Triptycene-Derived Photoresponsive Fluorescent Azo-Polymer as Chemosensor for Picric Acid Detection

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Supporting Information

ABSTRACT: Two new triptycene-based azobenzene-functionalized polymers (TBAFPs) have been synthesized using the well-known Pd-catalyzed Sonogashira cross-coupling polycondensation reaction between 2,6-diethynyltriphyene and (meta or para) dibromo-azobenzenes. Enhancement of the fluorescent emission intensity was observed upon trans \( \rightarrow \) cis isomerization of \(-N=\text{N}\) linkage in TBAFPs. The cis-lifetime of TBAFP1 is rather long (greater than 2 days). The resulting materials were tested as a potential chemosensor for the detection of picric acid (PA)—a water pollutant as well as chemical constituent of explosives used in warfare. PA was found to interact strongly with TBAFPs, which led to significant quenching of the latter’s fluorescence emission intensities. The binding constants are in the order of \(10^5\) M\(^{-1}\). TBAFPs were also able to detect PA in nanomolar concentrations.

INTRODUCTION

In recent decades, research related to polymers derived from monomers with azobenzene functional groups have attracted considerable attention.\(^1\) Azobenzene can exist in either trans or cis form with regard to the \(-N=\text{N}\) linkage with the former being thermodynamically more stable than the latter. The azobenzene unit undergoes photoisomerization because this chromophore is photoresponsive. Therefore, one of the most exciting properties of azobenzene-functionalized polymers is their photoresponsive nature, which is due to photoinduced isomerization of azo units. The potential applications of azo-polymers are, thus, mainly due to their unique ability to photoisomerize, photo-orient, and show refractive effect changes induced by light.\(^2,11\) These materials are, therefore, recognized as promising candidates for applications such as optical data storage,\(^12,13\) reversible holograms,\(^14\) reversible photomechanical systems,\(^15\) holographic media for high-capacity data storage,\(^16\) as adsorbents with tunable pore size for \(\text{CO}_2\) capture,\(^17\) and light-triggered drug release.\(^18\) Photochromic properties of azobenzene were also applied in the design of molecular machines,\(^19\) two dimensional vehicles,\(^20\) molecular scissors,\(^21\) molecular pedals,\(^22\) molecular sunflower,\(^23\) molecular lift,\(^24\) and host–guest recognition.\(^25\) Azo-polymers may have the azobenzene chromophore incorporated either in the side chains\(^26\) or in the polymer main chain.\(^27\)

Triptycene is the smallest member of a class of aromatic compounds known as "iptyocene" in which three or more arene rings are integrated via a bicyclo[2.2.2]octatriene bridgehead unit.\(^28\) Iptycene-based monomers are “exceptionally stable” and are reported to yield “high-performance polymers”.\(^29\) Potential applications of iptyocene-based polymeric materials include but are not limited to fluorescent sensors (for detection of trace quantities of explosives),\(^30\) thermally stable interlayer dielectric materials (for use in integrated circuits),\(^31\) low dielectric constant materials (for use as insulators),\(^32\) and as structural materials (with improved mechanical properties).\(^33,34\) More recently, triptycene-based porous network polymers are being projected as materials for selective capture and storage of small gas molecules such as \(\text{H}_2\) and \(\text{CO}_2\).\(^35,36\) The rigid three-dimensional framework of iptyocene motifs generate internal free volume in such polymers resulting in the aforementioned favorable properties.\(^29\)

Picric acid (PA) belongs to the family of nitroaromatic compounds (NACs).\(^37\) Nitrated aromatic molecules such as TNT, DNT, and others are chemical components of certain explosives.\(^37\) PA was also used extensively for this purpose in the last century.\(^38\) PA is also a useful industrial chemical employed in pharmaceutical and dye industries.\(^39\) PA is highly soluble in water, and its extensive use may lead to contamination of ground water and soil. This is a matter of environmental concern because PA toxicity may cause human health-related issues such as eye/skin irritation, anemia, lung damage, and even cancer.\(^40\) Therefore, development of probes to detect PA at very low concentrations is an active area of research. Till date, various highly sensitive probes have been designed to sense PA in low concentrations and these are based on small molecules,\(^41\) nanomaterial,\(^42,43\) gels,\(^44\) polymeric...
networks, and even metal organic frameworks. Most sensors detect PA using fluorescence spectroscopy. PA has an electron-deficient aromatic ring (due to the presence of electron-withdrawing nitro groups) that interacts with electron-rich fluorescent sensors rendering them nonfluorescent. This method of PA detection is most convenient because it is economical and a rapid testing technique.

Herein, we report for the first time, two triptycene-based linear polymers bearing azobenzene chromophores as integral units of the main chain. We have christened these polymers triptycene-based azobenzene-functionalyzed polymers (TBAFPs). These polymers are soluble in organic solvents and are fluorescent in nature. To the best of our knowledge, photoresponsive properties of triptycene-based azo-polymers have not been explored till date. Therefore, we have studied their photophysical properties in solution. Additionally, application of these polymers in sensing PA has been studied. It has been observed that using TBAFPs, trace quantities of PA can be detected with high sensitivity.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of Monomers.** 2,6-Diethynyltriptycene (DET) monomer (1) was prepared using a previously reported synthetic protocol using the Sonogashira coupling reaction between 2,6-dibromotriptycene and trimethylsilylacetylene. (E)-1,2-Bis(4-bromophenyl)diazene (2) was prepared by reacting 4-bromoaniline with KMnO₄ and FeSO₄ in dichloromethane (DCM) solvent (Scheme 1). Using the similar reaction conditions, (E)-1,2-bis(3-bromophenyl)diazene (3) was obtained in high yield (90%). Both molecules (2 and 3) were obtained as orange-colored solids, and these were characterized using Fourier-transform infrared (FTIR) and NMR spectroscopies that confirmed their purity. The presence of azo-linkage (−N=N−) was confirmed by the presence of a band centered at 1472 cm⁻¹ in the respective FTIR spectrum (Supporting Information, Figure S1). All signals in the ¹H and ¹³C{¹H}NMR spectra of 2 and 3 were correctly assigned (Supporting Information, Figures S2 and S3). In the ¹³C NMR spectra of 2 and 3, the peaks at 151 and 153 ppm were assigned to the carbon nuclei attached to the azo (−N=N−) functional group (Figures S4 and S5).

**Synthesis and Structural Characterization of Polymers.** Pd/Cu-catalyzed Sonogashira cross-coupling reaction is one of the most convenient and widely used method to yield C–C bonds between aryl halides and terminal acetylenes. 2,6-DET (1) and dibromo azobenzene monomers (2 or 3) were reacted in the presence of catalytic amount of Pd(PPh₃)₄ to yield the desired polymers (TBAFP1 and TBAFP2) in high yields (>90%) (Scheme 2). In these reactions carried out at 70 °C, dimethylformamide was used as the solvent, triethylamine (TEA) as the base, and cuprous iodide as the cocatalyst. TBAFPs are macromolecules that have triptycene and azobenzene units linked via ethynyl bridges. Although TBAFP1 is orange in color, TBAFP2 was obtained as a reddish brown solid. The number-average molecular weight (Mₙ) and the weight-average molecular weight (M_w) of TBAFPs were obtained from their respective gel permeation chromatography (GPC) analysis (Table 1 and Figures S6 and S7) in tetrahydrofuran (THF) (polystyrene was used as the standard). In case of TBAFP1, the dispersity (D_M = 2.44) corresponds to 16 repeating units (P_a = 16). On the other hand, for TBAFP2 having relatively lower Mₙ, the dispersity (D_M = 2.55) corresponds to nine repeating units (P_a = 9). TBAFPs were found to be easily soluble in halogenated (CDCl₃ and CH₂Cl₂) as well as nonhalogenated (tetrachloroethane)

**Scheme 1. Synthesis of Monomers**

**Scheme 2. Synthesis of Polymers TBAFP1 and TBAFP2**
drofuran and toluene) solvents (solubility chart of TBAFPs Table S1). The excellent solubility exhibited by these polymers was attributed to the presence of the bulky and rigid triptycene units that inhibits efficient packing of polymer chains.

The structure of polymers TBAFP1 and TBAFP2 were confirmed by FTIR and $^1$H NMR spectroscopy. In the FT-IR spectra of TBAFPs (Figure 1), the characteristic peak due to the azo (−$\equiv$N−$\equiv$) linkage was observed at 1468 cm$^{-1}$. The presence of −C≡C− linkages in the polymer backbone was confirmed from the presence of the weak band appearing at 2210 cm$^{-1}$. Additionally, absence of C≡H stretching band also confirmed the successful Sonogashira polycondensation reaction between DET and dibromoazobenzenes (2 and 3) leading to the formation of new C(sp$^2$)−C(sp) bonds.

Furthermore, the structures of the polymers (TBAFP1 and TBAFP2) were also confirmed by $^1$H NMR spectroscopy. In the NMR spectra of TBAFPs (Figure 2) recorded in CDCl$_3$ as the solvent, the signal at around $\delta$ = 5.50 ppm corresponds to the characteristic bridgehead protons of the triptycene unit. In TBAFP1, the protons in the phenyl ring that are in ortho position with respect to the azo (−N≡N−) group appear at 7.92 ppm. The remaining hydrogen nuclei bonded to the aromatic ring of triptycene and azobenzene unit are shifted upfield and appear in the range 7.60−7.00 ppm. Similarly, all signals appearing in the spectrum of TBAFP2 were assigned precisely (Figure 2). A broad feature in the powder X-ray diffraction (PXRD) pattern (Figure 3) indicated the amorphous nature of TBAFPs. Incorporation of rigid and bulky triptycene units in the main polymeric chain prevents their efficient interchain interactions and packing, which results in the observed amorphous nature of TBAFPs.

**Morphological Analysis of TBAFPs.** Figure 4 shows field-emission scanning electron microscopy (FESEM) micrographs of the TBAFPs. These polymers appear as nail-shaped nanorods with one broad end that gradually tapers to a relatively much narrower end. The diameter of the "nail-head" is in the range between 100 and 200 nm. The length of these nanonails varied between 400 and 500 nm. It can be observed that the broad ends of the "nanorods" exhibit flat cross-sections. There was no marked difference in the morphologies of TBAFP1 and TBAFP2.

**Thermal Property of TBAFPs.** Thermogravimetric analysis (TGA) of these polymers was performed to gauge their thermal stability (Figure 5). The thermal degradation temperature ($T_d$ at 10% weight loss) for the polymer, TBAFP1 (470 °C) is higher than that for TBAFP2 (214 °C), and this may be due to the relatively higher molecular weight in case of the former. The char yields of both polymers are slightly greater than 64% at 800 °C (Table 1). The presence of rigid and robust triptycene motifs in the polymer chains result in the high thermal stabilities observed for TBAFPs reported herein. Differential scanning calorimetry (DSC) traces were recorded for TBAFPs (Supporting Information, Figures

**Figure 1.** FTIR spectra of TBAFP2 (top), TBAFP1 (middle), and DET (bottom).

**Figure 2.** $^1$H NMR spectra of TBAFPs.

**Figure 3.** PXRD pattern of polymers (TBAFP1 and TBAFP2).

**Figure 4.** FESEM images of TBAFPs.
corresponds to the photoisomerization of TBAFP1 under UV Irradiation (Scheme 3). The band observed at 391 nm is due to \( \pi-\pi^* \) transition in azobenzene chromophore in the more stable trans form (Figure 7a). Upon irradiating the TBAFP1 solution with UV radiation (300 nm), the intensity of the \( \pi-\pi^* \) absorption band at 391 nm was observed to decrease gradually with the increased irradiation time (Figure 7a). After 20 min of UV irradiation, the \( \pi-\pi^* \) absorbance band shifted to a shorter wavelength and was then observed at 320 nm (Figure 7a). We attribute this spectral change to trans \( \rightarrow \) cis isomerization of the azo linkages in the polymer (TBAFP1) main chain upon exposure to UV radiation. The blue shift of \( \lambda_{\text{max}} \) corresponds to considerable decrease in the extent of conjugation in the cis-form.

In case of TBAFP2, the strong absorption band centered at 316 nm corresponds to the \( \pi-\pi^* \) transitions of trans-azobenzene units in the polymer main chain (Figure 7b). The intensity of this band also decreased when a THF solution of TBAFP2 was irradiated with UV light (300 nm) leading to photoinduced trans to cis isomerization (Figure 7b). The band appears at relatively shorter wavelength in the cis-form (than that due to trans-azobenzene units) because of further decrease in degree of conjugation in the main chain. The rate constants of photoinduced isomerization of TBAFPs were estimated from the first order kinetics expression \( \ln[(A_0 - A_t)/(A_0 - A_\infty)] = k_{\text{exp}} t \) where \( A_0, A_t, \) and \( A_\infty \) are the absorbance at \( t = 0 \) (before irradiation), \( t \), and \( t = \infty \), respectively, and \( k_{\text{exp}} \) is the rate constant.\(^{51}\) First-order rate constant for trans \( \rightarrow \) cis photoisomerization of polymer TBAFP1 and TBAFP2 were observed to be \( 5.53 \times 10^{-4} \) s\(^{-1} \) and \( 13.5 \times 10^{-4} \) s\(^{-1} \), respectively (Figure S10, Supporting Information).

Photoinduced Fluorescence Enhancement with Trans–Cis Isomerization. Before exposure to UV radiation, dilute solution of TBAFPs (THF as solvent and concentration \( = 10^{-7} \) M) shows very weak fluorescence upon excitation at 320 nm (Figure 8, at \( t = 0 \) min). This is also indicated from the very low quantum yields (\( \text{trans-TBAFP1}: \Phi_{\text{em}} = 403 \text{ nm and } \Phi = 0.0087, \) TBAFP2: \( \lambda_{\text{em}} = 425 \text{ nm and } \Phi = 0.0048 \)). The fluorescence emission spectra for these polymers were again recorded after irradiating solutions of TBAFPs with UV radiation. A noticeable increase in the fluorescence intensity was observed with UV irradiation (Figure 8a,b). Fluorescence enhancement upon photoisomerization (from trans \( \rightarrow \) cis) has been previously reported by others.\(^{52-56}\) These instances of fluorescence enhancement may be due to nonplanar/twisted geometry in the cis isomer in which photoinduced electron transfer is inhibited due to reduced extent of conjugation of the nitrogen lone pair of electrons and the \( \pi \) electrons of the fluorophore.\(^{51}\) Moreover, enhanced fluorescence emission in macromolecules containing an azobenzene unit has also been attributed to aggregation such as self-assembled bilayer aggregates.\(^{54,56-59}\) In case of TBAFP1, a 20 min UV irradiation resulted in the fluorescence intensity increase by 20 times relative to that before its exposure to UV light (Figure 8b).

Scheme 3. Photoisomerization of TBAFP1 under UV Irradiation

![Scheme 3](image-url)
An appreciable increase (seven times) in the quantum yield of TBAFP1 was observed after its exposure to UV radiation ($\lambda_{ex} = 320 \text{ nm}$, $\lambda_{em} = 386 \text{ nm}$ and $\Phi = 0.06$). This implies that upon isomerization of azobenzene units from the trans to the cis form, there is an enhancement of fluorescence for this material. Change in the quantum yield value of TBAFPs upon photoisomerization has been shown in Figure S11. Similarly, in case of TBAFP2, the quantum yield improved to 0.0478 ($\lambda_{em} = 425 \text{ nm}$), which is around 16 folds relative to the very weakly fluorescent TBAFP2 in its trans form [Figure 8b]. Weakly fluorescent TBAFP1 and TBAFP2 in the trans form have average radiative lifetime $\langle \tau \rangle$ of 1.12 and 1.21 ns, respectively (Figure 8c). TBAFPs emitted enhanced fluorescence after photoisomerization. The lifetime decay plots of these fluorescent TBAFPs after 20 minutes of UV irradiation are shown in Figure 8d. The average radiative lifetime $\langle \tau \rangle$ was observed to be 2.94 and 2.42 ns for TBAFP1 and TBAFP2, respectively. The fluorescence quantum yield measurements were performed using quinine sulfate as the reference in 1 N H$_2$SO$_4$ solution ($\Phi = 0.546$).

**Thermal Cis-to-Trans Isomerization.** The thermal cis–trans isomerization of azobenzene units is reported to be fast.$^{60,61}$ However, the rate of thermal back-isomerization from cis-form to trans-form is also dependent on the nature and conformation of the compound.$^{62,63}$ The energy barrier for this thermal cis–trans isomerization is around 90 kJ/mol.$^{11,61}$ Therefore, the thermodynamically unstable cis form relaxes back to stable trans form even at room temperature, rendering a relatively smaller cis-lifetime of few hours in case of azobenzene. On the other hand, for practical applications such as data storage and photochromic memory, a “two stable state system” is desired.$^{61,64}$ Attempts have been reported in the past to increase the cis-isomer’s lifetime. For example, the inclusion of azobenzene motifs in the main chain of a polyurethane enhances the cis-life by up to 4 days.$^{65}$ Bulky substituents were incorporated to prevent the thermal back isomerization of azo motifs, which increased the half-life by more than 5 days.$^{65}$ Conformational ring strain in azobenzene contained macrocycles was responsible for higher cis lifetime up to 19.7 days.$^{62}$ Similarly, cyclic peptides bearing azobenzene motifs were reported to exhibit relatively higher cis lifetime.$^{66}$
units have been reported to have a cis lifetime of nearly 40 days.67 These representative examples reiterate that the cis−trans isomerization of azo linkages present in the polymeric main chain is usually associated with large degree of geometric changes in the overall molecular con
figuration. In case of TBAFPs reported herein, the presence of bulky and rigid triptycene motif in these polymers are anticipated to improve the cis-lifetime of the azo linkages. Interestingly, very slow thermally driven cis−trans isomerization was observed even after keeping samples (previously treated with UV light) in dark for 2 days (Figure 9 a). In case of TBAFP1, an improvement in quantum yield (Φ = 0.08) (Figure 9b) was observed after incubation of the cis isomer in dark for 2 days at 25 °C. The quantum yield was relatively less (Φ = 0.06) before thermal cis-to-trans isomerization.

**Interaction of TBAFPs with PA.** TBAFPs are fluorescent in the cis form after photoisomerization. Additionally, TBAFPs have electron-rich arene rings of triptycene as well as nitrogen-rich azo (−N=−N−) linkages in the polymer framework. In this context, PA (a NAC) is relatively electron deficient due to the presence of three electron-withdrawing nitro groups in the arene ring. Therefore, it was expected that the relatively electron-rich polymer framework of TBAFPs would have facile interactions (hydrogen bonding/π−π/dipole−dipole interactions) with PA.43,47,68−71 With these premises in mind, we were curious to study the host−guest interaction between these polymers (TBAFPs) and PA. The fluorescence emission of TBAFPs was quenched in the presence of PA with an excellent binding affinity. TBAFPs were dissolved in THF and solution concentration was 2 × 10−7 mol L−1 in THF. For host−guest interaction between TBAFPs and PA, absorbance titration experiments were performed between cis-form of TBAFPs upon incremental addition of PA [Supporting Information, Figure S12]. In case of the fluorescence titration experiment, a steady decrease in the fluorescence intensity (fluorescence quenching) of TBAFPs was observed (Figure

![Figure 9.](image1)

**Figure 9.** Spectral changes in (a) absorption and (b) emission spectra of UV-irradiated TBAFP1 (THF solution) after 2 days of dark incubation.

![Figure 10.](image2)

**Figure 10.** Fluorescence quenching of (left) TBAFP1 (2 × 10−7 mol L−1) and (right) TBAFP2 (2 × 10−7 mol L−1) in the presence of PA as quencher in THF.

![Figure 11.](image3)

**Figure 11.** B−H fluorescence plot of 1:1 complexation between (left) PA and polymer TBAFP1 and (right) PA and polymer TBAFP2 recorded in THF.
formation of 1:1 complex (eq 1).

\[
\frac{F_0}{F_0 - F_i} = \frac{1}{A} + \left( \frac{1}{K_A} + \frac{1}{Q} \right)
\]  

(1)

In the above eq 1, "\(F_0\)" is fluorescence intensity of the TBAFPs in the presence of a quencher. The fluorescence intensity of TBAFPs in the presence of a quencher is "\(F\)". The concentration of the quencher (PA) is represented by \([Q]\). The constant \(A\) is associated with the emission quantum yield of the complexed and uncomplexed polymer. \(K\) is the binding constant of TBAFPs with PA.

Fluorescence quenching data revealed an excellent fit for 1:1 complexation between polymer TBAFPs and PA (Figure 11). The corresponding binding constant (\(K\)) for 1:1 complexation between polymers and PA were calculated to be \(3.39 \times 10^5\) and \(1.81 \times 10^5\) for polymers, TBAFP1 and TBAFP2, respectively. Interestingly, TBAFP1 shows considerably higher fluorescence quenching (78%) relative to TBAFP2 (57%), which clearly suggests its higher affinity toward PA. This inference was also supported by the higher magnitude of binding constant value calculated for TBAFP1.

Additionally, the quenching effect of TBAFPs by PA (as quencher) was studied by using the well-known Stern–Volmer equation: \(F_0/F = 1 + K_{sv}[Q]\), where \(F_0\) is the initial fluorescence intensity of TBAFPs in the absence of PA and \(F\) is the corresponding fluorescence intensity after adding PA having a concentration of \([Q]\), and \(K_{sv}\) is the quenching coefficient of TBAFPs for PA.

Using a plot of \(F_0/F\) (relative fluorescence intensity) versus \([Q]\), Stern–Volmer quenching constant (\(K_{sv}\)) was estimated from the slope of the linear plot (Figure 12). In case of titration of TBAFP1 and TBAFP2 with PA, \(K_{sv}\) was measured to be \(537,000\) and \(243,000\), respectively (Figure 12 and Table 2), indicating that TBAFPs interact efficiently with PA.

The PA “detection limit” of TBAFPs was also obtained from the fluorescence quenching plots (Figure 12). The limit of detection (LOD) was calculated using the following equation

\[
\text{LOD} = 3 \times \left( \frac{\text{SD}}{B} \right)
\]

where “SD” is standard deviation and “B” is the slope of the curve equations.

**Table 2. Binding Constant (\(K\)), Stern–Volmer Constant (\(K_{sv}\)) and Limit of Detection of TBAFPs With PA**

| polymers | binding constant \(K\) in \(M^{-1}\) with PA | Stern–Volmer constant \(K_{sv}\) in \(M^{-1}\) with PA | LOD values in nM |
|----------|---------------------------------|---------------------------------|-----------------|
| TBAFP1   | \(3.39 \times 10^5\)            | \(5.3 \times 10^5\)            | 144             |
| TBAFP2   | \(1.18 \times 10^5\)            | \(2.4 \times 10^5\)            | 151             |

The detection limits for PA were observed to be 144 and 151 nM for TBAFP1 and TBAFP2, respectively. These data suggest that fluorescent TBAFPs may be used for detecting PA present in ultra-trace quantities.

**CONCLUSIONS**

In summary, we report herein, two new triptycene-based polymers (TBAFPs) containing photoisomizable azobenzene groups in polymer main chain. The synthesis utilized Sonogashira cross-coupling reaction of DET with two different monomers bearing azobenzene functional groups. The UV–vis absorption spectra suggested that TBAFP1 has higher extended conjugation compared to TBAFP2. SEM images of TBAFPs indicate that these have well-defined morphology resembling that of nanodimensional nails. The photoinduced isomerization of azo groups (solution of TBAFPs in THF) resulted in noticeable fluorescence emission enhancement. Upon UV irradiation, the material obtained with azobenzene units in cis-orientation had considerably higher life-time (up to 2 days) suggesting that the cis- to trans-thermal isomerization was rather slow. The photo-switchable and fluorescence-emitting properties of TBAFPs under UV irradiation makes them promising candidates for various potential applications. Additionally, the fluorescent material obtained after UV-light irradiation was found to interact efficiently with PA. LOD estimation projects TBAFPs as potential chemosensor materials for detection of PA in nanomolar concentration. Thus, new polymers reported herein enrich the library of materials that exhibit strong interaction with PA and TBAFPs may have useful applications in the sensing of nitroaromatics.

**EXPERIMENTAL SECTION**

**Materials.** 4-Bromoaniline (97%) and 3-bromoaniline (97%) were purchased from Sigma-Aldrich. Ferrous sulfate \((FeSO_4 \cdot 7H_2O)\) and potassium permanganate \((KMnO_4)\) were purchased from Central Drug House (CDH) and used as received. The solvents dimethylformamide (DMF) [high-performance liquid chromatography (HPLC) grade] and TEA were purchased from CDH. TEA was dried in our laboratory. PA was purchased from Thomas Baker (Chemicals). Tetrakis-
(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (99%) and copper iodide (CuI) were purchased from Sigma-Aldrich and were used as received.

**General Methods and Instrumentation. Synthesis of Monomers 2 and 3. para-Dibromoazobenzene (2).** A 4-Bromoaniline (344 mg, 2 mmol) was dissolved in 20 ml of DCM and to this solution was added a previously mixed solid mixture of ferrous sulfate (FeSO₄·7H₂O) (1 gm, 3.59 mmol) and potassium permanganate (KMnO₄) (1 gm, 6.32 mmol). This reaction mixture was refluxed for 16 h at 35 °C. After the completion of reaction (confirmed by thin-layer chromatography and appearance of orange color), the reaction mixture was filtered using a Celite bed and washed with DCM. The filtrate was evaporated to obtain the crude product as an orange colored solid that was purified by column chromatography using 12–15% DCM in hexane. The final purified product was obtained as an orange crystalline solid. Yield (94%, 640 mg). The product obtained was characterized using NMR and infrared (IR) spectroscopies. ¹H NMR spectra were recorded on a BRUKER 400 MHz spectrometer using CDCl₃ as the solvent. ¹³C{¹H}NMR spectra were also recorded on a BRUKER 100 MHz spectrometer using CDCl₃ as the solvent. FT-IR spectra of the samples were recorded using KBr pellets.

**General Synthesis of TBAFPs.** Dibromoazobenzene monomer (2 or 3) (68 mg, 0.2 mmol), monomer 1 (DET) (60 mg, 0.2 mmol), CuI (2 mg, 0.02 mmol), and tetrakis(triphenylphosphine) palladium(0) (Pd(PPh₃)₄) (99%) and copper iodide (CuI) were purchased from Sigma-Aldrich and used as received.

**Polymer Characterization.** ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer using CDCl₃ solution of TBAFPs containing tetramethylsilane (TMS) as the internal standard. IR spectra of the TBAFPs were recorded using Shimadzu IR Affinity-1 spectrometer. TGA data were obtained using SDT Q600 (TA Instruments) at a scan rate of 10 °C/min under nitrogen flow (100 mL/min). Thermal properties of TBAFPs were also tested by using DSC (TG-DSC, STA 449 F3 Jupiter NETZSCH, Selb, Germany) with a heating or cooling rate of 10 °C/min.

**GPC Analysis.** Agilent PL-GPC 50 integrated GPC spectrometer was used to determine molecular weights and polydispersities of TBAFPs using THF as the eluent. Polymer solutions (sample concentration 1 mg/mL) were prepared in THF. The molecular weights of the polymers were determined using a standard calibration curve based on polystyrene standards and flow rate used was 1.0 mL/min at 25 °C.

**Photophysical Investigations (UV–Vis Absorption, Life Time Decay Plots, and Fluorescence Spectroscopies).** UV–vis spectra were recorded using a Shimadzu UV-2550 UV–vis spectrophotometer. Fluorescence spectra were recorded using the Horiba Jobin Yvon Fluoromax-4 spectrophotometer. UV–vis absorption and fluorescence spectra of polymer solutions (10⁻⁷ M polymer concentration in toluene) were measured using a 1 cm quartz cell. Lifetime decay plots of TBAFPs were recorded on a HORIBA Scientific Deltalight (Modular Fluorescence Lifetime System).

**Microscopic Analysis (FE-SEM Investigation).** For sample preparation, the following protocol was adapted. A suitably sized silicon wafer was cleaned using acetone (HPLC grade) and then rinsed with water (double distilled). The polymer solution (concentration 10⁻³ M in toluene) was dropcasted on the precleaned silicon wafer. The films thus obtained because of solvent evaporation were allowed to dry at room temperature for 1 h to remove any residual solvent. FE-SEM images of the dropcasted films (of TBAFPs) were captured using a Carl Zeiss ultra plus field emission scanning electron microscope. For high resolution imaging, a very thin layer of gold was deposited on the surface of the polymer sample using a Quorum Q150RS vacuum sputter to increase the electrical conductivity.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00497.

FTIR spectra of polymers monomers 2 and 3, ¹H NMR spectra of monomers 2 and 3, ¹³C NMR spectra of monomers 2 and 3, GPC traces of polymers TBAFPs, solubility Chart of polymers TBAFPs in various solvents, DSC traces of polymers TBAFPs, first-order rate constant for trans–cis photoisomerization of TBAFPs, change in the quantum yield value of TBAFPs upon photoisomerization, and absorbance titration of TBAFPs with incremental addition of PA (PDF)
N.D. thanks Indian Institute of Technology Patna for providing infrastructure and instrumental facilities required for this research. M.A. and R.B. thank Indian Institute of Technology Patna for providing research fellowship. S.M. thanks UGC, New Delhi for a Senior Research Fellowship.

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