

Highly Emissive Iptycene–Fluorene Conjugated Copolymers: Synthesis and Photophysical Properties

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ABSTRACT: Iptycene-type quinoxaline and thienopyrazine monomers were successfully synthesized via a condensation between 10-dihydro-9,10-ethanoanthracene-11,12-dione and the corresponding diamines. Copolymers based on fluorene and three iptycene monomers were prepared via Suzuki coupling reaction, and they exhibited good solubility in appropriate organic solvents. These copolymers are fluorescent in both solution and the solid state, emitting blue, greenish-blue, and red color due to the different electronic properties of the iptycene comonomers. The difference in their absorption and emission spectra was attributed to the donor–acceptor charge transfer interactions and/or polymer backbone conformational changes induced by steric effects. Moreover, the spectroscopic data clearly demonstrated the insulating effect of iptycene units, which prevented the aggregation of the polymer chains and the formation of excimers in the solid state.

Introduction

Iptycenes, especially triptycene and pentiptycene derivatives, have been extensively employed in our laboratory to design and synthesize novel functional materials.¹ Conjugated polymers containing these rigid, three-dimensional iptycene scaffolds have been found to display improved photostability and quantum yields in the solid state as well as enhanced solubility in common organic solvents. These enhancements were proposed to result from spatial isolation of the polymer backbones that significantly reduces interchain interaction in the solid state, which is believed to play a dominant role in determining the thin film optical properties of conjugated polymers.² Upon introducing iptycene units into the conjugated polymer, the three-dimensional bulky structures sterically isolate the polymer backbones and thereby reduce interchain electron/orbital coupling and self-quenching, which often accompanies these interactions. These features afforded novel, highly fluorescent conjugated polymers, such as poly(*p*-phenyleneethynylene)s (PPEs), which have been demonstrated to be ultrasensitive sensory materials. Sensor applications have been developed to take advantage of the ultrasensitive fluorescent quenching response of PPEs to vapors of electron-accepting analytes, such as 2,4,6-trinitrotoluene and 2,4-dinitrotoluene.^{1a–j} In addition, the rigid elaborated scaffolds also introduce additional free volume in the solid-state material, which facilitates rapid analyte diffusion into the polymer film to achieve faster and larger-amplitude responses.^{1i,j} This large free volume inherent to the iptycene scaffolds has also been exploited to achieve enhanced chromophore and liquid crystal alignments.^{1a–c}

On the basis of the advantages of iptycene-containing PPEs, we have been interested in extending this design concept into other conjugated systems, which have also shown excellent properties for numerous applications.³ Polyfluorenes (PFs) have been widely studied for polymer light-emitting diodes (PLEDs) because of their processability, high quantum yield, and good charge transport properties.⁴ However, the PLED applications of PFs often suffer from their poor electron-transporting properties, which results in a large electron-injection barrier and unbalance of charge carrier transport. Recent work found that copolymerization of fluorene with various electron-accepting and/or electron-transporting moieties could solve this problem.⁵ Hence, fluorene-acceptor-based conjugated copolymers have

attracted considerable attention.⁶ Pyridine, quinoxaline, benzothiadiazole, and thienopyrazine are good examples of acceptors that have been extensively studied. In addition to the improvement of charge injection and transport, the light-emitting color and efficiency of PLEDs based on the fluorene-acceptor copolymers were found to be easily tuned by the acceptors. Interestingly, photovoltaic devices with good efficiencies and field effect transistors with high electron mobility based on these kinds of copolymers were also recently demonstrated.^{6c,d}

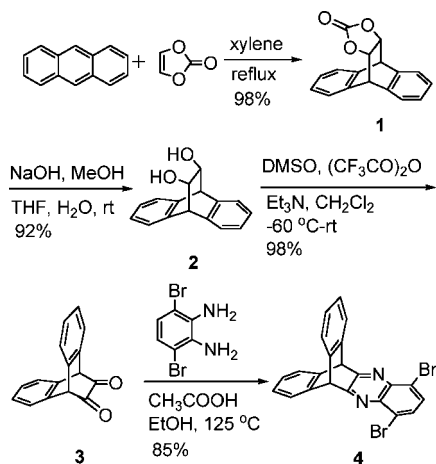
Inspired by the considerations above, we designed and synthesized three fluorene–iptycene-based conjugated polymers and investigated their properties. In this work, we present the synthesis of two triptycene-type quinoxaline and thienopyrazine acceptor monomers and the synthesis of the corresponding iptycene-type donor–acceptor copolymers using a palladium(0)-catalyzed Suzuki coupling reaction. These two copolymers were also compared with a regular fluorene–triptycene copolymer. The three copolymers have iptycene groups of different electronic properties installed in each repeating unit and expand the scope of both the iptycene “insulation” effect and the ability to tune the band structure of conjugated polymers.

Results and Discussion

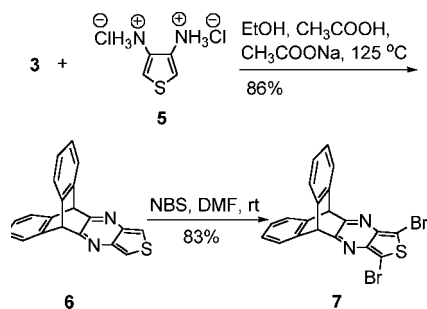
Monomer Synthesis. The triptycene-type monomers **4** and **7** were prepared from the condensation of a diketone with corresponding diamines (Scheme 1).⁷ The diketone compound **3** was prepared by a Diels–Alder reaction of anthracene and vinylene carbonate, followed by a base-assisted hydrolysis in a methanol/water/tetrahydrofuran (THF) mixture, leading to the diol product **2** in high yield.^{8d,9} Finally, an activated Swern oxidation using trifluoroacetic anhydride and dimethyl sulfoxide (DMSO) gave the target product **3** as a yellow solid.^{8a,d,9a,10} Monomer **4** was obtained as a white solid by condensing **3** with 3,6-dibromo-1,2-diaminobenzene, which was prepared from the reduction of dibromobenzothiadiazole.^{7a,11} A similar condensation between diketone **3** and 3,4-diaminothiophene hydrochloride (**5**),¹² which was easily prepared from a nitration of 2,5-dibromothiophene followed by a reduction with tin metal under acidic conditions,^{12a} afforded iptycene-type thieno[3,4-*b*]pyrazine (**6**) as a white solid. A bromination reaction of **6** with *N*-bromosuccinimide (NBS) in *N,N*-dimethylformide (DMF) gave the target thienopyrazine monomer **7** as a bright yellow solid.¹³ All of these new compounds are characterized by ¹H

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Scheme 1. Synthesis of Quinoxaline Monomer (4)



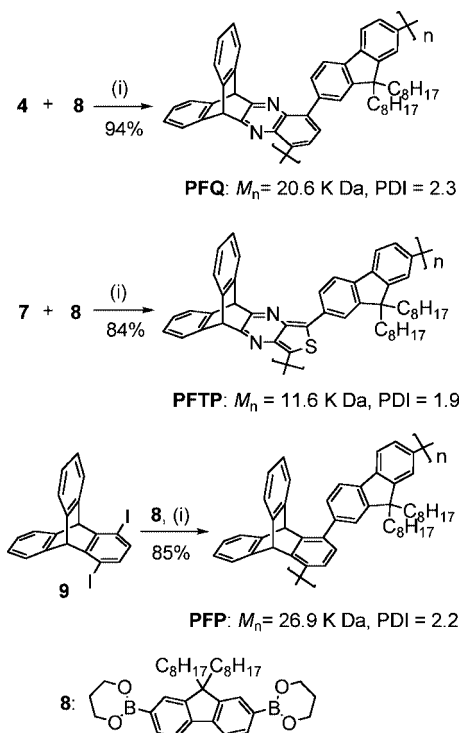
Scheme 2. Synthesis of Thienopyrazine Monomer (7)



and ^{13}C NMR spectroscopy as well as high-resolution mass spectrometry (see Supporting Information).

Polymer Synthesis. The synthetic strategy employed for the preparation of copolymers is based on the Suzuki reaction, using 9,9-dioctylfluorene-2,7-bis(trimethylboronate) (**8**) as the organoboron reagent.¹⁴ The polymerization was carried out in a mixture of toluene and aqueous potassium carbonate (2 M) containing a catalytic amount of tetrakis(triphenylphosphine)-palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) and Aliquat 336 (methyltrioctylammonium chloride) under vigorous stirring at 105 °C (Scheme 2).^{6a,15} For comparison, copolymer **PFP** containing a regular triptycene unit was also prepared from 1,4-diodotriptycene (**9**), which was prepared according to a reported procedure.¹⁶ All these copolymers were obtained in high yields and are readily dissolved in common organic solvents, such as chloroform, THF, toluene, and chlorobenzene. The molecular structures of these copolymers were verified by ^1H NMR spectroscopy (Figure 1), and the spectroscopic data are in good agreement with their structures. After standard purifications and drying, **PFP**, **PTQ**, and **PFTP** were obtained as white, greenish-yellow, and dark-red solids, respectively, indicating their different photophysical properties. Their molecular weights as determined by gel permeation chromatography (GPC) against polystyrene standards are within the range of 12K–27K Da, corresponding to degrees of polymerization of about 17–42 units, with polydispersity index (PDI) of around 2. The copolymers show high thermal stability, with decomposition temperature above 400 °C under nitrogen as measured by thermogravimetric analysis (TGA) (Table 1).

Polymer Characterization. The optical absorption and fluorescence spectra of **PFP**, **PFQ**, and **PFTP** in dilute chloroform solution are shown in Figure 2. **PFP** has an absorption maximum at 335 nm corresponding to the π – π^* transition of the polymer backbone that is blue-shifted by 50

Scheme 3. Polymer Synthesis^a

^a (i): $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , toluene, H_2O , Aliquat 336, 105 °C, 72 h.

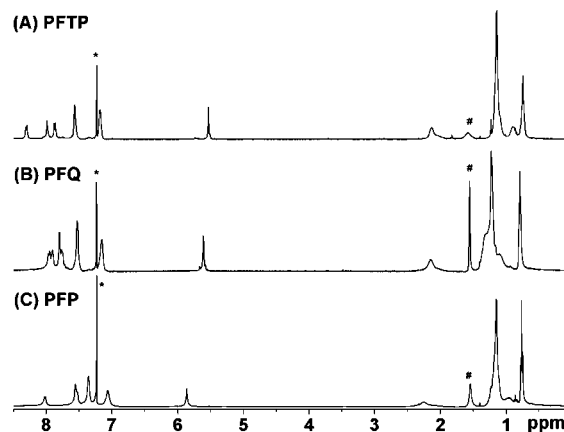


Figure 1. ^1H NMR spectra of the (A) **PFTP**, (B) **PFQ**, and (C) **PFP** in CDCl_3 , in which labels of * and # correspond to CHCl_3 and H_2O , respectively.

and 17 nm relative to the absorption of PF homopolymer¹⁷ and fluorene–phenylene copolymer,¹⁸ respectively. The impact of steric effects was previously invoked to explain the difference in electronic properties of conjugated polymers that differ only in the shape of the repeating unit because the steric repulsion between adjacent repeating units tends to increase their torsional angle, leading to weaker conjugation and bigger band gap.^{6a,18a,d,19} In this case, the observed blue shift may arise from the repulsive interaction between the bridgehead hydrogen of triptycene and the C-1 or C-3 hydrogen of the fluorene group. Both **PFQ** and **PFTP** have multiple absorption bands in solution (Figure 2), and the highest energy absorption bands centered at 328 and 345 nm, respectively, may be assigned to the fluorene segments of both polymers.²⁰ Additional long wavelength bands are observed at 395 and 530 nm for **PFQ** and **PFTP**, respectively. The substitution of phenylene by quinoxaline or

Table 1. Physical Data of Copolymers^a

| polymers | chloroform solution | | | | | T_d (°C) ^f | thin film | | | |
|----------|---|---|--------------------------|-------------------------------------|--------------------|-------------------------|---|---|--------------------------|--------------------|
| | $\lambda_{\text{max}}^{\text{ab}}$ (nm) | $\lambda_{\text{max}}^{\text{em}}$ (nm) | τ (ns) ^b | $E_{\text{g,op}}$ (eV) ^c | Φ_{re} | | $\lambda_{\text{max}}^{\text{ab}}$ (nm) | $\lambda_{\text{max}}^{\text{em}}$ (nm) | τ (ns) ^b | Φ_{re} |
| PFP | 335 | 381 | 0.48; 100% | 3.43 | 0.81 ^d | 430 | 337 | 391 | 0.34; 92% 0.76; 8% | 0.61 ^g |
| PFQ | 328 | 472 | 2.46; 100% | 2.84 | 0.70 ^d | 440 | 328 | 478 | 1.70; 86% | 0.49 ^g |
| PFTP | 395 | 622 | 3.04; 14% | 2.02 | 0.25 ^e | 405 | 396 | 623 | 3.04; 14% | 0.04 ^g |
| | 530 | | 523 | | | | 3.19; 25% | | | |

^a See Supporting Information for details of experimental conditions. ^b Fluorescence lifetime. ^c Band gap estimated from the onset of absorption spectrum in chloroform. ^d Fluorescence quantum yield relative to quinine sulfate in 0.1 N H₂SO₄ aqueous solution ($\Phi_{\text{re}} = 0.54$). ^e Fluorescence quantum yield relative to cresyl violet perchlorate in methanol ($\Phi_{\text{re}} = 0.54$).²⁵ ^f Onset decomposition temperature (5% weight loss) estimated by TGA under N₂. ^g Solid-state quantum yield relative to 9,10-diphenylanthracene in poly(methyl methacrylate) (PMMA) ($\Phi_{\text{re}} = 0.83$, 10⁻³ M).²⁸

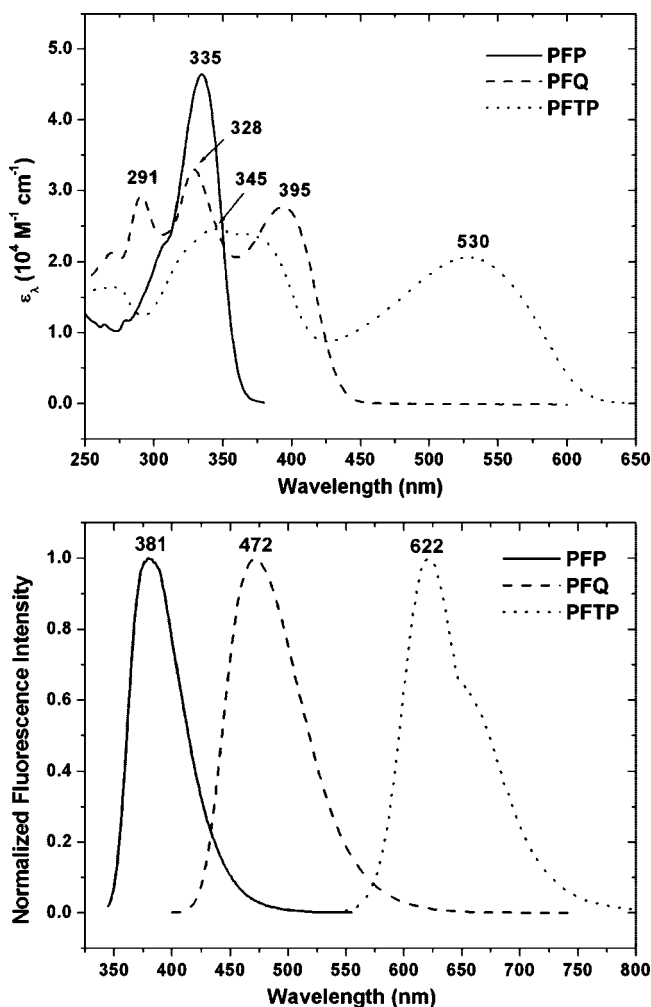


Figure 2. UV-vis absorption spectra displayed in molar extinction coefficients per repeating unit (top) and normalized fluorescence spectra (bottom) of **PFP**, **PFQ**, and **PFTP** in chloroform.

thienopyrazine units in the polymer backbone is observed to cause a significant red shift in the absorption band edge of these polymers relative to **PFP**. This difference is attributed to the intramolecular charge transfer (ICT) interactions that lead to an increase in the effective conjugation length and a reduction of band gap because quinoxaline and thienopyrazine are good acceptors.^{6,19} Previous studies by Kitamura and co-workers estimated that the lowest unoccupied molecular orbitals (LUMO) of quinoxaline and thienopyrazine are at -0.90 and -1.41 eV, respectively, which indicates that thienopyrazine is a stronger acceptor and is expected to have a stronger ICT interaction than quinoxaline.²¹ This is consistent with our observation that **PFTP** has a larger red shift than **PFQ**. However, it is also possible that the (five-membered ring) thiophene of thienopyrazine could

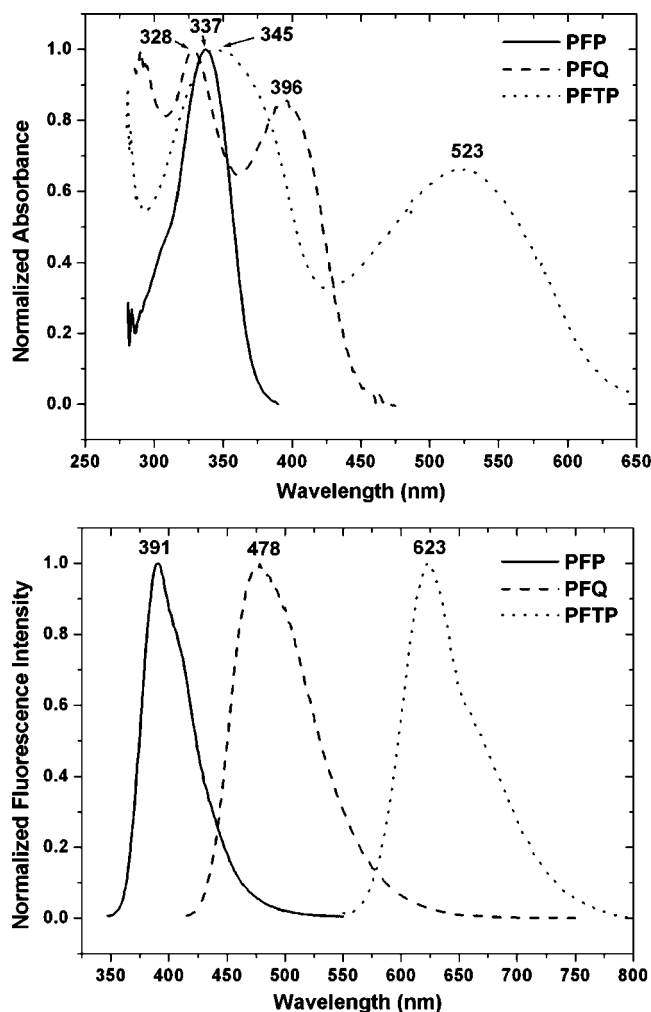


Figure 3. UV-vis absorption (top) and fluorescence spectra (bottom) of **PFP**, **PFQ**, and **PFTP** in the solid state.

result in a smaller torsional angle with fluorene than the phenylene (six-membered ring) of quinoxaline, which enhances the efficiency of ICT interaction and leads to a smaller band gap.^{6a,18,22} The optical band gaps of **PFP**, **PFQ**, and **PFTP**, determined from the onset of absorption, are 3.43, 2.84, and 2.02 eV, respectively (Table 1).

The three copolymers exhibited different emission colors when in solution, as shown in Figure 2 (bottom). The emission bands of **PFP**, **PFQ**, and **PFTP** have maxima at 381, 472, and 622 nm, respectively, roughly corresponding to blue, greenish-blue, and red light. Similar to their absorption spectra, this difference in the emission properties between the three copolymers can be understood in terms of the strength of the donor-acceptor interaction and/or the increased planarity of



Figure 4. Fluorescent images of thin films of **PFTP**, **PFQ**, and **PFP** under UV irradiation (365 nm).

thiophene-containing polymers, which leads to longer conjugation length and a smaller band gap.^{6,18a} The varied photophysical properties of **PFP**, **PFQ**, and **PFTP** also demonstrate that the photophysical properties of fluorene-based copolymers can be easily tuned using suitable comonomers, indicating the flexibility of structure manipulation of conjugated polymers. The emission bands of all polymers are relatively narrow, without significant vibronic peaks/shoulders, which may be smeared out by large inhomogeneous optical broadening of polymers.²³ Additionally, the spectra demonstrate a significant red shift of the emission with respect to absorption (Stokes shift), valued at 46, 77, and 92 nm for **PFP**, **PFQ**, and **PFTP**, respectively, which indicates the presence of a large conformation difference between the ground and the excited states of the copolymers. This may be explained by the sterically imposed structural twisting of the polymer backbone in its ground state. The polymer backbone in the excited state has more quinonoid character, which induces planarization.^{3,24} Furthermore, the progressively larger Stokes shift from **PFP**, **PFQ**, to **PFTP** suggests that the Stokes shift is increased by the donor—acceptor charge transfer interactions. Table 1 summarizes the quantum yields and fluorescence lifetimes of **PFP**, **PFQ**, and **PFTP** together with other photophysical properties. The large Stokes shifts observed are also consistent with the fluorescence lifetime results (Table 1).²⁶ It is noteworthy that the presence of a large Stokes shift in conjugated polymers has been considered an advantage for designing polymer laser materials because the red-shifted emission will limit self-absorption.²⁷

The absorption and emission spectra of **PFP**, **PFQ**, and **PFTP** in the solid state (Figure 3) are almost identical to their spectra in solution, indicating the success of polymer chain insulation by iptycene units.^{14,i,j,16} Further evidence came from the absence of any shoulder peaks and/or tails at the longer wavelength range, which are often observed for various conjugated polymers and are proposed to result from strong polymer interchain interactions, leading to formation of aggregates and excimers.⁶ Figure 4 shows the fluorescent images of thin films of **PFP**, **PFQ**, and **PFTP** irradiated by a 365 nm UV light. The moderately strong and pure emissions indicate that these copolymers retain their pristine single-chain photophysical properties in a thin film. Solid-state fluorescence quantum yields of **PFP**, **PFQ**, and **PFTP** films were found to be 0.61, 0.49, and 0.04, respectively (Table 1). The low quantum yield of **PFTP** may be due to the photodegradation of its thieno-[3,4-*b*]pyrazine units, which was recently reported by Jenekhe and co-workers.²⁹

Conclusion

Iptycene-type quinoxaline and thienopyrazine monomers (**2** and **5**) were successfully synthesized via a condensation between 10-dihydro-9,10-ethanoanthracene-11,12-dione (**1**) and corresponding diamines. Three fluorene-based copolymers (**PFTP**, **PFQ**, and **PFP**) containing different iptycene units were prepared via Suzuki coupling reactions, and they exhibited good solubility in appropriate organic solvents. These copolymers are fluorescent in solution and the solid state, emitting blue, greenish-blue, and red color, respectively. The difference in absorption/emission spectra was attributed to the donor—acceptor

charge transfer interactions and conformation change in the polymer backbone induced by steric effects. Moreover, we clearly demonstrated the insulation effect of iptycene units, which prevented intermolecular interactions between the chromophores and the formation of excimers in the solid state. It will be interesting to further tune the electronic and optical properties of this class of copolymers.

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Supporting Information Available: Experimental details and NMR spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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