



# Synthesis, structures, and properties of a fluoranthene-based biphenol polymer as a fluorescent nano-thermometer



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## HIGHLIGHTS

- PNIPAm was labeled using a fluorogen of fluoranthene-based biphenol.
- FL thermometer with both aggregation- and concentration-enhanced emission feature.
- Emission mechanism involves protonation equilibrium in PN4 water solution.
- The inter- or intra-polymer aggregation caused AIE mechanism in PN4 water solution.
- The FL intensity at 50 °C is about 7-fold higher than at 15 °C for PN4.

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## ABSTRACT

In this work, we explored a direct way of labeling poly(N-isopropylacrylamide) (PNIPAm) and developed a fluorescent thermometer with desired feature of aggregation-enhanced emission. A fluoranthene-based biphenol polymer, PNIPAm-MAh-4 (**PN4**), consisting of N-isopropylacrylamide (NIPAm) and 4-(9-(2-(4-hydroxyphenyl)ethynyl)-7,10-diphenylfluoranthene-8-yl)-phenol (**4**) units as temperature-responsive and fluorescent signaling parts, respectively, was synthesized. The aqueous solution of **PN4** exhibits weak fluorescence (FL) below 30 °C, whereas shows FL enhancement above 30 °C. The FL intensity increases with temperature monotonically until 50 °C, and the maximum FL intensity at 50 °C is about 7-fold higher than that at 15 °C. The FL enhancement is found to be associated with a heat-induced polymer chain conformation transition from hydrated coil to dehydrated globule. And the possible mechanisms for emission responses of PN4 against temperature, concentration and aggregation are suggested, respectively. The plausible mechanism of the sensitivity of the emission intensity to temperature or polymer state involves the deprotonation equilibrium and formation of the less fluorescent form of PN4. Meanwhile, the polymer possesses high reversibility of the FL response. Therefore the polymer **PN4** is expected to have great potential as a fluorescent thermometer with high sensitivity and reversibility, and our work explores its utilities in molecular probes, biotechnology, multistimuli-responsive nanomaterials and smart polymer machines.

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## 1. Introduction

In the last years, the dye-functionalized thermo-responsive polymers have drawn significant attention for the development of sensory materials, and various fluorescent [1–6] and UV/Vis [7–9] temperature sensors by incorporating dye groups into thermo-responsive polymers have been reported. A majority of such sensors are based on dye-functionalized stimuli-responsive

poly(N-isopropylacrylamide) (PNIPAm), owing to its lower critical solution temperature (LCST) [10–12] in aqueous solution around 32 °C. The biocompatibility of PNIPAm and its near-body-temperature LCST have stimulated the exploration of its utilization in biotechnology, especially in the development of temperature-responsive drug delivery systems [1], and the polymer is known being widely used in optical and electronic devices [13,14], biomedical systems [15,16], and chemosensors [1,17]. In the meanwhile, fluorescence (FL) technique is a powerful tool in the study of conformational change of polymer chains at a molecular level, and fluorescent groups have been incorporated into PNIPAm chains to study the physical and chemical properties of PNIPAm through FL technique [18,19]. These

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fluorescent sensors can be divided into three categories: the type-I exhibits thermo-induced FL enhancement [2,4,20–23], the type-II shows heat-induced FL quenching [3,24,25], and the type-III manifests selective emission behavior within certain temperature range [26]. However, the FL enhancement-type thermometers [2,20–23] are regarded as good candidate sensors owing to their high signal-to-noise ratio [4]. Another important issue is certainly the development of efficient luminescent materials. The concentration-quenching and aggregation-caused quenching (ACQ) effects, however, have been the troublesome obstacles to the development of luminogens as chemical sensors, bioluminescence probes and smart materials. On one hand, conventional luminophores are generally flat disk-like aromatic molecules, which usually meet with strong molecular interactions in concentrated solutions. It is the general belief that concentration quenching is ubiquitous to most aromatic hydrocarbons and their derivatives [27]. Owing to the common concentration-quenching effect, researchers have to utilize fluorophores in very dilute solutions [28,29], which obviously causes many problems. Emissions in dilute solutions are usually weak, leading to poor sensitivity in fluorescent sensors, especially for trace-amount bioassays [30–34]. Although inorganic quantum dots (QDs) could overcome these disadvantages, a series of new problems are brought about, such as pains-taking synthetic effort and high cytotoxicity [35–37]. In some bioassay cases, concentration-quenching cannot be avoided even in dilute solutions [38–41]. On the other hand, luminophore aggregation has mostly been linked with the ACQ phenomena. The attachment of the non-conjugated groups to the aromatic rings is known to be passive and sometimes even destructive. Despite of various attempts to interfere with luminogen aggregation, the approaches have shown only limited success because the aggregate formation is an intrinsic process when luminogens are located within short enough distance [42]. Therefore, it is desirable if we can develop a system, in which light emission is enhanced rather than quenched by aggregation and concentration. It will make our life much easier if the aggregation could work to our benefit, and there is no more to be done to artificially interrupt the very natural process of luminophore aggregation [42]. Further as we know, planar luminogens such as pyrene prefer to clustering just as discs pile up due to strong  $\pi$ - $\pi$  stacking interactions, which usually turn “off” their emission, whereas nonplanar propeller-like ones such as hexaphenylsilole (HPS) behave oppositely, with their light emissions turned “on” by cluster formation, due to the restricted intramolecular rotation (RIR) in the aggregates [42]. On the basis of our mechanistic understanding, a nonplanar propeller-shaped dye unit is certainly our favorite choice for aggregation-enhanced emission purpose. According to the structural design principle elaborated above, we first synthesized a **partially propeller-shaped** and fluoranthene-based biphenol as the fluorescent unit (compound **4**, Scheme 1). Then, a thermo-responsive polymer ended with the fluorescent unit **4**, PNIPAm-MAh-4 (**PN4** or compound **8**, Scheme 2), was synthesized through acylation reaction of compound **4** and PNIPAm-MAh (compound **7**, Scheme 2). The as-prepared polymer **PN4** is working in a desired feature of aggregation-enhanced emission. Meanwhile, the emission intensity of PN4 series is strongly temperature dependent. As expected, **PN4** shows heat-induced FL enhancement in aqueous solution, which exhibits relatively **weak** FL below 30 °C, while showing FL enhancement above 30 °C. The observed maximum intensity at 50 °C is about **7-fold** higher than that at 15 °C. The possible mechanisms for emission responses of PN4 against temperature, concentration and aggregation are suggested, respectively. The high reversibility of the polymer thermometer is also presented.

## 2. Experimental

### 2.1. General Information

Fourier transform infrared (FT-IR) spectra were recorded on an NEXUS-470 spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained from a DRX-400 NMR instrument with tetramethylsilane as internal standard. Mass spectra were obtained on an Agilent 1100 Series LC/MSD Trap XCT mass spectrometer, equipped with an electrospray ionization (ESI) source. Average molecular weights ( $M_w$  and  $M_n$ ) and polydispersity indexes (PDIs) were estimated by a waters 150C Gel permeation chromatography (GPC) equipped with Waters 515 HPLC pump, Waters 2414 differential refractive index (RI) detector and four columns at 40 °C, using monodispersed polymethylmethacrylate (PMMA) as calibration standard. DMF was used as eluent at a flow rate of 1.0 mL/min. UV-Vis spectra were taken on a Persee TU-1901 spectrophotometer with a temperature controller. The fluorescence measurements were carried out on a Hitachi FL-4500 spectrofluorometer with a temperature controller. The emission spectra were recorded with an excitation wavelength at 390 nm, except the quantum yield measurement excited at 360 nm. Dynamic light scattering (DLS) measurements were performed with a Nano ZS-90 particle size analyzer (Malvern Instruments, UK), and equipped with a He-Ne laser (633 nm, 4 mW). The accompanying Malvern Instruments DTS v4.10 software package was used to perform measurements and data analysis. The apparent hydrodynamic radius ( $R_h$ ) can be extracted from the Stokes-Einstein equation as follows

$$R_h = k_B T / 6\pi\eta D \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $\eta$  is the solvent viscosity,  $T$  is the absolute temperature and  $D$  is the diffusion coefficient. The pH values were obtained using a Beckman 360 pH meter.

### 2.2. Materials

N-isopropylacrylamide (NIPAm, Shanghai Chemical Reagents Co., 98%) was recrystallized from toluene and n-hexane (1:3). Maleic anhydride (MAh, Beijing Chemical Reagents Co., 99%) was recrystallized from anhydrous chloroform. 2,2-Azobis(isobutyronitrile) (AIBN, Shanghai Chemical Reagents Co., 98%) was recrystallized from ethanol twice. 1,4-dioxane (Tianjin Chemical Reagents Co., 99%) was distilled in the presence of sodium slices. Tetrahydrofuran (THF, Beijing Chemical Reagents Co.) was distilled from sodium benzophenone ketyl under argon immediately prior to use. Magnesium powder, potassium hydroxide, iodine,  $\text{MgSO}_4$ , CuI and  $\text{PdCl}_2$ , dichloromethane, chloroform, ethyl acetate, methanol, ethanol, petroleum ether and ortho-xylene (Beijing Chemical Reagents Co., analytical pure grade) were used as received. The pH buffers from Sigma-Aldrich were used as received. The solvents cyclohexane ( $\text{C}_6\text{H}_{12}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), dimethyl sulfoxide (DMSO), ethylene glycol (EG), methanol ( $\text{CH}_3\text{OH}$ ) and THF for absorption (Abs) and FL measurements were spectrophotometric or HPLC grade ( $\geq 99.9\%$ ) from Sigma-Aldrich and were used as received. Compound **4** was synthesized according to a reference procedure [43,44]. **PNIPAm** with  $M_n = 17,200$  and  $42,900 \text{ g mol}^{-1}$  were synthesized according to a procedure described previously [3], and the detailed reaction conditions for the preparation of PNIPAm, the number-average molecular weight ( $M_n$ ) and polydispersity index ( $M_w/M_n$ ) of PNIPAm determined by GPC are provided in Table 1. **PNIPAm-MAh-4** (compound **8** or **PN4**) was synthesized according to the reported method [45,46]. In this work, **PN4** with different molar mass, **PN4a** ( $M_n = 17,000 \text{ g mol}^{-1}$ ) and **PN4b** ( $M_n = 42,700 \text{ g mol}^{-1}$ ) were prepared and used, and the  $M_n$  and polydispersity index tabulated in Table 2 were obtained by GPC

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