

## Research Article

# Amphiphilic Fluorescent Well-Defined Living Polymer from Indole-3-Carboxaldehyde and 4-Bromo-1, 8-Naphthalic Anhydride: Synthesis and Characterization

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We reported a well-defined amphiphilic fluorescent polymer bearing indole repeating units with naphthalimide pendants obtained by ATRP followed by chemical modification. The obtained polymer poly (N-allyl indole-2-(4-hydroxybutyl)-1, 8-naphthalimide) (PAIHN) was characterized by <sup>1</sup>H NMR, FTIR, and GPC. The polymer showed a specific fluorescence emission maximum at 538 nm excited at 435 nm in aqueous solution. The amphiphilic nature of the polymer was investigated in aqueous solution using two spectroscopic methods, namely, absorption and emission spectroscopy. The Critical Micellar Concentration values obtained by UV-visible and fluorescence are in good agreement with each other. The micelles were characterized by TEM at concentration of 0.014 mg/mL. The polymer PAIHN prepared after tweaking exhibits green fluorescence at 538 nm due to the significant effect of naphthalimide moieties, whereas before tweaking the polymer poly (1-allyl indole-3-carbaldehyde) (PAIC) exhibits blue fluorescence at 425 nm due to indole repeating units of the polymer.

## 1. Introduction

Amphiphilic property in polymers is a consequence of presence of segments of opposite philicity, that is, hydrophobic and hydrophilic segments, which are covalently bonded. This gives rise to unique properties at surfaces as well as in bulk due to the differential solvation of the hydrophilic and hydrophobic segments where the hydrophobic part forms the inner core and hydrophilic part forms the outer shell to form micellar structure in aqueous media [1, 2]. The major driving force behind this phenomenon is the decrease in free energy of the system due to the removal of the hydrophobic blocks from the aqueous media, while hydrophilic blocks stabilize the system. The characteristic self-organization of these materials in the presence of selective media often results in the formation of different types of supramolecular structures such as polymeric micelles [3] and nanoparticles [4] in aqueous environment with a right balance of solvophobic and solvophilic moieties [5].

The amphiphilic polymer architecture generally consists of block copolymers and several research groups have reported the synthesis and applications thereof where one block is hydrophilic while the other is hydrophobic [6]. Synthesis of amphiphilic diblock copolymers poly [2-(N, N-dimethylamino)ethyl methacrylate]-b-poly (stearyl methacrylate) with different molecular weights through RAFT and their self-assembly in mixed solvent was studied by Liu et al. [7]. Lu et al. reported the synthesis of amphiphilic copolymers polyacrylamide-b-poly (p-methacrylamido) acetophenone thiosemicarbazone (PAM-b-PMATC) which could be potentially used as drug carriers and tracer to determine the drug release behavior in drug delivery [8]. Functionalization of the polymer is another way of achieving amphiphilicity as has been done by Manolova et al. in preparing amphiphilic derivatives of fullerenes by the reaction of C<sub>60</sub> and C<sub>70</sub> with precursor poly(oxyethylene) or poly(oxypropylene) polymers possessing amino end-groups [9]. Certain aromatic moieties possess inherent fluorescent

properties such as naphthalene or pyrene, which when transformed to hydrophilic groups serve both as the hydrophilic moiety and as the fluorescent probe. Thus, when attached to the polymer backbone they generate the amphiphilic property in the polymer and eliminate the need to attach fluorescent tags in biological systems. In a pioneering work, Hoskins et al. prepared amphiphilic fluorescent polymers by grafting different types and levels of hydrophobic pendant groups having intrinsic fluorescent properties to a water soluble homopolymer backbone poly allyl amine [10]. Du et al. reported a novel well-defined amphiphilic fluorescent polymer containing asymmetric perylene bisimide synthesized by combining reaction of perylene anhydride with amino functional polyhedral oligomeric silsesquioxane (POSS) and ATRP of *N*-isopropylacrylamide [11].

Therefore, we intended to transform hydrophobic indole-based polymer into amphiphilic polymeric architecture by using naphthalimide-based hydrophilic fluorophore. Naphthalimide moiety was introduced in polymer, since amphiphilic polymer with intrinsic fluorescence is generally labeled with naphthalene or pyrene moiety [8]. Since the polymer was fluorescent prior to modification, hence, we have tried to focus on the changes which will occur after attachment of fluorophore in the polymer backbone. Further, we studied self-aggregation property of modified polymer in aqueous medium. Since amphiphilic character is strongly affected by the molecular weight and molecular weight distribution of the polymer [12], hence, living radical polymerization technique "ATRP" was selected which afforded accurate control over molecular weight distribution, chain ends, and polymer architecture. Further, a hydrophilic moiety, namely, a naphthalimide-based fluorophore 6-(2-aminoethylamino)-2-(4-hydroxybutyl)-1, 8-naphthalimide (AAHN), by functionalization on free aldehyde group of each polymeric repeat unit through imide linkage, was introduced for achieving amphiphilic character in polymer.

## 2. Experimental Section

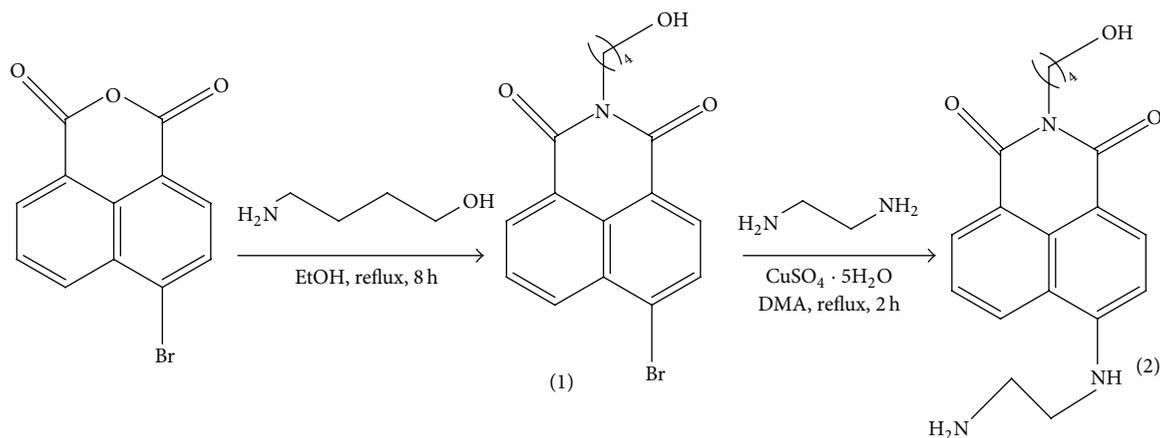
**2.1. Materials.** Indole-3-carboxaldehyde (97%, Aldrich), 2,2'-bipyridyl (99%, Himedia), 4-bromo-1, 8-naphthalic anhydride (95%, Aldrich), 4-amino-1-butanol (98%, Aldrich), ethylenediamine (97%, Spectrochem), dimethylacetamide (DMA) (AR grade, Merck, India), absolute ethanol (99%, s. d. fine), acetonitrile (HPLC grade, Merck, India), methanol (99%, s. d. fine), and 2-bromoisobutylbromide (98%, Aldrich) were used as received. CuBr (98%, Aldrich) was purified by consecutive washing with glacial acetic acid in order to remove residual CuBr<sub>2</sub> [13]. It was further filtered, washed with absolute ethanol and diethyl ether, and dried under vacuum. Toluene (AR grade, Merck, India) was dried and purified as per the methods given by Grabchev [14].

**2.2. Measurements.** <sup>1</sup>H NMR spectra were recorded at 300 MHz resonance frequency in a JEOL AL300 FT NMR at 25°C in DMSO-d<sub>6</sub> and CDCl<sub>3</sub> using trimethylsilane (TMS) as an internal reference. FTIR spectra were recorded on a Varian Excalibur 3000 (Palo Alto, CA) spectrophotometer

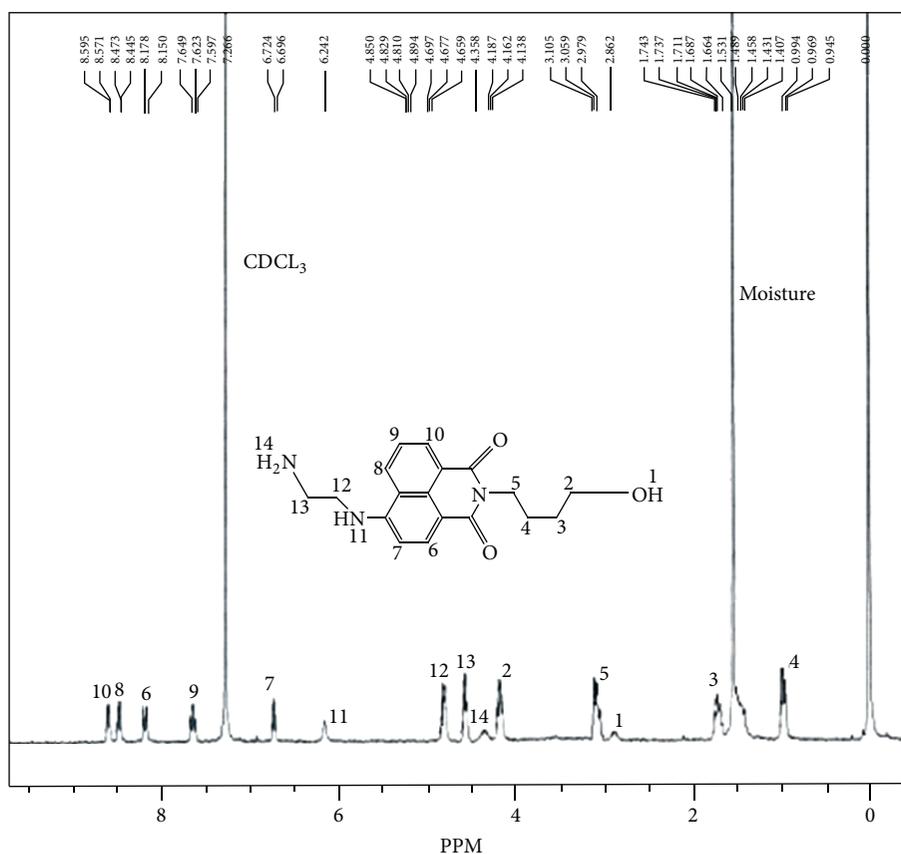
in the region 4000–400 cm<sup>-1</sup> on KBr disc. The absorption spectra were recorded on Perkin Elmer-Lambda 35 UV-VIS spectrophotometer connected with PTP-1 Peltier system at 25°C in the range 200–700 nm. The optical path length of measurement cell was 10 mm. Fluorescence measurements were taken on Fluorolog3-11 spectrophotometer from Horiba Jobin-Yvon, USA, with excitation at 435 nm using a 10 mm path length quartz cuvette in the wavelength range 430–700 nm. All fluorescence experiments were carried out at 25°C. Average molecular weights ( $M_n$  and  $M_w$ ) and molar mass distribution ( $\overline{M}_w$ ) of the modified polymer were determined at 40°C on polymer laboratories PL GPC-220 with THF as an eluent, at a flow rate of 1.0 mL/min. Molecular weights were calculated using monodisperse polystyrene standard. TEM micrographs were taken on Technai FEI operated at 120 kV.

**2.3. Synthesis of Fluorophore AAHN.** The fluorophore AAHN was prepared by small modification in procedures [15] reported. It was prepared in two steps.

- (i) 4-Bromo-1, 8-naphthalic anhydride (1 mmol, 277 mg) was taken in absolute ethanol (15 mL) followed by the addition of 4-amino-1-butanol (1.5 mmol, 134 mg). The reaction was refluxed for 8 h, cooled, and poured in crushed ice. Product was precipitated, filtered, and washed with cold water. The precipitate was then dried under vacuum at 20°C for 4 h to give light yellow-colored solid **1** with 65% yield.
- (ii) **1** (1 mmol, 348 mg) was added in DMA (10 mL) followed by the addition of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.1 mmol, 25 mg) and was kept in a thermostat maintained at 80°C. Ethylenediamine (1.5 mmol, 0.1 mL) was added dropwise and the reaction was refluxed for 5 h. Further, the reaction was cooled and the precipitated solid was filtered followed by washing with cold DMA. The compound was dried under vacuum at 20°C for 3 h to give dark yellow-colored solid **2** with 60% yield. Schematic representation of fluorophore synthesis is given in Scheme 1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 0.95–0.99 (t, *J* = 7.5 Hz, 2H, H<sup>4</sup>), 1.66–1.76 (m, 2H, H<sup>3</sup>), 2.86 (br, 1H, H<sup>1</sup>), 2.98–3.11 (t, *J* = 7.8 Hz, 2H, H<sup>5</sup>), 4.14–4.19 (t, *J* = 7.5 Hz, 2H, H<sup>2</sup>), 4.36 (br, 2H, H<sup>14</sup>), 4.66–4.70 (t, *J* = 7.2 Hz, 2H, H<sup>13</sup>), 4.89–4.95 (q, *J* = 7.5 Hz, 2H, H<sup>12</sup>), 6.14 (s, 1H, H<sup>11</sup>), 6.50–6.72 (d, *J* = 7.2 Hz, H<sup>7</sup>), 7.60–7.65 (t, *J* = 7.8 Hz, 1H, H<sup>9</sup>), 8.15–8.18 (d, *J* = 8.4 Hz, 1H, H<sup>6</sup>), 8.45–8.47 (d, *J* = 8.4 Hz, 1H, H<sup>8</sup>), 8.57–8.60 (d, *J* = 7.2 Hz, 1H, H<sup>10</sup>) (Figure 1); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 24.67, 25.95, 44.05, 57.71, 122.10, 122.88, 128.32, 128.79, 128.99, 129.74, 130.90, 131.33, 131.50, 132.50, 154.11, 162.95 (Figure 2); FTIR ( $\nu$ , cm<sup>-1</sup>): 3700–3400 (O–H stretching), 3043 (N–H stretching (1° amine) and C–H stretching (aromatic)), 1695, 1666 (C=O stretching), 1587 (N–H bending), 1569 (C=C stretching (aromatic)), 1233 (C–N stretching (amine)), 1058 (C–O stretching (Hydroxyl)), 778 (N–H wagging) (Figure 3).

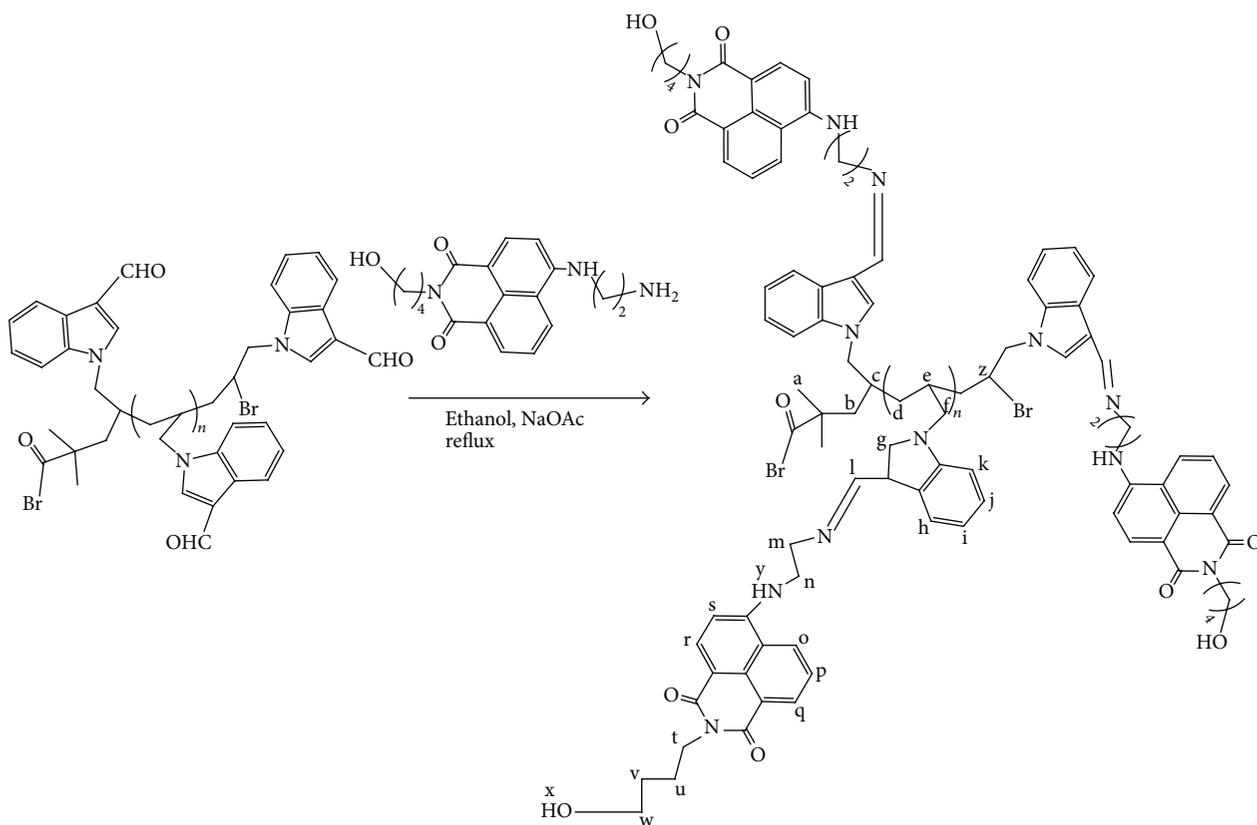


SCHEME 1: Synthesis of fluorophore AAHN (2).

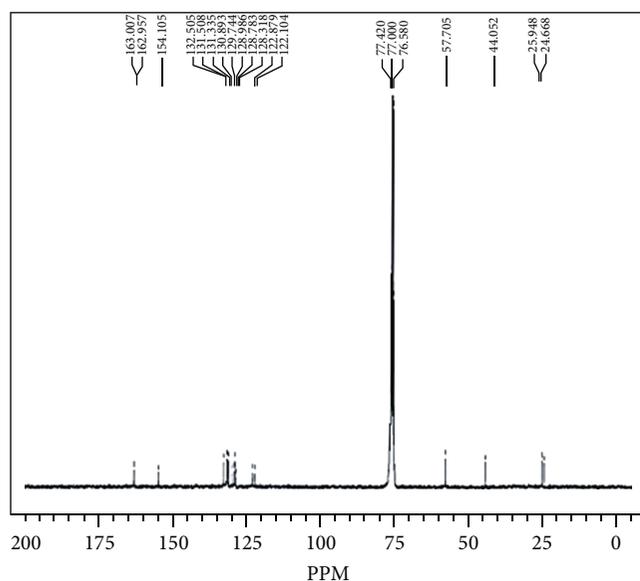
FIGURE 1:  $^1\text{H}$  NMR spectrum of the fluorophore AAHN in  $\text{CDCl}_3$ .

2.4. *Synthesis of Fluorescent Polymer by Chemical Modification of Poly (1-allyl indole-3-carbaldehyde) (PAIC)*. Polymer of substituted indole PAIC was prepared by the ATRP protocol as reported elsewhere [16, 17]. Chemical modification of PAIC was carried out by taking PAIC (0.015 mmol, 114 mg), AAHN (0.75 mmol, 24.50 mg), and ethanol (20 mL) into a 100 mL round-bottomed flask. Then sodium acetate was added (0.75 mmol, 61.50 mg) and stirred until the reagents fully dissolved in ethanol. Finally the reaction was put into

a thermostatic oil bath and kept refluxing at  $85^\circ\text{C}$  for 6 h. The completion of reaction was monitored by TLC. After it was cooled to room temperature, the solvent was removed under reduced pressure and precipitated in diethyl ether as brown-colored solid. The precipitated polymer was washed with cold diethyl ether repeatedly until no absorption of dye was observed and finally the crude polymer poly (N-allyl indole-2-(4-hydroxybutyl)-1, 8-naphthalimide) (PAIHN) was purified by repeated precipitation into diethyl ether and dried



SCHEME 2: Schematic representation of chemical modification of PAIC.

FIGURE 2:  $^{13}\text{C}$  NMR spectrum of AAHN in  $\text{CDCl}_3$ .

in vacuum oven at  $20^\circ\text{C}$ . The resultant polymer was used for GPC and spectral studies. Schematic representation of chemical modification of PAIC is given in Scheme 2.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.23 (s, 6H,  $\text{H}^{\text{a}}$ ), 1.42–1.65 (b,

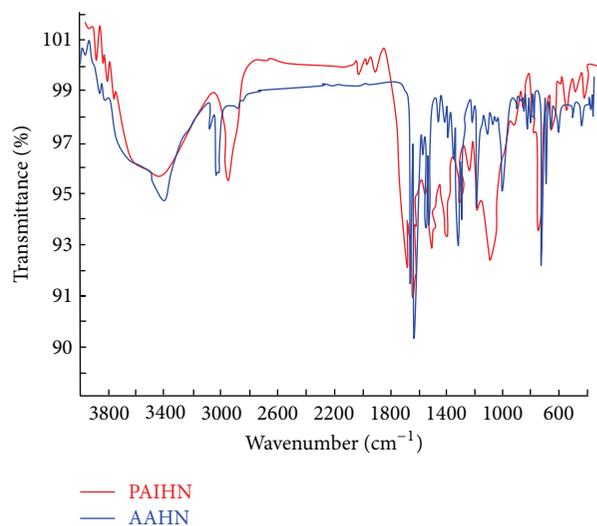


FIGURE 3: FTIR spectra of AAHN and PAIHN in KBr.

245H,  $\text{H}^{\text{b,d,u,v}}$ ), 2.01–2.20 (b, 50H,  $\text{H}^{\text{c,e}}$ ), 2.95 (s, 40H,  $\text{H}^{\text{x}}$ ), 3.15–3.26 (b, 100H,  $\text{H}^{\text{z,l}}$ ), 4.55–4.89 (b, 320H,  $\text{H}^{\text{f,m,n,w}}$ ), 5.92 (b, 40H,  $\text{H}^{\text{y}}$ ), 7.00–7.71 (b, 200H,  $\text{H}^{\text{i,k,g,p,s}}$ ), 8.06–8.25 (b, 80H,  $\text{H}^{\text{h,j}}$ ), 8.25–8.40 (b, 80H,  $\text{H}^{\text{q,r}}$ ), 8.48–8.63 (m, 120H,  $\text{H}^{\text{l,o}}$ ), (Figure 4); FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3700–3400 (O–H stretching), 2966 (O–H and  $2^\circ$  amine), 1680 (C=O & C=N stretching),

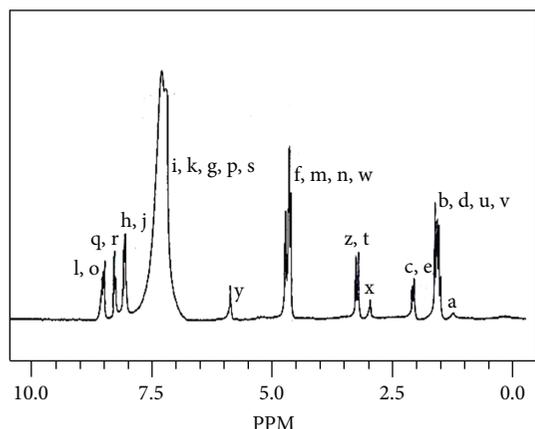


FIGURE 4:  $^1\text{H}$  NMR spectrum of modified fluorescent polymer PAIHN in  $\text{CDCl}_3$ .

1610 (N–H bending), 1515 (C=C stretching (aromatic)), 1412, 1286 (C–N stretching (amine)), 1078 (C–O str of  $1^\circ$  alcohol), 780 (N–H wagging) (Figure 3).

**2.5. Determination of Critical Micellar Concentration (CMC) by UV-Visible and Fluorescence Spectroscopy.** CMC of the polymer PAIHN was determined by absorption as well as emission phenomenon. It may be noted that due to the high composition of hydrophobic moieties in the polymer PAIHN, the polymer could not be dispersed directly into water. Therefore, the polymer was first dissolved in minimum amount of acetone (0.1 mL) and water. The mixture was sonicated to yield a clear solution followed by evaporation of acetone in nitrogen atmosphere and addition of distilled water to obtain a final stock solution of PAIHN of 1 mg/mL and the concentration was varied from  $3.5 \times 10^{-6}$  to  $1 \times 10^{-1}$  mg/mL by diluting the stock solution with distilled water. All the solutions were equilibrated at  $25^\circ\text{C}$  for 24 h, well shielded from light. The CMC determinations were carried out at  $25^\circ\text{C}$  and the values were calculated from the interception point of two tangent straight lines passing through the plotted points.

### 3. Results and Discussion

**3.1. Fluorophore Synthesis and Chemical Modification of Polymer.** Chemical modification leads to many changes in chemical as well as physical properties of polymer. Thus, designing and incorporating suitable fluorophore result in tunable fluorescent polymer. Attempts were carried out to chemically modify PAIC such that the emitting color of the polymer solution could be tuned from initial blue to green. The attachment of many polar groups onto one hydrophobic polymer chain affords the polymer high amphiphilicity. Thus, in an effort to gain amphiphilicity naphthalimide unit containing hydroxyl group was attached to the polymer PAIC. PAIHN was self-assembled into micellar aggregates with hydrophobic polymer backbone segments as the core and hydrophilic hydroxyl group segments as the corona.

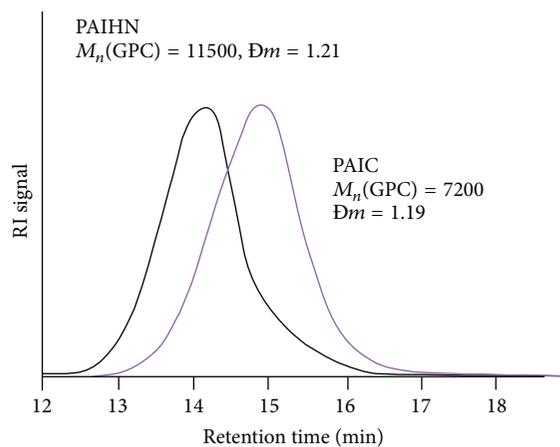


FIGURE 5: GPC chromatogram of PAIC and PAIHN.

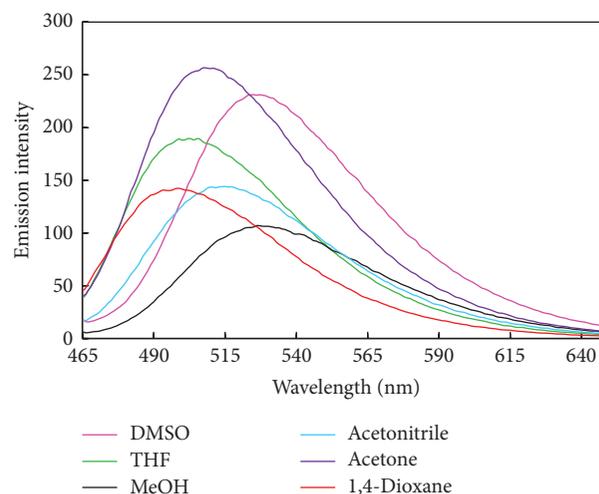


FIGURE 6: Fluorescence spectra of PAIHN in different solvents.

A detailed discussion regarding the characterization of PAIHN along with amphiphilicity and fluorescence properties is given below.

**3.2. Comparative  $^1\text{H}$  NMR Analysis of AAHN and PAIHN.** The homopolymer of N-allyl indole-3-carboxaldehyde was synthesized by atom transfer radical polymerization in the presence of 2,2'-bipyridyl, CuBr, and 2-bromoisobutryl bromide as ligand, catalyst, and initiator, respectively, in the ratio 200 : 4 : 2 : 4. In the case of fluorophore AAHN, all the aromatic protons of the naphthalimide unit appeared in the range  $\delta$  7.00–8.63 ppm, whereas methylene protons appeared upfield in the ranges  $\delta$  1.42–1.65 and 3.15–4.89 ppm, respectively (Figure 1). The  $^{13}\text{C}$  NMR spectrum shows all the different carbons of the fluorophore AAHN (Figure 2). The functionalization of aldehyde group in PAIC was verified by  $^1\text{H}$  NMR spectrum. From Figure 4, it can be seen that there is no NMR signal in the range  $\delta$  9.0–10.0 which is specific

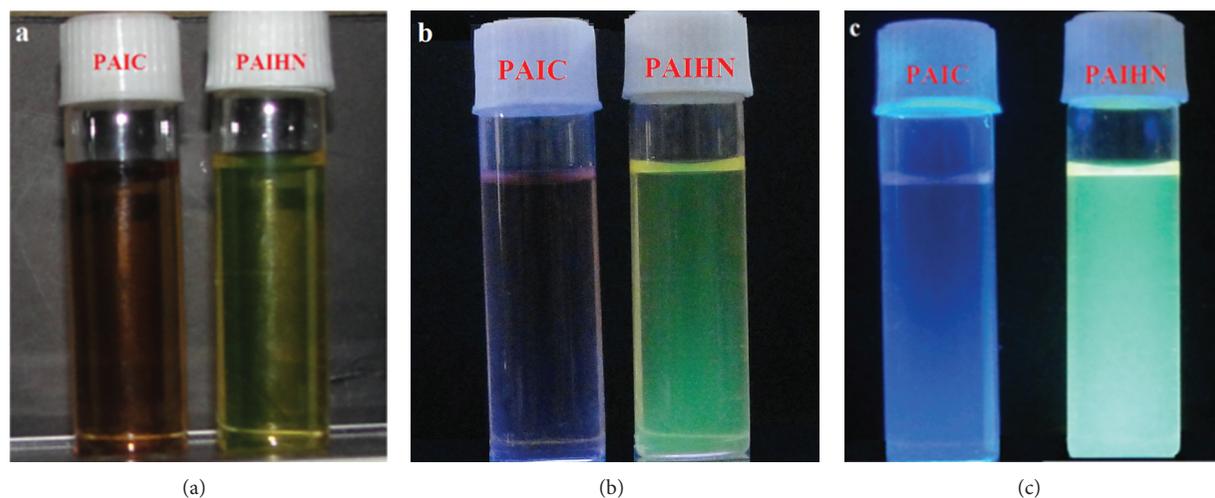


FIGURE 7: Photographs exhibiting the color of PAIC and PAIHN in (a) normal light, (b) UV light (354 nm), and (c) UV light (365 nm).

for aldehyde protons. In addition to this, imine proton signal emerges in the aromatic region in the range  $\delta$  8.48–8.63 ppm.

**3.3. Comparative FTIR of AAHN and PAIHN.** The analysis of the FTIR spectrum of the fluorophore AAHN (Figure 3) and its comparison with that of the modified polymer PAIHN (Figure 3) indicates that the intensity of the absorption band of the C=O group decreases as well as it shifts to longer wavelength side ( $1680\text{ cm}^{-1}$ ) since carbonyl absorption of amides occurs at lower frequency than normal carbonyl absorption due to resonance effect. This indicates the presence of naphthalimide moiety containing amide functional group in the polymer. Also, the band regarding primary amine disappears in PAIHN and a broad band characteristic of hydroxyl group is observed which may be attributed to the introduction of hydroxyl group in the polymer chain. Band for secondary amine is not seen separately which may be due to merging of bands (hydroxyl and secondary amine). A new small band should be observed at  $1676\text{ cm}^{-1}$  due to C=N stretching in the modified polymer, but it might be possible that it is superimposed with the band at  $1680\text{ cm}^{-1}$ . Also, a band corresponding to C–O stretching in primary alcohol can be observed at  $1078\text{ cm}^{-1}$ . Thus, the FTIR spectrum of PAIHN suggested the success of the modification reaction.

**3.4. Determination of Molecular Weight of PAIC and PAIHN by GPC.** The number average molecular weight ( $M_n$ ) of the modified polymer PAIHN ( $M_n = 11500$ ) is larger than the unmodified polymer PAIC ( $M_n = 7200$ ) due to incorporation of bulky naphthalimide units (Figure 5).

Both the polymers PAIC and PAIHN have narrow molar mass dispersion ( $\text{Đ}_m$ ) as 1.19 and 1.21, respectively, indicating controlled molecular weight and well-defined structures. Characterizations of PAIC and PAIHN in terms of molecular weight and molar mass dispersion are given in Table 1.

TABLE 1: Characterization of indole-based polymer PAIC and chemically modified fluorescent polymer PAIHN by GPC.

Sample	$M_n$	$\text{Đ}_m$
PAIC	7200	1.19
PAIHN	11500	1.21

**3.5. Fluorescence Characteristics of PAIHN.** The emission spectra of PAIHN in dimethyl sulfoxide, tetrahydrofuran, acetone, methanol, acetonitrile, and 1,4-dioxane are illustrated in Figure 6. The spectra showed solvent dependency, since the fluorescence maximum shows a bathochromic shift with increased solvent polarity. The emission spectra follow the order methanol > DMSO > acetonitrile > acetone > THF > 1,4-dioxane, that is, order of decreasing solvent polarity. Thus, the obtained polymer exhibits excellent solubility in various organic polar solvents such as tetrahydrofuran, N, N-dimethyl formamide, and dimethyl sulfoxide at room temperature which may be due to the polar hydroxyl group attached to the bulky pendant of naphthalimide derivative linked through imide bond to the indole-based polymer. The bulky pendant AAHN reduces the packing force and increases the free volume of the polymer, thus resulting in good polymer solubility. The only discrepancy is seen in case of methanol, where PAIHN exhibits a pronounced red shift in the wavelength of maximum emission which may be due to the hydrogen bonding property of methanol [18].

PAIC and PAIHN dissolved in acetonitrile were investigated in normal as well as UV light for their change in color. Naked eye observation of PAIC and PAIHN exhibited brown and green coloration, whereas when exposed to UV light (354 and 365 nm) PAIC shows strong blue fluorescence and PAIHN emits bright green fluorescence as can be seen from Figures 7(a), 7(b), and 7(c). Thus, chemical modification has changed the fluorescence property of polymer bathochromically from blue (PAIC) to green (PAIHN).

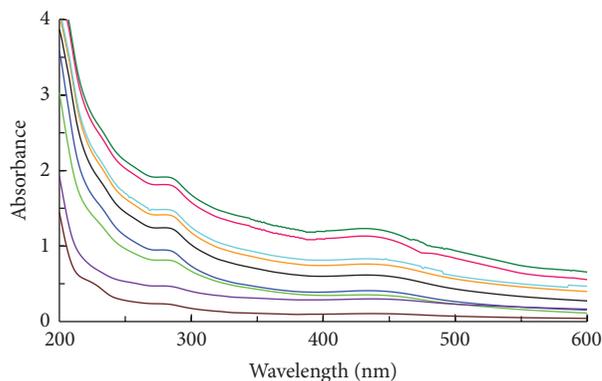


FIGURE 8: UV-visible absorption spectra of PAIHN at various concentrations ( $3.5 \times 10^{-6}$  to  $1 \times 10^{-1}$  mg/mL) in aqueous solution.

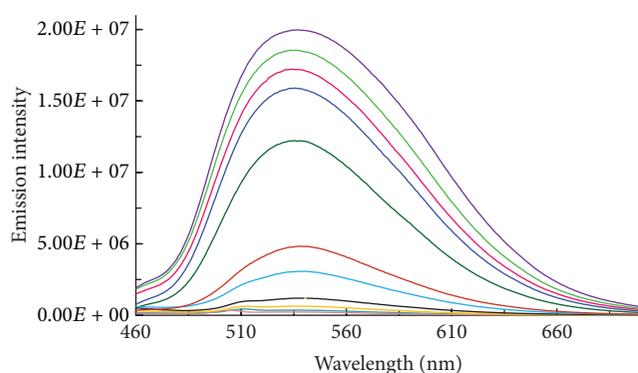


FIGURE 9: Fluorescence emission spectra at various concentrations of PAIHN ( $3.5 \times 10^{-6}$  to  $1 \times 10^{-1}$  mg/mL) in aqueous solutions, excited at 435 nm.

**3.6. Determination of CMC for the Study of Amphiphilic Nature of Polymer.** Since the polymer PAIHN itself exhibits intrinsic fluorescent properties, hence, there was no need of adding any external fluoroprobe for the determination of CMC [19]. Thermodynamic stability of the polymeric micelles in aqueous solutions is inversely proportional to the CMC value [20] thus lower CMC values indicate more stable polymeric micelles [21, 22]. CMC of polymer PAIHN was determined by employing the intensity change upon micelle formation in aqueous solution [19]. On gradually increasing the concentration of PAIHN, absorbance increases with no change in spectral maxima as can be seen in Figure 8. A similar trend was observed in case of fluorescence where polymer exhibits no change in spectral maxima on increasing polymer concentration with specific emission maximum at 538 nm excited at 435 nm (Figure 9). As a result, on increasing polymer concentration, a point is reached, that is, CMC, where the aqueous solution becomes saturated with PAIHN amphiphiles. At this point, further increase in concentration of PAIHN results in the formation of micelles in the solution. For CMC determination of PAIHN, plots of absorbance and fluorescence as a function of concentration of PAIHN are shown separately in Figures 10 and 11. The point at which the two straight lines intersect each other is considered

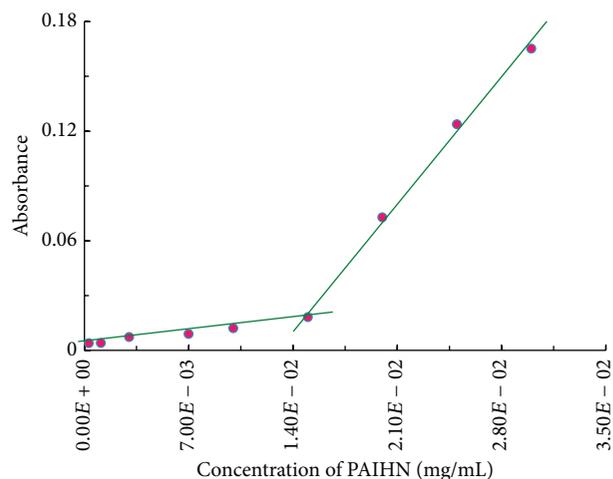


FIGURE 10: Plot of absorbance versus concentration of PAIHN for the determination of CMC.

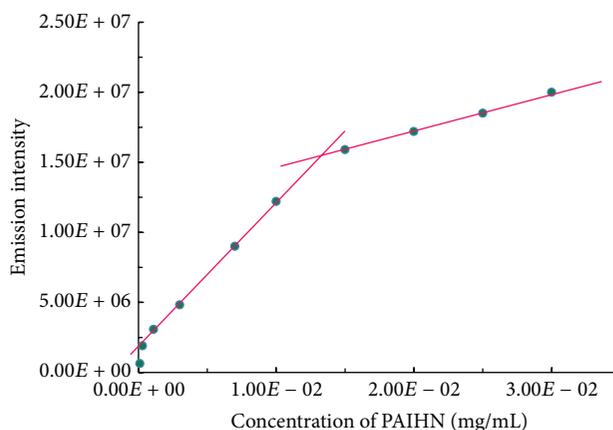


FIGURE 11: Plot of emission intensity versus concentration of PAIHN for the determination of CMC.

to be the respective CMC with the values of 0.015 mg/mL and 0.013 mg/mL obtained using absorption and emission spectroscopy.

The results obtained by the two spectroscopic methods are summarized in Table 2. As can be seen, after micelle formation, absorbance and fluorescence increase with concentration but with different rate. Such observations were reported earlier also [23].

The successful formation of micelles was confirmed by TEM measurement where Figure 12 shows the TEM image of the micelles formed by PAIHN at concentration of 0.014 mg/mL. It can be seen that the micelles have opted a spherical morphology.

## 4. Conclusion

In this paper, fluorescent amphiphilic polymer bearing indole repeating units with naphthalimide pendants was obtained by ATRP followed by chemical modification. The polymer showed a specific fluorescence emission maximum at 538 nm

TABLE 2: Critical micelle concentration of PAIHN obtained by UV-visible and fluorescence methods.

Sample	CMC <sub>UV-Vis.</sub> <sup>a</sup>	CMC <sub>Fluo.</sub> <sup>a</sup>
PAIHN	0.015	0.013

<sup>a</sup>Unit of CMC is given in mg/mL.

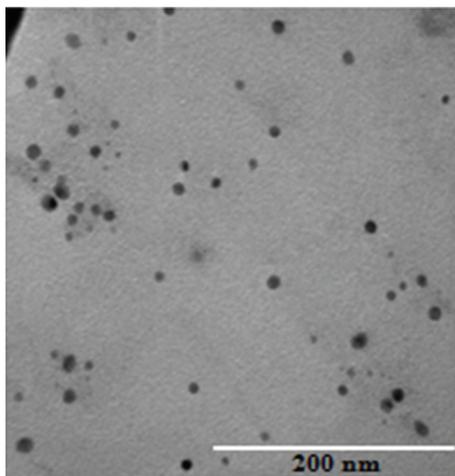


FIGURE 12: TEM micrograph showing micelles of the modified fluorescent polymer PAIHN ( $M_{nGPC} = 11500$ ,  $\bar{D}m = 1.21$ ) of concentration 0.014 mg/mL at room temperature.

excited at 435 nm in aqueous solution. The amphiphilic nature of the polymer was investigated using two spectroscopic methods, namely, absorption and emission spectroscopy. The two methods revealed critical micelle concentrations of PAIHN solution to be 0.015 and 0.013 mg/mL, respectively; thus, the results of these two methods have evidenced fair agreement with each other. TEM studies also supported self-assembled micelles of PAIHN in water. These results demonstrate the possibility of preparing modified amphiphilic polymers with tunable fluorescence.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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### References

- [1] K. A. Janes, P. Calvo, and M. J. Alonso, "Polysaccharide colloidal particles as delivery systems for macromolecules," *Advanced Drug Delivery Reviews*, vol. 47, no. 1, pp. 83–97, 2001.
- [2] G. S. Kwon and K. Kataoka, "Block copolymer micelles as long-circulating drug vehicles," *Advanced Drug Delivery Reviews*, vol. 16, no. 2-3, pp. 295–309, 1995.
- [3] N. Nishiyama and K. Kataoka, "Current state, achievements, and future prospects of polymeric micelles as nanocarriers for drug and gene delivery," *Pharmacology and Therapeutics*, vol. 112, no. 3, pp. 630–648, 2006.
- [4] W. Wang, X. Qu, A. I. Gray, L. Tetley, and I. F. Uchegbu, "Self-assembly of cetyl linear polyethylenimine to give micelles, vesicles, and dense nanoparticles," *Macromolecules*, vol. 37, no. 24, pp. 9114–9122, 2004.
- [5] A. Halperin, M. Tirrell, and T. P. Lodge, "Tethered chains in polymer microstructures," *Advances in Polymer Science*, vol. 100, pp. 30–71, 1991.
- [6] W. Jiang, Y.-D. Wang, Q. Gan et al., "Preparation and characterization of copolymer micelles formed by poly(ethylene glycol)-polylactide block copolymers as novel drug carriers," *The Chinese Journal of Process Engineering*, vol. 6, no. 2, pp. 289–295, 2006.
- [7] C. Liu, P. Ni, X. Fang, and X. Zhou, "Synthesis of amphiphilic diblock copolymers poly[2-(N,N-dimethylamino) ethyl methacrylate]-b-poly(stearyl methacrylate) and their self-assembly in mixed solvent," *Colloid and Polymer Science*, vol. 287, no. 1, pp. 45–55, 2009.
- [8] X. Lu, S. Gong, L. Meng et al., "Novel fluorescent amphiphilic block copolymers: controllable morphologies and size by self-assembly," *European Polymer Journal*, vol. 43, no. 7, pp. 2891–2900, 2007.
- [9] N. Manolova, I. Rashkov, F. Beguin, and H. van Damme, "Amphiphilic derivatives of fullerenes formed by polymer modification," *Journal of the Chemical Society*, no. 23, pp. 1725–1727, 1993.
- [10] C. Hoskins, P. K. T. Lin, L. Tetley, and W. P. Cheng, "Novel fluorescent amphiphilic poly(allylamine) and their supramacromolecular self-assemblies in aqueous media," *Polymers for Advanced Technologies*, vol. 23, no. 3, pp. 710–719, 2012.
- [11] F. Du, J. Tian, H. Wang, B. Liu, B. Jin, and R. Bai, "Synthesis and luminescence of POSS-containing perylene bisimide-bridged amphiphilic polymers," *Macromolecules*, vol. 45, no. 7, pp. 3086–3093, 2012.
- [12] P. Singh, A. Srivastava, and R. Kumar, "Synthesis of amphiphilic poly(N-vinylcaprolactam) using ATRP protocol and antibacterial study of its silver nanocomposite," *Journal of Polymer Science A*, vol. 50, no. 8, pp. 1503–1514, 2012.
- [13] N. I. Georgiev, V. B. Bojinov, and P. S. Nikolov, "Design and synthesis of a novel pH sensitive core and peripherally 1,8-naphthalimide-labeled PAMAM dendron as light harvesting antenna," *Dyes and Pigments*, vol. 81, no. 1, pp. 18–26, 2009.
- [14] I. Grabchev, "Photophysical characteristics of polymerizable 1,8-naphthalimide dyes and their copolymers with styrene or methylmethacrylate," *Dyes and Pigments*, vol. 38, no. 4, pp. 219–226, 1998.
- [15] K. Kawai, K. Kawabata, S. Tojo, and T. Majima, "Synthesis of ODNs containing 4-methylamino-1,8-naphthalimide as a fluorescence probe in DNA," *Bioorganic and Medicinal Chemistry Letters*, vol. 12, no. 17, pp. 2363–2366, 2002.

- [16] A. Srivastava, V. Mishra, P. Singh, and R. Kumar, "Coumarin based polymer and its silver nanocomposite as advanced antibacterial agents: synthetic path, kinetics of polymerization and applications," *Journal of Applied Polymer Science*, vol. 126, no. 2, pp. 395–407, 2012.
- [17] A. Srivastava, P. Singh, R. Kumar, S. K. Verma, and R. N. Kharwar, "Indole based polymer and its silver nanocomposite as advanced antibacterial agents: synthetic path, kinetics of polymerization and applications," *Polymer International*, vol. 62, no. 2, pp. 210–218, 2013.
- [18] S. A. Barghouthi, J. Perrault, and L. H. Holmes, "Effects of solvents on the fluorescence emission spectra of -anilino-8-naphthalene sulfonic acid: a physical chemistry experiment," *The Chemical Educator*, vol. 3, no. 5, pp. 1–10, 1998.
- [19] J. Liaw, T. Aoyagi, K. Kataoka, Y. Sakurai, and T. Okano, "Permeation of PEO-PBLA-FITC polymeric micelles in aortic endothelial cells," *Pharmaceutical Research*, vol. 16, no. 2, pp. 213–220, 1999.
- [20] K. Kataoka, A. Harada, and Y. Nagasaki, "Block copolymer micelles for drug delivery: design, characterization and biological significance," *Advanced Drug Delivery Reviews*, vol. 47, no. 1, pp. 113–131, 2001.
- [21] A. V. Kabanov, E. V. Batrakova, and V. Y. Alakhov, "Pluronic block copolymers as novel polymer therapeutics for drug and gene delivery," *Journal of Controlled Release*, vol. 82, no. 2-3, pp. 189–212, 2002.
- [22] J.-P. Xu, J. Ji, W.-D. Chen, and J.-C. Shen, "Novel biomimetic surfactant: synthesis and micellar characteristics," *Macromolecular Bioscience*, vol. 5, no. 2, pp. 164–171, 2005.
- [23] T. S. Singh and S. Mitra, "Interaction of charge transfer fluorescence probe with non-ionic surfactants: estimation of physico-chemical properties and association constant," *European Journal of Chemistry*, vol. 1, no. 4, pp. 341–347, 2010.



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