart material and in detection and bio-imaging applications.

Experimental section

Measurements and materials

The ^1H and ^{13}C NMR spectra were recorded on Bruker 600 MHz spectrometer. FT-IR spectra were recorded on PerkinElmer Spectrum BX FT-IR system using KBr pellets at 25 °C. Size exclusion chromatography (SEC) was performed on Waters 515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using three linear Styragel HR1, HR2 and HR4 columns. Tetrahydrofuran (THF) was used as eluent and the flow rate is 0.3 mL/min. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) data are reported relative to polystyrene standards. UV-vis and emission spectra were performed on UNIC 4802 UV/VIS double beam spectrophotometer in a 1.0 cm length quartz cell and Hitachi F-4600 fluorescence spectrophotometer, respectively. TEM was performed on a JEM-2100F operating at 200 kV accelerating voltage. Number distributions were recorded using a Nano-ZS 90 Zetasizer of Malvern (UK) instrument. All samples were filtered with syringe filters (0.8 μm pore size, Cellulose Acetate filter media) prior to the DLS measurements, and all data were averaged over three time measurements. Cell culture and in vitro fluorescence imaging were performed following the procedure reported by our group previously.[19c] All solvents were purified by the standard procedures just before use. THF was further dried over sodium benzophenone ketyl, distilled onto $LiAlH_4$ under nitrogen, and distilled under high vacuum just before use. All chemicals were used as received without further purification otherwise denoted. 2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (Me-TEG-Ts) was prepared according to the reported literature and the structure was confirmed by ^{1}H NMR (Fig. S14, see the ESI†).[21] Monomer **2** was synthesized according to Scheme 2. Compound **3** and **4** were prepared according to the reported literatures with slight modifications.[22]



Scheme 2 Synthesis of monomer **2**

Synthesis of 3. Methyl gallate (4.00 g, 21.72 mmol), Me-TEG-Ts (27.63 g, 86.89 mmol), KI (2.90 g, 17.38 mmol), and K_2CO_3 (30.00 g, 217.21 mmol) were mixed in dry CH_3CN (150 mL). After the reaction solution was refluxed overnight, the solvent was removed by evaporation under reduced pressure. The residue was dissolved in water and extracted with CH_2Cl_2. The organic phase was washed successively with aqueous $NaHCO_3$ and brine, and then dried over anhydrous $MgSO_4$. After concentrated, the residue was purified by column chromatography using CH_2Cl_2/MeOH (v/v = 40/1) as eluent to afford compound **3** as a yellow oil (11.09 g, 82% yield). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.28 (s, 2H, ArH), 4.24−4.17 (m, 6H, CH_2), 3.88−3.84 (m, 7H, CH_2 and CH_3), 3.79 (t, J = 6.0 Hz, 2H, CH_2), 3.74−3.69 (m, 6H, CH_2), 3.67−3.61 (m, 12H, CH_2), 3.55−3.51 (m, 6H, CH_2), 3.36 (s, 9H, CH_3).

Synthesis of 4. Under an atmosphere of nitrogen, $LiAlH_4$ (0.87 g, 22.92 mmol) was added to a solution of **3** (7.17 g, 11.51 mmol) in dry THF (140 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h, and at room temperature for another 4 h, then quenched by dropwise addition of water. After filtered off the resulting precipitate, the filtrate was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and washed with H_2O and brine. After drying over anhydrous $MgSO_4$, the solvent was evaporated to dryness under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2/MeOH (v/v = 50:1 to 40:1) as eluent to afford compound **4** as a yellow oil (5.44 g, 80% yield). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 6.61 (s, 2H, ArH), 4.56 (s, 2H, $ArCH_2$), 4.17−4.11 (m, 6H, CH_2), 3.83 (t, J = 6.0 Hz, 4H, CH_2), 3.77 (t, J = 6.0 Hz, 2H, CH_2), 3.72−3.69 (m, 6H, CH_2), 3.66−3.61 (m, 12H, CH_2), 3.53 (t, J = 6.0 Hz, 6H, CH_2), 3.36 (s, 9H, CH_3).

Synthesis of 5. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.45 g, 7.58 mmol) and 4-dimethyl-aminopyridine (0.49 g, 4.04 mmol) were added to a solution of **4** (3.00 g, 5.06 mmol) and 4-nitrobenzoic acid (1.27 g, 7.58 mmol) in dry CH_2Cl_2 (30 mL) under an atmosphere of nitrogen. The resulting mixture was stirred at room temperature for 10 h before portioned between water and CH_2Cl_2. The organic phase was washed sequentially with aqueous

$NaHCO_3$ and brine, and then dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated to dryness under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2/MeOH (v/v = 50/1) as eluent to afford compound **5** as a yellow oil (3.08 g, 82% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.29 (d, J = 12.0 Hz, 2H, ArH), 8.22 (d, J = 6.0 Hz, 2H, ArH), 6.67 (s, 2H, ArH), 5.27 (s, 2H, $ArCH_2$), 4.18−4.13 (m, 6H, CH_2), 3.85 (t, J = 6.0 Hz, 4H, CH_2), 3.78 (t, J = 6.0 Hz, 2H, CH_2), 3.74−3.70 (m, 6H, CH_2), 3.67−3.62 (m, 12H, CH_2), 3.53 (t, J = 3.0 Hz, 6H, CH_2), 3.36 (s, 9H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 164.39, 152.69, 150.47, 138.67, 135.36, 130.75, 130.41, 123.47, 108.35, 72.21, 71.82, 71.80, 70.69, 70.57, 70.44, 70.42, 70.40, 70.39, 69.60, 68.85, 67.67, 58.93. HRMS m/z: calcd for $C_{35}H_{54}NO_{16}$ $[M + H]^+$, 744.3443; found, $C_{35}H_{54}NO_{16}$, 744.3438. Anal. Calcd for $C_{35}H_{53}NO_{16}$: C, 56.52; H, 7.18; N, 1.88. Found: C, 56.46; H, 7.20; N, 1.89.

Synthesis of 6. A solution of compound **5** (3.00 g, 4.03 mmol) in ethanol (60 mL) was charged with 10% Pd/C (0.30 g). The mixture was stirred at room temperature for 6 h under an atmosphere of H_2. After filtration through Celite, the solvent was evaporated to dryness under reduced pressure. Then purified the crude product by column chromatography with CH_2Cl_2/MeOH (v/v = 60/1 to 50/1), afforded **6** as a yellow oil (2.71 g, 94% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.86 (d, J = 12.0 Hz, 2H, ArH), 6.65 (s, 2H, CH), 6.63 (d, J = 6.0 Hz, 2H, ArH), 5.17 (s, 2H, $ArCH_2$), 4.17−4.10 (m, 8H, CH_2 and NH_2), 3.83 (t, J = 3.0 Hz, 4H, CH_2), 3.78 (t, J = 6.0 Hz, 2H, CH_2), 3.73−3.70 (m, 6H, CH_2), 3.66−3.61 (m, 12H, CH_2), 3.53 (t, J = 6.0 Hz, 6H, CH_2), 3.36 (s, 9H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 166.35, 152.55, 151.07, 138.11, 131.93, 131.68, 119.24, 113.68, 107.77, 72.20, 71.85, 71.84, 70.72, 70.60, 70.47, 70.44, 70.42, 70.41, 69.64, 68.78, 66.02, 58.95. HRMS m/z: calcd for $C_{35}H_{56}NO_{14}$ $[M + H]^+$, 714.3701; found, $C_{35}H_{56}NO_{14}$, 714.3711. Anal. Calcd for $C_{35}H_{55}NO_{14}$: C, 58.89; H, 7.77; N, 1.96. Found: C, 58.85; H, 7.82; N, 1.90.

Synthesis of 7. A mixture of formic acid (2.18 g, 47.28 mmol) and acetic anhydride (0.97 g, 9.46 mmol) was stirred at room temperature for 2 h under nitrogen atmosphere. Subsequently, a solution of compound **6** (2.70 g, 3.78 mmol) in dry ethyl acetate (60 mL) was added dropwise to the aforementioned mixture under an ice bath. The resulting mixture was stirred at 0 °C for 1 h, and then warmed to room temperature for another 4 h. After removal of the solvent, the residue was dissolved in CH_2Cl_2 and washed successively with H_2O, aqueous $NaHCO_3$, and brine, and then dried over anhydrous $MgSO_4$. After the solvent was removed by evaporation, the crude product was purified by column chromatography using CH_2Cl_2/MeOH (v/v = 50/1 to 40/1) as eluent to afford the desired product **7** as a yellow oil (2.08 g, 74% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.83 (d, J = 12.0 Hz, 0.4H, CHO), 8.41 (s, 0.6H, ArH and CHO), 8.10−7.99 (m, 3H, ArH), 7.65 (d, J = 6.0 Hz, 1.4H, NH and ArH), 7.12 (d, J = 6.0 Hz, 0.6H, NH), 6.64 (d, J = 6.0 Hz, 2H, ArH), 5.21 (s, 2H, $ArCH_2$), 4.17−4.12 (m, 6H, CH_2), 3.83 (t, J = 3.0 Hz, 4H, CH_2), 3.78 (t, J = 3.0 Hz, 2H, CH_2), 3.72−3.70 (m, 6H, CH_2), 3.66−3.61 (m, 12H, CH_2), 3.53 (t, J = 6.0 Hz, 6H, CH_2), 3.36 (s, 9H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 165.71, 161.43, 159.47, 152.58, 141.53, 138.14, 131.60, 131.48, 130.88, 125.60, 119.03, 117.12, 107.90, 107.76, 72.23, 71.83, 71.81, 70.69, 70.58, 70.44, 70.42, 70.40, 69.60, 68.77, 68.73, 66.55, 58.93. HRMS m/z: calcd for $C_{36}H_{56}NO_{15}$ $[M + H]^+$, 742.3650; found, $C_{36}H_{55}NO_{15}$, 742.3635. Anal. Calcd for $C_{36}H_{55}NO_{15}$: C, 58.29; H, 7.47; N, 1.89. Found: C, 58.12; H, 7.60; N, 1.85.

Synthesis of 2. Under an atmosphere of nitrogen, triethylamine (0.27 g, 2.70 mmol) was added to a solution of **7** (0.50 g, 0.67 mmol) in dry CH_2Cl_2 (10 mL). After the resulting mixture was stirred at 0 °C for 20 min, a solution of triphosgene (0.18 g, 0.59 mmol) in dry CH_2Cl_2 (12 mL) was added dropwise to the mixture via a syringe. The reaction mixture was stirred at 0 °C for another 2 h. Then the resulting solution was washed with H_2O, aqueous $NaHCO_3$ and brine, and dried over anhydrous $MgSO_4$. After the solvent was evaporated, the crude product was purified by column chromatography using CH_2Cl_2/MeOH (v/v = 80/1 to 70/1) as eluent to afford the desired product **2** as a light yellow oil (0.38 g, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.09 (d, J = 6.0 Hz, 2H, ArH), 7.45 (d, J = 6.0 Hz, 2H, ArH), 6.66 (s, 2H, ArH), 5.23 (s, 2H, $ArCH_2$), 4.17−4.13 (m, 6H, CH_2), 3.84 (t, J = 6.0 Hz, 4H, CH_2), 3.78 (t, J = 6.0 Hz, 2H, CH_2), 3.67−3.61 (m, 12H, CH_2), 3.53 (t, J = 6.0 Hz, 6H, CH_2), 3.36 (s, 9H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 165.88, 152.67, 142.45, 131.53, 131.04, 124.55, 119.39, 117.50, 107.99, 72.28, 71.92, 71.91, 70.78, 70.65, 70.54, 70.52, 70.50, 70.48, 69.69, 68.88, 66.52, 59.00. HRMS m/z: calcd for $C_{36}H_{54}NO_{14}$ $[M + H]^+$, 724.3544; found, $C_{36}H_{54}NO_{14}$, 724.3550. Anal. Calcd for $C_{36}H_{53}NO_{14}$: C, 59.74; H, 7.38; N, 1.94. Found: C, 59.50; H, 7.42; N, 1.88.

Representative copolymerization procedure for P3HT-*b*-PPI (poly(1_{30}-*b*-2_{60}). A 10 mL oven-dried flask was charged with 2,5-dibromo-3-hexylthiophene (98.00 mg, 0.30 mmol), dry THF (3.0 mL), and a stirring bar. After a solution of isopropylmagnesium chloride (0.15 mL, 2.00 M solution in THF, 0.30 mmol) was added via a syringe, the resulting mixture was stirred at room temperature for 2 h. Ni(dppp)Cl_2 (5.42 mg, 10.0 μmol, $[\text{monomer}]_0/[\text{Ni}]_0 = 30/1$) was then added to the reaction mixture under an atmosphere of nitrogen, and the progress of the polymerization was monitored by SEC until the molecular weight of the yielded P3HT (poly-$\mathbf{1}_{30}$) ceased to increase. SEC analysis of an aliquot removed from the reaction mixture showed that the poly-$\mathbf{1}_{30}$ prepared in situ exhibited the following characteristics: M_n = 5.30 kDa, M_w/M_n = 1.36. After removing a small amount of the reaction mixture to another oven-dried flask under an atmosphere of nitrogen for further analyses, monomer **2** (43.40 mg, 0.06 mmol, $[\mathbf{2}]_0/[\text{Ni}]_0 = 60/1$)

in 0.8 mL THF was then added to the reaction solution by a syringe. After the reaction mixture was stirred at room temperature for about 12 h, methanol (2.0 mL) was added to the reaction solution to quench the polymerization. Then the solution was pour into a large amount of *n*-hexane which caused a dark-purple solid to precipitate. The solid was isolated via filtration, and washed with cold methanol and *n*-hexane to remove residual metal salts, unreacted monomer and oligomers. The resulting purple solid was then dried under vacuum to afford the desired block copolymer poly($\mathbf{1}_{30}$-*b*-$\mathbf{2}_{60}$) (45.80 mg, 86% yield, over the two steps). SEC: M_n = 24.0 kDa, M_w/M_n = 1.22. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.80−7.34 (br, PPI, ArH), 6.98 (s, P3HT, ArH), 6.75−6.45 (br, PPI, ArH), 6.30−6.05 (br, PPI, ArH), 5.92−5.44 (br, PPI, CH_2), 4.30−3.08 (br, PPI, OCH_2 and OCH_3 of TEG chains), 2.83−2.79 (br, P3HT, thiophene-CH_2), 1.79−0.80 (br, P3HT, alkyl chains). FT-IR: 2955, 2925, 2850, 1717, 1600, 1450, 1262, 1103, 803 cm^{-1}.

Synthesis of homopolymer of 2 (poly-$\mathbf{2}_{30}$). This polymer was prepared according to the reported literature with slightly modifications.[17] A stirring solution of monomer **2** (65.15 mg, 0.09 mmol in THF (1.6 mL) was treated with Ni(dppp)Cl_2 (1.63 mg, 3.0 μmol, $[\mathbf{2}]_0/[\mathrm{Ni}]_0$ = 30/1). After stirred at 25 °C for 12 h under a nitrogen atmosphere, it was poured into a large amount of *n*-hexane. The precipitated yellow solid was washed several times with cold *n*-hexane and then dried under vacuum to afford the desired PPI polymer poly-$\mathbf{2}_{30}$ (55.40 mg, 85% yield). SEC: M_n = 14.5 kDa, M_w/M_n = 1.25. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.80–7.27 (br, ArH), 6.85–6.55 (br, ArH), 6.30–5.90 (br, ArH), 5.87–5.54 (br, $ArCH_2$), 4.25−3.05 (br, OCH_2 and OCH_3 of TEG chains). FT-IR (KBr, 25 °C): 2850, 1717, 1600, 1438, 1262, 1103, 876 cm^{-1}.

†Electronic supplementary information. Additional spectroscopies and SEC chromatograms.

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Multiresponsive of highly water-soluble poly(3-hexylthiophene)-*block*-poly(phenylisocyanide) block copolymers†

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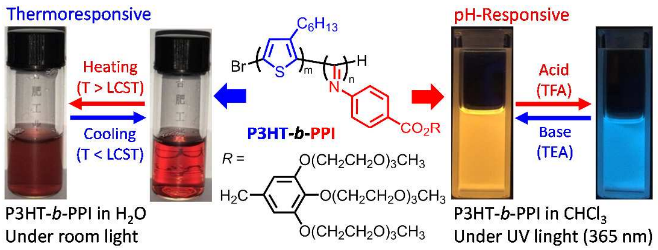

Highly water-soluble block copolymers containing conjugated poly(3-hexylthiophene) and hydrophilic poly(phenyl isocyanide) segments were found to responsive to multiple stimuli such as temperature, pH and solvents.