

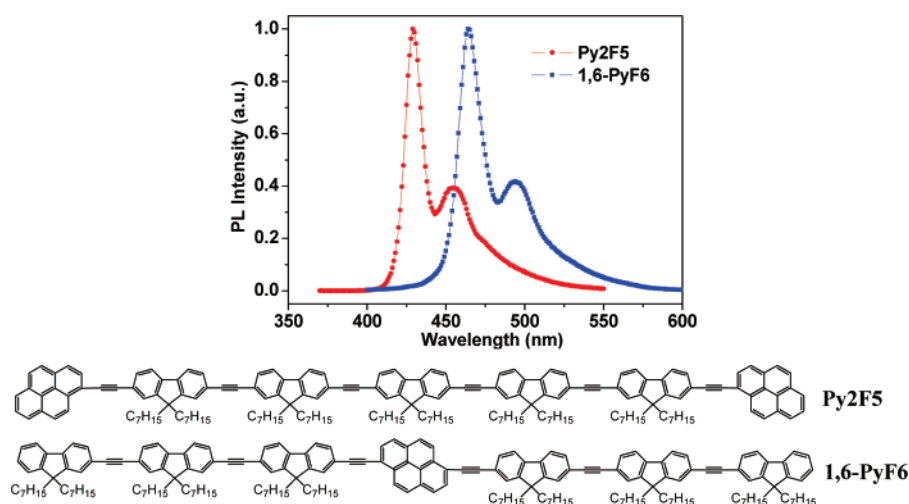
Oligo(2,7-fluorene ethynylene)s with Pyrene Moieties: Synthesis, Characterization, Photoluminescence, and Electroluminescence

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A series of highly fluorescent, pyrene-modified oligo(2,7-fluorene ethynylene)s were synthesized and fully characterized. Different emissions were observed between pyrene-end-capped and pyrene-centered oligo(2,7-fluorene ethynylene)s. Moreover, these oligomers were applied to fabricate organic light-emitting diodes (OLEDs), and bright blue or green electroluminescence (EL) with good device performances was achieved in multilayer OLEDs. These pyrene-modified oligo(2,7-fluorene ethynylene)s could be used as optoelectronics materials or models to investigate fluorescent structure–property relationship of fluorene derivatives.

1. Introduction

Organic materials with extended π -conjugated systems, such as conjugated polymers¹ and monodisperse conjugated oligomers,² have been intensively studied in recent years because of their potential applications in photonics and optoelectronics, such as field-effect transistors (FETs),^{3–5} OLEDs,^{6,7} solar cells,⁸ and solid-state lasers,⁹ and the academic interest on the structure–property relationship of molecules. Purified by precipitation,

conjugated polymers are typically characterized by chemical composition and distribution in chain length. The polydispersity in chain lengths leads to complex structural characteristics of the thin films and makes it very difficult for researchers to establish a proper structure–property relationship.¹⁰ In contrast, monodisperse conjugated oligomers are structurally uniform

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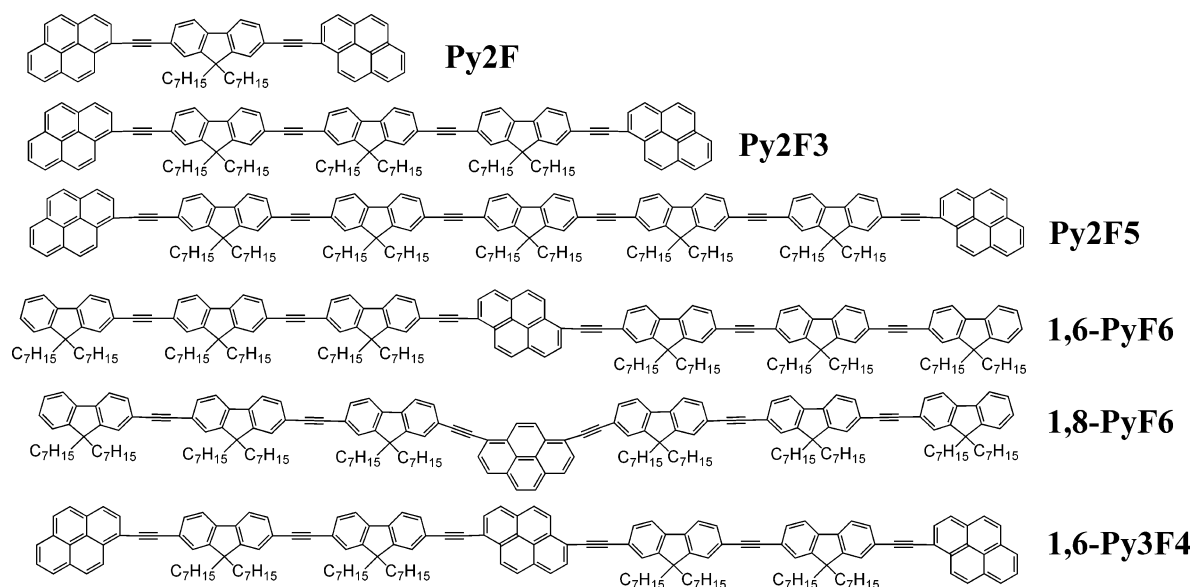
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SCHEME 1



with superior chemical purity accomplished by recrystallization or column chromatography. Thus, oligomers generally possess more predictable and reproducible properties, facilitating systematic investigation of structure–property relationship and optimization. So there exists intensive interest in preparing conjugated oligomers as model systems for conjugated polymer investigations or as a distinct class of materials themselves.¹¹

Recent studies have shown that fluorene-based materials hold great potential applications,¹² such as highly thermal stable and efficient emissive materials for OLEDs and carrier transport materials for FETs.¹³ Chemically, fluorene derivatives are interesting since they contain a rigid biphenyl plane and the facile substitution at the C₉ site, which provides the possibility of improving the solubility and processability and of controlling interchain interactions to prevent excimer formation in the excited state.^{14,15} Monodisperse oligofluorenes, which constitute an important class of π -conjugated organic materials because of their excellent chemical, thermal, and photochemical stabilities as well as the ease of structure tuning to adjust the electronic and morphological properties, have been extensively investigated and explored for various functional properties including EL and liquid crystalline and two-photon absorption properties for optoelectronic applications in the past few years. They are

capable of self-organization into uniaxially aligned, defect-free films for the realization of strongly polarized and highly efficient organic EL at a performance level consistently better than that of polymer analogues.¹⁶ On the other hand, pyrene-containing molecular rods have been reported by Leroy-Lhez et al.¹⁷ These π -conjugated oligomers exhibit intensive visible electronic absorption and fluorescence emission properties. Here we synthesized and characterized a series of well-defined, pyrene-modified oligo(2,7-fluorene ethynylene)s based on the previous works of other group and ourselves¹⁸ in order to study the influence of pyrene on the PL and EL properties of the oligomers. These oligomers exhibited good solubility, stable thermal properties, and strong PL emission. Moreover, multi-layer OLEDs using these oligomers as emissive layers were fabricated and investigated.

2. Results and Discussion

2.1. Synthesis of Oligomers. The well-defined, pyrene-containing oligo(2,7-fluorene ethynylene)s (Scheme 1) were synthesized in moderate yields by the Pd/Cu-catalyzed Sonogashira coupling reaction. The synthetic routes are illustrated in Scheme 2. Compounds **1**, **2**, **7**, and **12** were prepared according to references' methods.¹⁸ 1,6-Diethynylpyrene and 1,8-diethynylpyrene¹⁹ (**13** and **14**), synthesized by reference's method, served as cores of pyrene-centered oligomers. Initial Sonogashira coupling of alkyne **1** with an excess amount of diiodide **2** yielded intermediate **3**. The excess diiodide **2** was used to suppress the formation of troublesome byproduct 1,4-di(pyren-1-yl)buta-1,3-diyne from self-coupling of **1**. Then treatment of **3** with 3-methyl-1-butyne-3-ol was followed by

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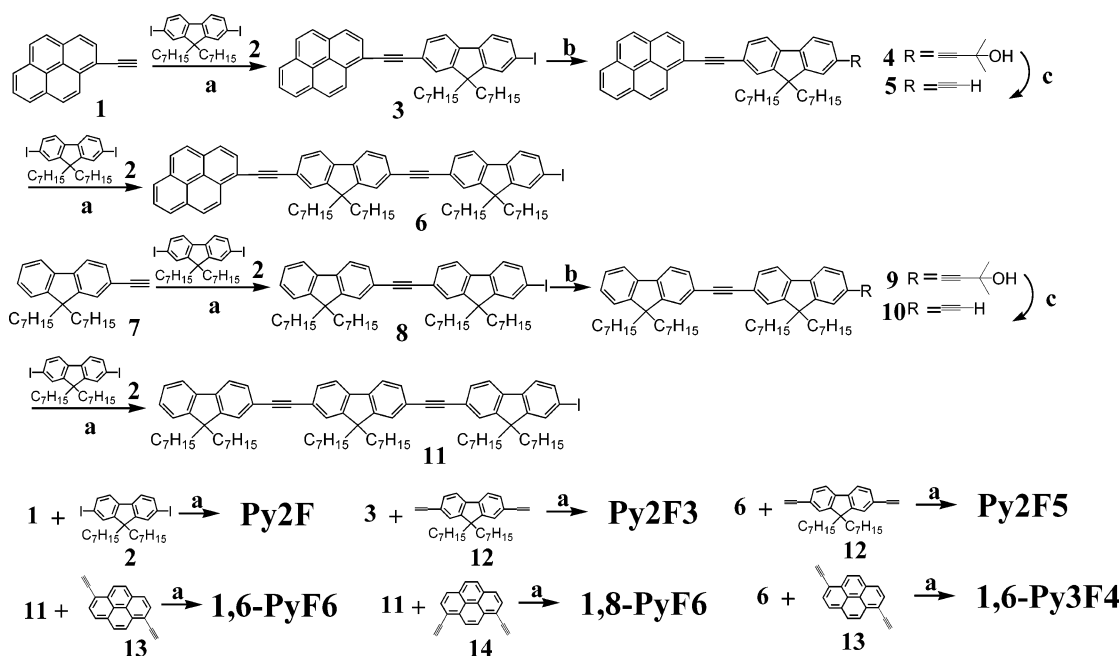
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^a Reagents and conditions: (a) CuI, Pd(PPh₃)₂Cl₂, Ph₃P, NEt₃, N₂, reflux; (b) 3-methyl-1-butyn-3-ol, CuI, Pd(PPh₃)₂Cl₂, Ph₃P, NEt₃, N₂, reflux; (c) KOH, 2-propanol, reflux.

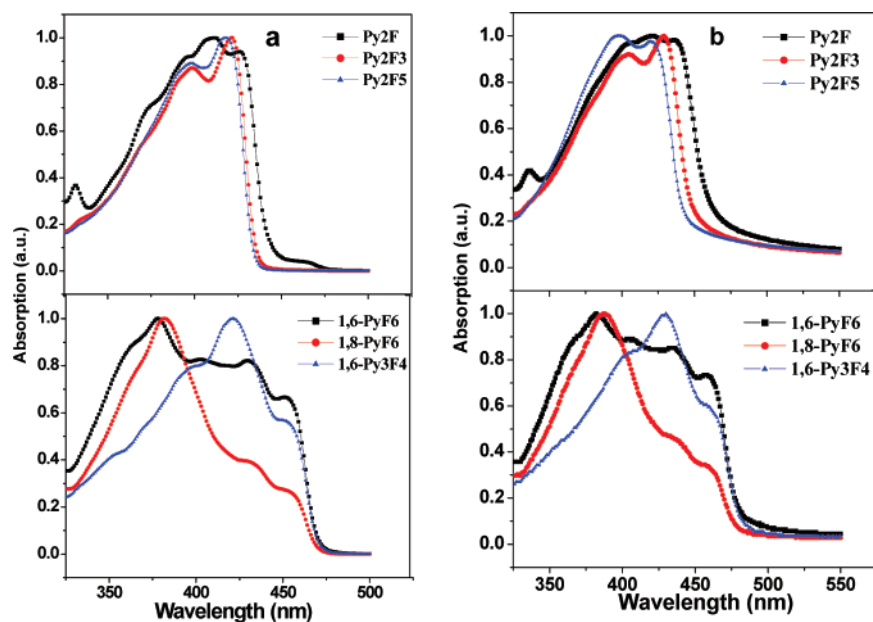


FIGURE 1. Absorption spectra of oligomers in CH₂Cl₂ solutions (a) and in thin neat films (b).

deprotection and coupling cycles to afford intermediate **6**. Similar procedures were performed to get intermediates **8** and **11**. Intermediates **4** and **9** were separated by column chromatography (silica gel, hexane/dichloromethane/ethyl acetate as eluent) and used in the next reaction without characterization. Final coupling in the presence of Pd/Cu catalyst led to our desired oligomers successfully. Compound **Py2F**,^{18b} which had been reported elsewhere, was used for comparative investigation. All of these oligomers were highly soluble in common organic solvents, such as CH₂Cl₂, CHCl₃, tetrahydrofuran (THF), and toluene, due to the *n*-heptyl substituents, and their molecular structures were verified by ¹H and ¹³C NMR spectroscopy, MALDI-TOF MS measurement, and element analysis. No

melting points of these oligomers were detected by differential scanning calorimetry (DSC), and the glass transition temperatures were not clearly observed. The decomposition temperatures (*T*_d) measured by thermogravimetric analysis (TGA) (10 °C/min, N₂) were in the range of 382–414 °C with 5% loss of initial weight.

2.2. Optical Properties. The normalized absorption spectra of oligomers in dilute CH₂Cl₂ solutions and in thin neat films are shown in Figure 1. For pyrene-end-capped oligomers **Py2F**, **Py2F3**, and **Py2F5**, their optical absorption spectra in solution were similar to those of oligo(2,7-fluorene ethynylene)s^{18a} but with a certain red shift. Their maximum absorption peaks of **Py2F**, **Py2F3**, and **Py2F5** were located at 426, 421, and 418

TABLE 1. Photophysical Properties of Oligomers

compound	$\lambda_{\text{Abs.}}^a$ (nm)		$\lambda_{\text{Em.}}$ (nm)		Φ	E_g^b (eV)	$E^{\text{ox}}_{1/2}^c$ (V)	HOMO/LUMO ^d (eV)	T_d (°C)
	CH ₂ Cl ₂ ($\epsilon \times 10^5$)	film	CH ₂ Cl ₂	film					
Py2F	426 (1.23), 411 (1.30)	436	436, 464	492	0.78	2.78	0.42	−4.82/−2.04	382
Py2F3	421 (2.53), 398 (2.21)	429	430, 456	489	0.93	2.83	0.47	−4.87/−2.04	404
Py2F5	418 (4.20), 398 (3.79)	420	429, 455	476	0.98	2.85	0.45	−4.85/−2.00	410
1,6-PyF6	450 (0.70), 430 (0.89), 378 (1.06)	456	464, 494	472, 504	0.81	2.63	0.45	−4.85/−2.22	392
1,8-PyF6	452 (0.61), 430 (0.87), 382 (1.24)	459	465, 495	472, 504	0.82	2.64	0.42	−4.82/−2.18	401
1,6-Py3F4	451 (2.05), 421 (3.63), 398 (2.87)	457	465, 495	475, 504	0.84	2.63	0.49	−4.89/−2.26	414

^a Mole absorption coefficient (ϵ): M^{−1} cm^{−1}. ^b Determined from UV–vis absorption spectra. ^c $E^{\text{ox}}_{1/2}$ = half-wave oxidation potential; potentials vs Ag/AgCl, working electrode Pt, 0.1 M Bu₄NPF₆–CH₂Cl₂, scan rate 100 mV/s. ^d HOMO = $E^{\text{ox}}_{1/2}$ + 4.4 eV; LUMO = HOMO − E_g (eV).

nm, respectively, which could be ascribed to the π – π^* transition of the molecular backbone.²⁰ The interesting thing was that the maximum absorption peak blue-shifted as the molecular chain length increased, which was opposite to the findings for oligo-(2,7-fluorene ethynylene)s.^{18a} We inferred that the lowest-lying energy chromophore of this series of compounds should localize on the pyrene-containing segments with a certain extension through ethynylene and fluorene units. However, with the increment of the molecular length, the conjugated backbone containing ethynylene unit(s) might have complicated intramolecular conformations, which might not be necessary to have a planar one all the time except for the case of **Py2F**. Two pyrene units in **Py2F** could conjugate into the whole molecule backbone efficiently, resulting in longest absorption wavelength. On the other hand, with the elongation of chain length due to the accumulation of the fluorene units, two pyrene units might not conjugate to the whole molecular backbone efficiently at one time, thus the influence of pyrene became weaker and the absorption spectra showed the characteristic of oligo(2,7-fluorene ethynylene).

1,6-PyF6 and **1,6-Py3F4**, containing pyrene in the middle of the molecular backbone, exhibited almost the same maximum absorption peaks at ~451 nm, which were red-shifted by ~33 nm compare to that of pyrene-end-capped oligomer **Py2F5**. Broad absorption band (from 360 to 420 nm) with continuously large molar absorption coefficient (ϵ) (Table 1) was observed for **1,6-Py3F4**, which indicated that this molecule could be excited at a relative wide range with an efficient energy transfer. The red-shifted absorption peak, which might be arising from the pyrene core, could also be observed from other π -conjugated systems, such as poly(fluorene-co-perylene),²¹ poly(fluorene-co-anthracene),²² and poly(*p*-phenylene ethynylene-co-anthracene).²³ **1,8-PyF6** exhibited a similar maximum absorption peak in comparison to that of **1,6-PyF6**, but the relative absorption intensity changed, which might be due to the interruption of delocalization of the π -electrons along the oligomer backbone by the 1,8-pyrene linkage. Consequently, different location of pyrene units had different influence on the oligomers' absorption spectra. The strongly red-shifted absorption spectra were observed from these pyrene-centered oligomers with respect to those of pyrene-end-capped ones. This should be ascribed to the better π -conjugation of the disubstituted pyrene core, and the vibronic features of pyrene were a good indication.

Solid-state absorption spectra of all oligomers were almost identical, but had a slightly bathochromic shift (2–10 nm) compared to those in solutions, which indicated that these oligomers exhibited very similar conformations in both states.²⁴ By inspecting the edge of the absorption spectra, the energy band gaps (E_g) of oligomers were obtained (Table 1). It was observed that the E_g values slightly decreased with the increment of the molecular length. Moreover, the obvious difference between E_g of **Py2F5** (2.85 eV) and that of **1,6-PyF6** (2.63 eV) indicated that different position of pyrene in oligomers would inevitably result in different energy states of the whole molecules.

The normalized PL emission spectra of oligomers, excited at 380 nm, in dilute CH₂Cl₂ solutions and in thin neat films are shown in Figure 2. The emission peaks were independent of excitation wavelength, and the excitation spectra, given in Supporting Information, were similar to their absorption spectra. In CH₂Cl₂ solutions, **Py2F**, **Py2F3**, and **Py2F5** showed a main emission peak at 436, 430, and 429 nm, respectively, with a shoulder peak at 464, 456, and 455 nm, respectively. In comparison with the emission spectrum of 1,1'-(9,9-dimethyl-9H-fluorene-2,7-diyl)dipyrene (**DPF**),²⁵ **Py2F** emitted light at longer wavelength in CH₂Cl₂ solution. Emission difference between **Py2F** and **DPF** should be ascribed to the ethynylene linkages that elongated the conjugation length of the molecule and made the molecule more planar. The blue-shifted emission of **Py2F3** and **Py2F5** with respect to that of **Py2F** was ascribed to the same reason for blue-shifted absorption spectra of them. On the other hand, although the shapes of absorption spectra of **1,6-PyF6**, **1,8-PyF6**, and **1,6-Py3F4** were different, these compounds exhibited quit similar emission spectra. We inferred that these compounds had similar transition energy gaps resulting from the existence of disubstituted pyrene moieties in both oligomers. By exciting these compounds at 380 nm, they exhibited quite similar main emission peaks at about 465 nm with shoulder peaks at about 495 nm, actually emanating from disubstituted pyrene, which exhibited distinct red-shifted emissions (~35 nm) in comparison with those of oligomers end-capped with pyrene moieties, such as **Py2F5**.

In thin neat films, the main emission peaks of **Py2F**, **Py2F3**, and **Py2F5** were located at 492, 489, and 476 nm, respectively, with the disappearance of the fine structures of spectra. Emissions were strongly red-shifted compared to those in solutions (≥ 47 nm). In terms of **DPF**,²⁵ it exhibited an emission peak at 460 nm in film as reported, which was blue-shifted (32 nm) with respect to that of **Py2F**. In some ways, the extended structure between pyrene and fluorene resulting from the triple

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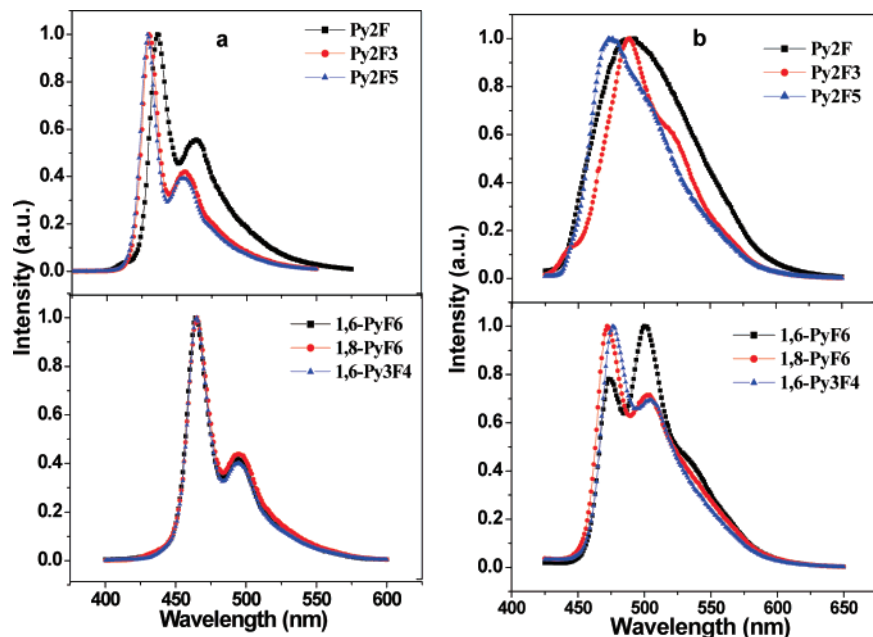


FIGURE 2. PL emission spectra of oligomers in CH_2Cl_2 solutions (a) and in thin neat films (b).

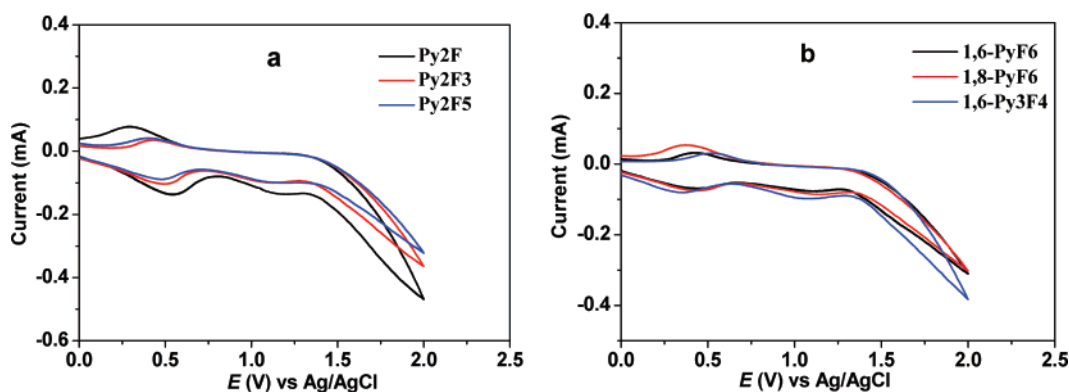


FIGURE 3. Cyclic voltammogram of oligomers (0.5 mM) in 0.1 M Bu_4NPF_6 –THF; scan rate 100 mV/s.

bonds reduced the steric hindrance of the bulky rigid pyrene and made the molecule more planar.^{21,22,26} The strongly red-shifted emission of **Py2F** in thin neat film should be due to the facile formation of excimers between pyrene units,²⁷ which caused the low-energy emission.

All the synthesized oligomers were highly fluorescent. The PL quantum yields were measured in degassed cyclohexane solutions using 9,10-diphenylanthracene (DPA, $\Phi = 0.95$)²⁸ as a standard. The PL quantum yields of these oligomers were in the range of 0.78–0.98, which became higher with the increment of the molecular length. Moreover, **Py2F5** ($\Phi = 0.98$) exhibited higher quantum yields than those of oligomers with similar chain length, **1,6-PyF6** ($\Phi = 0.81$), **1,8-PyF6** ($\Phi = 0.82$), and **1,6-Py3F4** ($\Phi = 0.84$). The difference of quantum yields might be that excitons were confined to the whole backbone of **Py2F5**, thereby giving higher quantum yields, whereas in the case of pyrene-centered oligomers, some energy loss might happen during the excitons migration.²⁹

2.3. Cyclic Voltammetric Studies. The electrochemical properties of these oligomers were investigated by cyclic voltammetry at room temperature, and the results are listed in Table 1. Figure 3 shows cyclic voltammograms (CVs). All these compounds displayed two oxidation peaks, the first was reversible, and the second was irreversible. The half-wave oxidation potential ($E^{\text{ox}}_{1/2}$) was in the range of 0.42–0.49 V. HOMO and LUMO levels of these oligomers were determined by the $E^{\text{ox}}_{1/2}$ and E_g (Table 1). HOMO levels ($\text{HOMO} = E^{\text{ox}}_{1/2} + 4.4 \text{ eV}$) were in the range of -4.82 to -4.89 eV , which were higher than that of the most widely used hole-transport material 4,4'-bis(1-naphthylphenylamino)biphenyl (NBP) ($\text{HOMO} = -5.5 \text{ eV}$, $\text{LUMO} = -2.4 \text{ eV}$) and thus might be beneficial for the hole injection and transport.³⁰ LUMO levels ($\text{LUMO} = \text{HOMO} - E_g$) were in a range of -2.00 to -2.26 eV . Results obtained here further supported that LUMO, HOMO, as well as the energy gap of these oligo(2,7-fluorene ethynylene)s could be easily modified or tuned by introduction of the pyrene into

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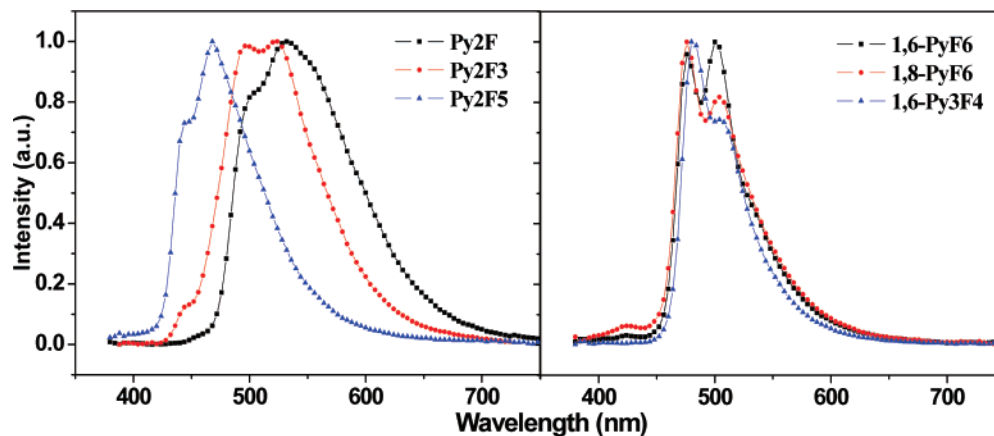


FIGURE 4. Normalized electroluminescence (EL) spectra of oligomers.

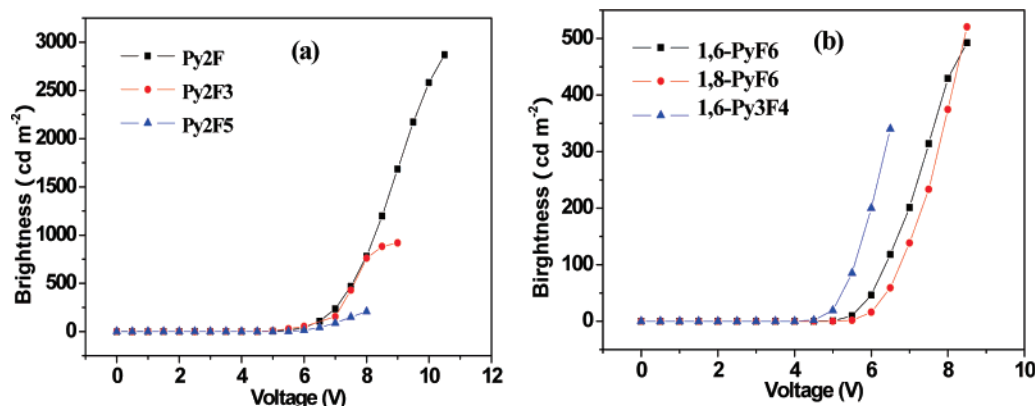


FIGURE 5. Brightness–voltage diagrams for devices based on oligomers.

the different position of conjugated oligo(2,7-fluorene ethynylene) backbone.

2.4. Electroluminescent Properties. To investigate the EL properties of these oligomers, devices with the same configurations of ITO/poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) (30 nm)/oligomer (50 nm)/1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) (20 nm)/Al (100 nm), for the purpose of comparison, were fabricated. The EL spectra and current density–voltage–brightness characteristics were measured under ambient conditions. For oligomers **Py2F**, **Py2F3**, and **Py2F5**, the EL emissions were observed from green (532 nm) to blue (468 nm) with the increment of the fluorene moieties (Figure 4). The EL emission of **Py2F** was significantly red-shifted (40 nm) in comparison with that of PL emission in film, while the EL emission of **Py2F5** was slightly blue-shifted (8 nm). Although similar emission color in solutions and in thin neat films were obtained for these compounds, EL emissions present different color. Since **Py2F** had the shortest chain length among **Py2F**, **Py2F3**, and **Py2F5**, we thought that **Py2F** had the highest chain mobility. Materials with repeating fluorene units had been reported to undergo a process of alignment in an electric field, and molecules with the high chain mobility more easily formed excimers than molecules with low chain mobility.³¹ Due to the higher chain mobility of **Py2F** compared to that of **Py2F3** and **Py2F5**, it was more possible for **Py2F**

molecules to align under the electric field. Thus, the pyrene groups on one **Py2F** molecule could be close to the pyrene groups on the neighboring molecule, and when the distance between the two fluorophores was appropriate, excimers were formed under the electric excitation. It is well-known that excimers could result in a red-shifted EL emission, so **Py2F** exhibits more significantly red-shifted EL spectrum than **Py2F3** and **Py2F5**.

On the other hand, for the EL spectra of **1,6-PyF6**, **1,8-PyF6**, and **1,6-Py3F4**, similar green emissions dominated with very narrow bands from 472 to 504 nm, which were similar to their PL emission spectra in films except for slight red shifts. The similarity between PL and EL spectra of these pyrene-centered oligomers indicated that both PL and EL originated from the same radiative decay process of singlet excitons.³²

The brightness–voltage characteristics for the EL devices based on these oligomers are shown in Figure 5, and the device performances are summarized in Table 2. The turn-on voltages of these devices were in the range of 4.3–5.4 V. The device based on **Py2F** exhibited maximum brightness at 2869 cd m^{−2} at 10.5 V and a highest external quantum efficiency of 0.64%. While with the increase of the fluorene moiety, the device based on **Py2F3** and **Py2F5** exhibited a substantial decrease of maximum brightness from 918 cd m^{−2} at 9.0 V to 207 cd m^{−2} at 8.0 V as well as the external quantum efficiency of **Py2F3** (0.41%) and **Py2F5** (0.15%). The devices based on the other

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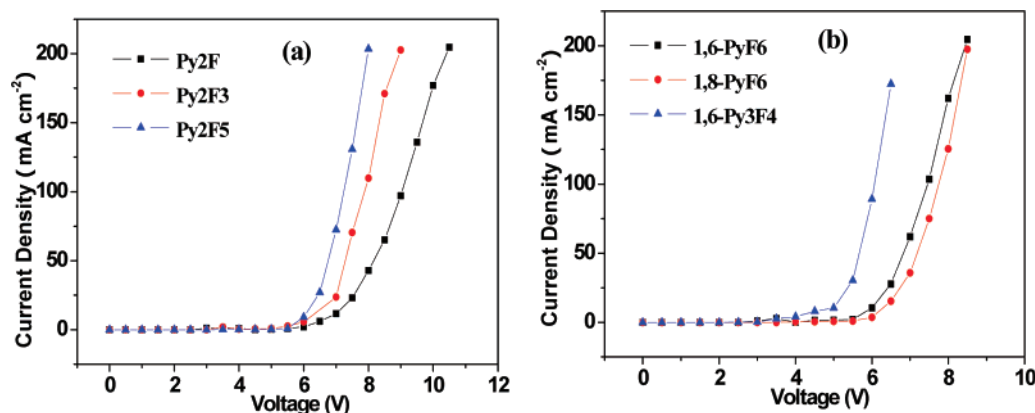


FIGURE 6. Current density–voltage diagrams for devices based on oligomers.

TABLE 2. Summary of Device Performances

device	EL (nm)	fwhm (nm)	turn-on voltage (V)	η_{ext} (%, 100 cd m^{-2})	$\eta_{\text{max, ext}}$ (%)	$\eta_{\text{max, L}}$ (cd A^{-1})	L_{max} (cd m^{-2} , V)
Py2F	532	113	4.5	0.57	0.64	2.03	2869, 10.5
Py2F3	496, 524	94	4.3	0.32	0.41	1.06	918, 9.0
Py2F5	468	76	5.4	0.08	0.15	0.21	207, 8.0
1,6-PyF6	476, 500	60	4.9	0.21	0.22	0.44	493, 8.5
1,8-PyF6	476, 504	63	5.4	0.19	0.22	0.44	520, 8.5
1,6-Py3F4	480, 504	54	4.4	0.13	0.14	0.28	340, 6.5

three **1,6-PyF6**, **1,8-PyF6**, and **1,6-Py3F4** exhibited comparable brightness, 493 cd m^{-2} at 8.5 V, 520 cd m^{-2} at 8.5 V, and 340 cd m^{-2} at 6.5 V, respectively, as well as an external quantum efficiency, 0.22, 0.22, and 0.14%, respectively. The interesting thing was the decrease of the devices' performances as chain length elongated, for which the exact reason was not very clear yet. One possible explanation for this phenomenon was that the oligomers with more fluorene units were more easily crystallized than the oligomers with fewer fluorene units. Geng et al. reported that the chain length of oligofluorenes played an important role in solid morphology, and with increasing the chain length, the oligofluorenes tended to be crystallized.³³ Due to the fact that our oligomers also had fluorene units, we thought that increasing the chain length (that was increasing the fluorene units) would also cause the oligomers to be crystallized. It was well-known that crystallization was disadvantageous to the electroluminescent properties of organic materials. As a result, the maximum luminance of these oligomers decreased with the chain length.

The current–voltage characteristics for EL devices are illustrated in Figure 6. From Figure 6a, it was obviously observed that the current density became greater with the increase of oligomeric length. This result was in accordance with the previously reported dependence of carrier mobility on oligomer length, that is, the mobilities of both carriers increased with the backbone length.³⁴ By comparison, relatively greater current density could also be observed in oligomers with more pyrene moieties.

3. Conclusions

In summary, a series of well-defined, pyrene-modified oligo(2,7-fluorene ethynylene)s with high quantum yields have been

synthesized and fully characterized. The results, obtained through inspecting the emission spectra of these pure oligomers, demonstrated a certain structure–property relationship of these oligomers. Furthermore, bright blue or green EL emission with good device performances was achieved in multilayer OLEDs based on these oligomers, which indicated that they were promising light-emitting materials for OLEDs.

4. Experimental Section

1-(2-(2-Ethynyl-9,9-diheptyl-9H-fluoren-7-yl)ethynyl)-pyrene (3): 1-Ethynylpyrene (**1**) (0.2 g, 1 mmol), 9,9-diheptyl-2,7-diiodo-9H-fluorene (**2**) (3 g, 5 mmol), cuprous iodide (10 mg, 0.05 mmol), Pd(PPh₃)₂Cl₂ (3.5 mg, 0.005 mmol), triphenylphosphine (PPh₃, 5 mg, 0.02 mmol), and 150 mL of dry triethylamine were placed in a 250 mL round bottle flask equipped with a Teflon-covered magnetic stir bar. After the solution was purged with nitrogen for 30 min, it was refluxed under nitrogen for 4 h. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/dichloromethane as eluent). In this way, 0.59 g (83% yield) of **3** was obtained: ¹H NMR (CDCl₃) δ 0.65 (m, 4H), 0.81 (t, 6H, $J = 7.5$ Hz), 1.08 (br, 12H), 1.17–1.20 (m, 4H), 1.94–2.05 (m, 4H), 7.46 (d, 1H, $J = 8$ Hz), 7.65–7.71 (m, 5H), 8.02–8.14 (m, 4H), 8.19–8.24 (m, 4H), 8.72 (d, 1H, $J = 8.5$ Hz) ppm; ¹³C NMR (CDCl₃) δ 14.3, 22.8, 24.0, 29.2, 30.2, 40.5, 55.8, 89.4, 93.4, 96.4, 118.2, 120.2, 122.0, 122.7, 124.6, 124.8, 125.9, 126.2, 126.5, 127.5, 128.4, 128.6, 129.9, 131.2, 131.4, 131.5, 131.6, 132.1, 136.3, 140.4, 140.8, 150.6, 153.7 ppm. MS (MALDI) (m/z): 712.2 (M^+).

1-(7-Ethynyl-9,9-diheptyl-9H-fluoren-2-ylethynyl)pyrene (5): **3** (712 mg, 1 mmol), 3-methyl-1-butyn-3-ol (126 mg, 1.5 mmol), cuprous iodide (10 mg, 0.05 mmol), Pd(PPh₃)₂Cl₂ (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol), and 100 mL of dry triethylamine were placed in a 150 mL round bottle flask equipped with a Teflon-covered magnetic stir bar. After the solution was purged with nitrogen for 30 min, it was refluxed under nitrogen for 8 h. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was purified

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through column chromatography (silica gel, hexane/dichloromethane/ethyl acetate as eluent) to get **4**. Then **4**, 500 mg of KOH, and 100 mL of 2-propanol were placed in a 150 mL round bottle flask equipped with a Teflon-covered magnetic stir bar. After the solution was purged with nitrogen for 30 min, it was refluxed under nitrogen for 4 h. The solvent was then removed, and the crude product was purified by column chromatography (silica gel, hexane/dichloromethane as eluent) to afford **5** (476 mg, 78% total yield): ^1H NMR (CDCl_3) δ 0.63–0.65 (m, 4H), 0.80 (t, 6H, $J = 7.5$ Hz), 1.07 (br, 12H), 1.16–1.19 (m, 4H), 1.99–2.04 (m, 4H), 3.17 (s, 1H), 7.50–7.52 (m, 2H), 7.67–7.68 (m, 2H), 7.71–7.75 (m, 2H), 8.02–8.16 (m, 4H), 8.20–8.25 (m, 4H), 8.73 (d, 1H, $J = 1.0$ Hz) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 22.8, 24.0, 29.2, 30.2, 32.1, 40.6, 55.6, 77.6, 84.9, 89.4, 96.4, 118.2, 120.2, 120.4, 121.0, 122.6, 124.7, 124.8, 124.9, 125.9, 125.9, 125.9, 126.2, 126.5, 126.8, 127.6, 128.4, 128.6, 129.9, 131.2, 131.4, 131.6, 132.2, 140.9, 141.5, 151.3, 151.6 ppm. MS (MALDI) (m/z): 610.5 (M^+).

1-[7-(9,9-Diheptyl-7-iodo-9H-fluoren-2-ylethynyl)-9,9-dihexyl-9H-fluoren-2-ylethynyl]pyrene (6): **5** (610 mg, 1 mmol), **2** (1842 mg, 3 mmol), cuprous iodide (10 mg, 0.05 mmol), $\text{Pd}(\text{PPh}_3)_2 \cdot \text{Cl}_2$ (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol), and 100 mL of dry triethylamine were placed in a 150 mL round bottle flask equipped with a Teflon-covered magnetic stir bar. After the solution was purged with nitrogen for 30 min, it was refluxed under nitrogen for 4 h. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/dichloromethane as eluent). In this way, 790 mg (72% yield) of **6** was obtained: ^1H NMR (CDCl_3) δ 0.61–0.67 (m, 8H), 0.79–0.83 (m, 12H), 1.05–1.08 (m, 24H), 1.16–1.20 (m, 8H), 1.94–2.00 (m, 4H), 2.05–2.06 (m, 4H), 7.33–7.34 (m, 2H), 7.54–7.60 (m, 4H), 7.66–7.77 (m, 6H), 8.03–8.17 (m, 4H), 8.21–8.26 (m, 4H), 8.75 (d, 1H, $J = 9.0$ Hz) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 22.9, 23.1, 24.0, 29.2, 29.3, 30.3, 32.1, 32.1, 40.7, 40.8, 55.4, 55.6, 89.3, 90.6, 93.4, 96.5, 118.2, 119.9, 120.1, 120.2, 120.3, 121.9, 122.4, 123.1, 124.6, 124.8, 124.7, 125.7, 125.9, 126.1, 126.2, 126.5, 127.1, 127.5, 127.8, 128.4, 128.6, 129.9, 130.8, 131.0, 131.2, 131.4, 131.5, 131.5, 132.1, 132.3, 136.2, 140.3, 140.9, 141.2, 141.7, 150.5, 151.2, 151.4, 151.5, 153.6 ppm. MS (MALDI) (m/z): 1096.9 (M^+).

2-((9,9-Diheptyl-9H-fluoren-2-yl)ethynyl)-9,9-dihexyl-7-iodo-9H-fluorene (8): The procedure was analogous to that described for **3** (86% yield): ^1H NMR (CDCl_3) δ 0.60 (br, 8H), 0.78–0.82 (m, 12H), 1.05–1.06 (m, 24H), 1.15–1.19 (m, 8H), 1.92–1.99 (m, 8H), 7.31–7.35 (m, 3H), 7.43 (d, 1H, $J = 8.5$ Hz), 7.52–7.56 (m, 4H), 7.64–7.70 (m, 5H) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 22.8, 23.9, 24.0, 29.2, 30.2, 30.3, 32.0, 40.5, 40.7, 55.4, 55.7, 90.5, 91.2, 93.3, 119.9, 120.1, 120.2, 121.7, 121.9, 122.6, 123.1, 126.1, 126.2, 127.1, 127.8, 130.8, 131.0, 132.4, 136.2, 140.4, 140.5, 140.7, 141.7, 150.5, 151.1, 151.3, 153.7 ppm. MS (MALDI) (m/z): 872.7 (M^+).

2-((9,9-Diheptyl-9H-fluoren-2-yl)ethynyl)-7-ethynyl-9,9-dihexyl-9H-fluorene (10): The procedure was analogous to that described for **5** (73% yield): ^1H NMR (CDCl_3) δ 0.60 (br, 8H), 0.78–0.82 (m, 12H), 1.05 (br, 24H), 1.16–1.19 (m, 8H), 1.95–1.99 (m, 8H), 3.15 (s, 1H), 7.31–7.35 (m, 3H), 7.47–7.50 (m, 2H), 7.54–7.57 (m, 4H), 7.63–7.70 (m, 4H) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 22.8, 24.0, 29.2, 30.2, 32.0, 40.6, 40.7, 55.4, 55.5, 77.5, 84.9, 90.5, 91.2, 119.9, 120.1, 120.2, 120.3, 120.9, 121.7, 122.6, 123.1, 126.2, 126.8, 127.1, 127.8, 130.8, 131.0, 131.5, 140.7, 141.5, 141.7, 151.1, 151.3, 151.4 ppm. MS (MALDI) (m/z): 771.2 (M^+).

2-((9,9-Diheptyl-7-iodo-9H-fluoren-2-yl)ethynyl)-7-((9,9-dihexyl-9H-fluoren-2-yl)ethynyl)-9,9-dihexyl-9H-fluorene (11): The procedure was analogous to that described for **6** (77% yield): ^1H NMR (CDCl_3) δ 0.61 (br, 12H), 0.78–0.83 (m, 18H), 1.06 (br, 36H), 1.17–1.18 (m, 12H), 1.94–2.02 (m, 12H), 7.33–7.34 (m, 3H), 7.44 (d, 1H, $J = 8.0$ Hz), 7.52–7.58 (m, 8H), 7.66–7.71 (m, 7H) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 14.3, 22.8, 23.9, 24.0, 29.2, 29.2, 29.3, 30.2, 30.3, 32.0, 32.1, 40.5, 40.7, 40.8, 55.4, 55.5, 55.7, 90.6, 90.9, 91.1, 91.2, 93.4, 119.9, 120.1, 120.2, 121.6, 121.9, 122.1,

122.4, 122.4, 123.1, 126.1, 126.2, 127.1, 127.8, 130.8, 131.0, 132.3, 136.2, 140.3, 140.6, 140.7, 140.8, 141.0, 141.7, 150.5, 151.0, 151.2, 151.3, 151.3, 153.6 ppm. MS (MALDI) (m/z): 1256.9 (M^+).

1-(2-(9,9-Diheptyl-2-(2-(9,9-dihexyl-2-(2-(9,9-dihexyl-2-(2-(pyren-1-yl)ethynyl)-9H-fluoren-7-yl)ethynyl)-9H-fluoren-7-yl)ethynyl)-9H-fluoren-7-yl)ethynyl)pyrene (Py2F3): The procedure was analogous to that described for **6** (62% yield): ^1H NMR (CDCl_3) δ 0.68 (br, 12H), 0.79–0.83 (m, 18H), 1.09 (br, 36H), 1.18–1.20 (m, 12H), 2.01–2.07 (m, 12H), 7.58–7.61 (m, 8H), 7.69–7.77 (m, 10H), 8.03–8.17 (m, 8H), 8.21–8.26 (m, 8H), 8.75 (d, 2H, $J = 9.0$ Hz) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 22.9, 24.1, 29.3, 30.3, 32.1, 55.6, 55.6, 89.4, 91.1, 96.5, 118.2, 120.3, 120.3, 120.4, 120.3, 122.3, 122.5, 124.7, 124.9, 125.9, 125.9, 126.2, 126.2, 126.5, 127.6, 128.4, 128.6, 129.9, 131.0, 131.2, 131.4, 131.5, 131.6, 132.2, 141.0, 141.2, 151.4, 151.5, 151.5 ppm. MS (MALDI) (m/z): 1580.0 (M^+). Anal. Calcd for $\text{C}_{121}\text{H}_{126}$: C, 91.96; H, 8.04. Found: C, 91.99; H, 8.01.

1-(2-(9,9-Diheptyl-2-(2-(9,9-dihexyl-2-(2-(9,9-dihexyl-2-(2-(pyren-1-yl)ethynyl)-9H-fluoren-7-yl)ethynyl)-9H-fluoren-7-yl)ethynyl)-9H-fluoren-7-yl)ethynyl)pyrene (Py2F5): The procedure was analogous to that described for **4** (48% yield): ^1H NMR (CDCl_3) δ 0.64–0.68 (m, 20H), 0.79–0.83 (m, 30H), 1.07–1.09 (m, 60H), 1.17–1.22 (m, 20H), 2.02–2.07 (m, 20H), 7.57–7.61 (m, 16H), 7.70–7.77 (m, 14H), 8.03–8.17 (m, 8H), 8.21–8.27 (m, 8H), 8.75 (d, 2H, $J = 9.0$ Hz) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 22.9, 24.0, 24.0, 29.3, 29.4, 30.03, 30.3, 32.1, 40.8, 55.0, 55.6, 89.4, 91.1, 96.5, 118.2, 120.3, 120.3, 120.4, 122.2, 122.3, 122.5, 124.6, 124.8, 124.9, 125.9, 126.2, 126.5, 127.6, 128.4, 128.6, 129.9, 131.0, 131.2, 131.4, 131.5, 131.6, 132.1, 141.0, 141.1, 151.4, 151.4, 151.5 ppm. MS (MALDI) (m/z): 2347.6 (M^+). Anal. Calcd for $\text{C}_{179}\text{H}_{198}$: C, 91.51; H, 8.49. Found: C, 91.50; H, 8.57.

1,6-Bis((7-((9,9-dihexyl-9H-fluoren-2-yl)ethynyl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)pyrene (1,6-PyF6): The procedure was analogous to that described for **4** (48% yield): ^1H NMR (CDCl_3) δ 0.63–0.69 (m, 24H), 0.79–0.83 (m, 36H), 1.06–1.10 (m, 72H), 1.16–1.20 (m, 24H), 1.97–2.07 (m, 24H), 7.32–7.36 (m, 6H), 7.55–7.62 (m, 16H), 7.70–7.79 (m, 16H), 8.23 (d, 4H, $J = 8.0$ Hz), 8.29 (d, 2H, $J = 8.0$ Hz), 8.78 (d, 2H, $J = 9.5$ Hz) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 22.9, 24.0, 29.2, 29.3, 30.3, 32.1, 32.1, 40.7, 40.8, 55.4, 55.5, 55.6, 89.3, 90.6, 91.1, 91.2, 91.2, 97.0, 118.9, 119.9, 120.3, 120.4, 121.7, 122.2, 122.4, 123.1, 124.6, 125.5, 126.2, 126.6, 127.1, 127.8, 128.4, 130.3, 130.8, 131.0, 131.0, 131.3, 131.3, 132.3, 140.7, 140.9, 140.9, 141.0, 141.3, 141.7, 151.1, 151.3, 151.4, 151.4, 151.5, 151.6 ppm. MS (MALDI) (m/z): 2507.8 (M^+). Anal. Calcd for $\text{C}_{190}\text{H}_{226}$: C, 90.92; H, 9.08. Found: C, 90.89; H, 9.12.

1,8-Bis((7-((9,9-dihexyl-9H-fluoren-2-yl)ethynyl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)pyrene (1,8-PyF6): The procedure was analogous to that described for **4** (52% yield): ^1H NMR (CDCl_3) δ 0.63–0.69 (m, 24H), 0.79–0.83 (m, 36H), 1.06–1.10 (m, 72H), 1.17–1.19 (m, 24H), 1.97–2.09 (m, 24H), 7.34–7.35 (m, 6H), 7.56–7.62 (m, 16H), 7.71 (m, 10H), 7.74–7.79 (m, 6H), 8.11 (s, 2H), 8.20 (d, 2H, $J = 8.5$ Hz), 8.29 (d, 2H, $J = 7.5$ Hz), 8.92 (s, 2H) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 14.3, 22.8, 22.9, 24.0, 29.2, 29.3, 30.3, 32.1, 40.7, 40.8, 55.4, 55.5, 55.6, 89.2, 90.6, 91.0, 91.1, 91.2, 97.0, 118.9, 119.9, 120.2, 120.3, 120.4, 121.6, 122.2, 122.3, 123.1, 124.6, 125.5, 126.2, 126.8, 127.1, 127.8, 128.3, 130.3, 130.8, 131.0, 131.3, 131.6, 132.1, 140.7, 140.9, 141.0, 141.3, 141.7, 151.0, 151.2, 151.3, 151.4, 151.5 ppm. MS (MALDI) (m/z): 2507.3 (M^+). Anal. Calcd for $\text{C}_{190}\text{H}_{226}$: C, 90.92; H, 9.08. Found: C, 90.93; H, 9.09.

1,6-Bis((7-((9,9-dihexyl-7-(pyren-1-ylethynyl)-9H-fluoren-2-yl)ethynyl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)pyrene (1,6-Py3F4): The procedure was analogous to that described for **4** (40% yield): ^1H NMR (CDCl_3) δ 0.69 (br, 16H), 0.81–0.84 (m, 24H), 1.11 (br, 48H), 1.19–1.22 (m, 16H), 2.07–2.09 (m, 16H), 7.61–7.64 (m, 8H), 7.71–7.72 (m, 4H), 7.75–7.79 (m, 12H), 8.04–

8.13 (m, 6H), 8.17 (d, 2H, $J = 8.0$ Hz), 8.22–8.31 (m, 14H), 8.75–8.80 (m, 4H) ppm; ^{13}C NMR (CDCl_3) δ 14.3, 22.9, 24.1, 29.2, 29.3, 30.3, 32.1, 40.8, 55.6, 89.3, 89.4, 91.1, 91.2, 96.5, 97.0, 118.2, 118.9, 120.4, 122.3, 122.4, 122.5, 124.6, 124.6, 124.8, 124.8, 125.5, 125.9, 126.2, 126.2, 126.5, 126.6, 127.5, 128.4, 128.6, 129.9, 130.3, 131.1, 131.2, 131.4, 131.4, 131.5, 132.1, 132.3, 140.9, 141.0, 141.1, 141.2, 151.4, 151.5 ppm. MS (MALDI) (m/z): 2187.7 (M^+). Anal. Calcd for $\text{C}_{168}\text{H}_{170}$: C, 92.17; H, 7.83. Found: C, 92.11; H, 7.90.

Fabrication and Characterization of OLEDs. All of the devices were fabricated on bare ITO substrates that were subsequently cleaned by detergent, deionized water, acetone, and ethanol. PEDOT:PSS was spin-coated on ITO glass and was baked at 100 °C for 2 h. Compounds **Py2F**, **Py2F3**, **Py2F5**, **1,6-PyF6**, **1,8-PyF6**, and **1,6-Py3F4** were spin-coated onto the PEDOT:PSS layer from their toluene solutions. Films of TPBI and Al cathode were formed by vacuum deposition under a pressure of 3×10^{-4} Pa. The deposition rate for TPBI and Al cathode layers was 1 and 5 Å/s, respectively. The thickness of the thin films was monitored by a quartz crystal oscillator placed near the substrates and was calibrated

ex situ by an Ambios Technology XP-2 surface profilometer. EL spectra were recorded with a Photo Research PR-650 spectrophotometer. Current–voltage characteristics were measured with a Hewlett-Packard 4140B semiconductor parameter analyzer. A Newport 2835-C multifunction optical meter was used to measure the luminescence output.

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Supporting Information Available: General information, excitation spectra, and NMR and mass spectra of intermediates and oligomers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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