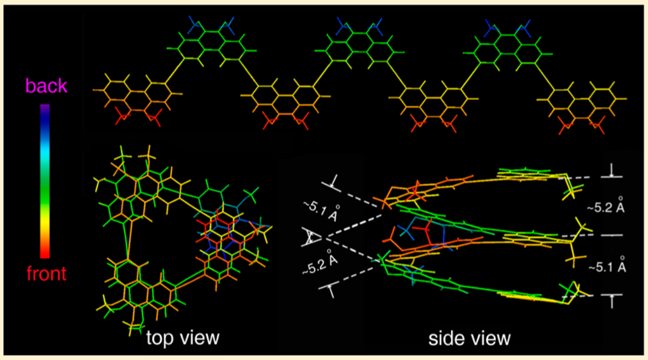
JOC The Journal of Organic Chemistry
Article
pubs.acs.org/joc

Oligo(3,6-phenanthrene ethynylenes): Synthesis, Characterization, and Photoluminescence

Jichao Li, Gongfang Hu, Ningning Wang, Tao Hu, Qiaodong Wen, Ping Lu,* and Yanguang Wang*

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

S *Supporting Information*



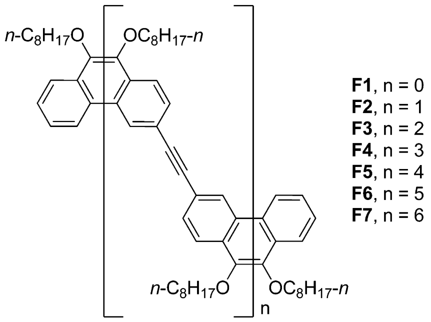
ABSTRACT: A series of highly fluorescent, oligo(3,6-phenanthrene ethynylenes) (**F1**−**F7**) were synthesized, and their photophysical behavior was systematically investigated. They emitted light with highly emissive quantum yields, up to 0.92. Emissive wavelengths of these compounds relied on the number of phenanthrene blocks existing in the oligomers. Red-shifted emissions were observed as the number of phenanthrenes increased. On the basis of theoretical calculations, helical structures could be formed for **F4**−**F7**, indicating that the excimer emissions might be observed for **F4**−**F7** due to the intramolecular $\pi-\pi$ stackings of phenanthrenes in the helical structures. However, excimer emissions were only observed for **F5**−**F7** in dilute cyclohexane and for **F6** and **F7** in dilute methylene chloride, respectively. No excimer emission was observed for **F4**−**F7** in dilute tetrahydrofuran due to the degree of solvation.

■ INTRODUCTION

In 1987, the first organic light-emitting diode device was designed by Tang and Van Slyke at Eastman Kodak.[1] Over the past three decades, vast quantities of investigations have been made on developing new materials and optimizing device architectures to realize the full-color, flat-panel display with improved efficiency and lifetime.[2−4] There was an upsurge of interest in research into polymer electroluminescence since Burroughes and co-workers reported a highly efficient green light-emitting polymer based device using 100 nm thick films of poly(*p*-phenylenevinylene) (PPV).[5] Since then, conjugated polymers and oligomers based on various aromatic building blocks have received considerable attention, owing to their intriguing photoluminescent (PL) and electroluminescent (EL) properties as well as their promising applications in the field of OLEDs.[2,6,7] Fluorophores, with high quantum yields, a good range of color, and favorable hole/electron mobilities, were introduced to the conjugated polymers in order to gain novel emitters that can drastically improve the performance of OLEDs.[8−10]

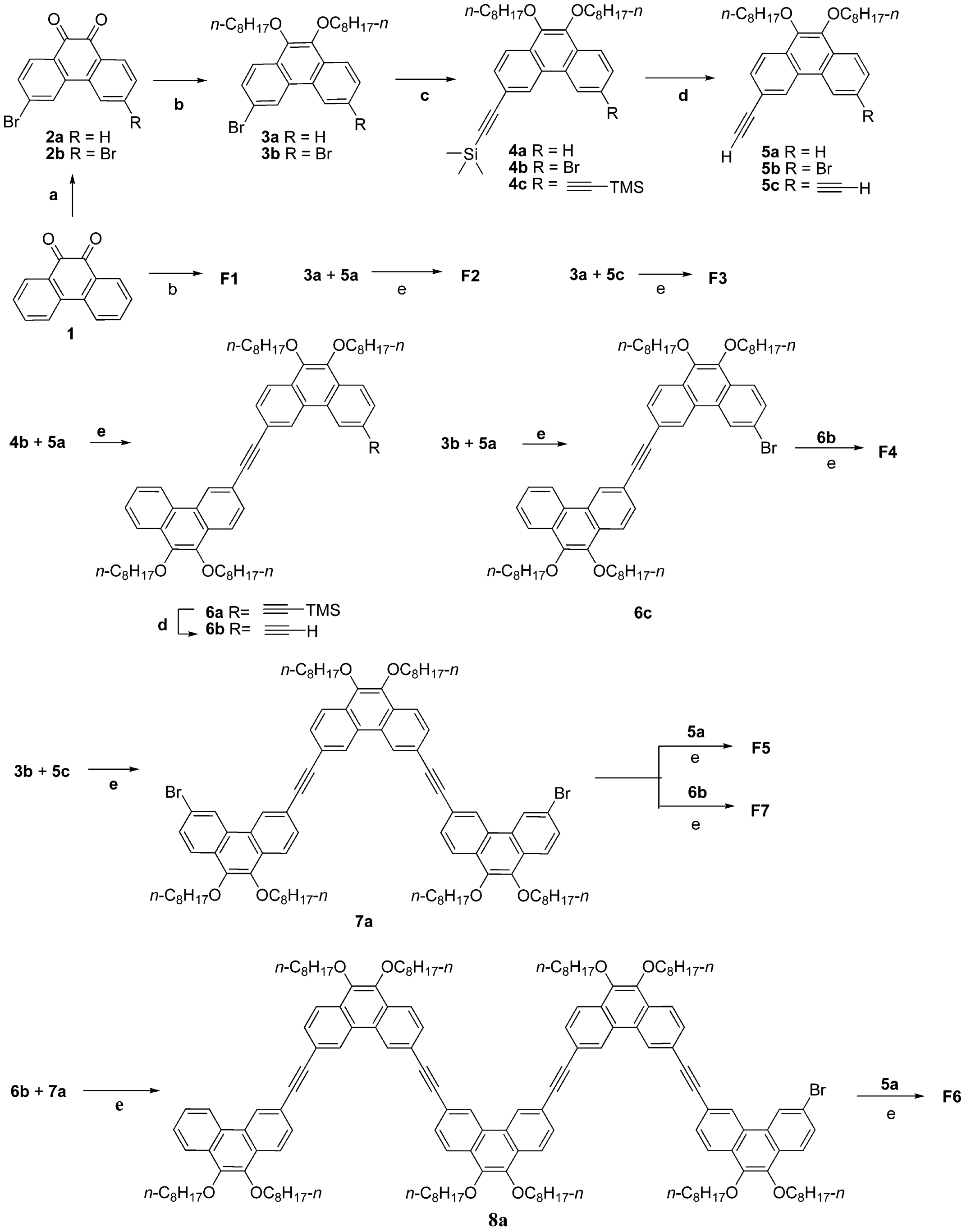
Phenanthrene and its derivatives have been extensively studied and developed as the desired blue light-emitting materials due to their specific optical and electrochemical properties.[11−16] Furthermore, it has been demonstrated that the thermal stability or glass-state durability of materials could be significantly improved when phenanthrene was integrated in the core structures.[17] Previously, we introduced fluorene or pyrene moieties into the backbone of the acetylene-linked carbazole oligomers and investigated the effects of chemical structure on the electronic, photonic, and morphological properties.[18−21] Encouraged by these results, we synthesized the seven oligo(3,6-phenanthrene ethynylenes) **F1**−**F7** (Scheme 1) in order to improve optoelectronic performance. The oligo(3,6-phenanthrene ethynylenes) were analogously constructed with respect to the fact that phenanthrene is rigid and highly fluorescent. From a synthetic point of view, the phenanthrene moiety can be easily modified at its 3,6-positions or 9,10-positions of the phenanthrene ring through covalent bonding, while the reactivity of the 2,7-positions is relatively poor. Thus, 3,6-positions of phenanthrene were chosen to construct the chain of the oligomers for a relatively stretched configuration and an efficient conjugation length in which the undesirable optical defects arising from the dispersed molecular size could be prevented. Meanwhile, the 9,10-positions of phenanthrene were intentionally substituted by two alkoxy groups so as to increase the product solubility as well as to serve as the electron donors in these structures. Therefore, these designed oligomers would combine the merits of well-defined structures and superior chemical

Scheme 1. Structures of Oligomers F1−F7



Received: December 31, 2012

Scheme 2. Synthesis of F1−F7[a]



[a]Reagents and conditions: (a) Br_2, benzoyl peroxide, *hν*, $PhNO_2$, 60 °C; (b) $Na_2S_2O_8$, K_2CO_3, Bu_4NBr, *n*-$C_8H_{17}Br$, H_2O/THF, room temperature, 48 h; (c) TMSCCH, CuI, $Pd(PPh_3)_4$, Ph_3P, NEt_3, N_2, reflux; (d) KF, MeOH/THF, N_2, reflux; (e) CuI, $Pd(PPh_3)_4$, Ph_3P, NEt_3, N_2, reflux.

purities possessed by small molecules and might be used as models for understanding the fluorescent structure−property relationship in detail.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Oligomers. Oligo-(3,6-phenanthrene ethynylenes) **F1**−**F7** were synthesized from phenanthrene-9,10-dione (**1**) as the starting material, and the Pd/Cu-catalyzed Sonogashira coupling strategy was used to build the ethylnylene-linked molecules (Scheme 2). Free radical bromination of **1** afforded **2a,b** in 68% and 79% yields, respectively, when the molar ratio of the bromine was used in a suitable amount.[22] As the mechanism of this radical bromination has been seldom discussed in the literature, we postulated a possible mechanism for this transformation (Scheme S1, Supporting Information). Treatment of **2a,b** with $Na_2S_2O_8$ followed by K_2CO_3, 1-bromooctane, and Bu_4NBr in the presence of H_2O/THF (1/1 v/v) for 48 h at room temperature afforded **3a,b** in 45% and 48% yields, respectively. The Pd/Cu-catalyzed coupling of **3a** as well as **3b** and ethynyltrimethylsilane provided **4a,c** in 90% and 89% yields, respectively. When the ratio of **3b** to ethynyltrimethylsilane was changed to 1.1/1, **4b** was prepared in 80% yield. Subsequent deprotection of **4a,c** with

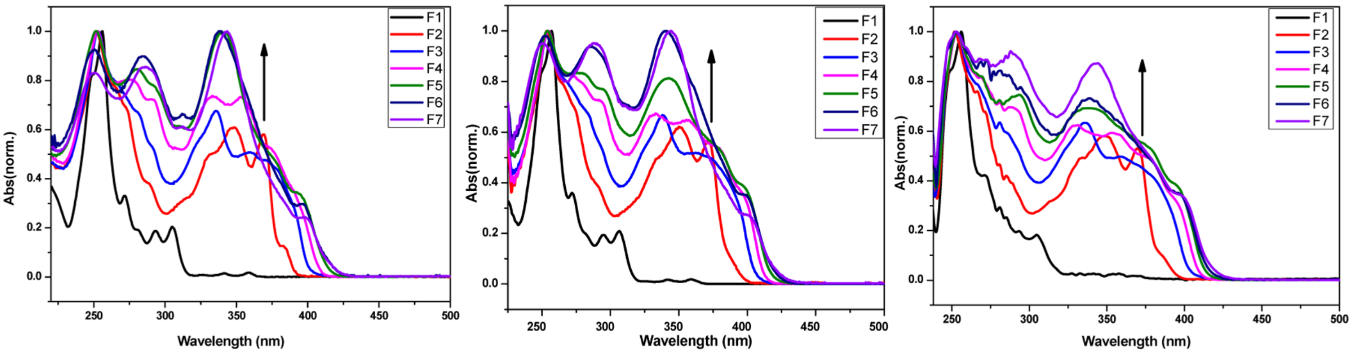


Figure 1. UV spectra of **F1**−**F7** in CH (left), DCM (middle), and THF (right), measured at 1 × 10^{-5} mol/L.

Table 1. UV Absorption Data of F1−F7[a]

	λ_{abs}, nm (ε, M^{-1} cm^{-1})		
	CH	DCM	THF
F1	256, 272, 293, 304	256, 271, 294, 305	256 (4800), 271 (2000), 293 (1000), 306 (800)
F2	253, 348, 369, 384	254, 351, 372	252 (5500), 349 (3200), 370 (3000)
F3	253, 336, 385, 392	253, 338, 379, 392	253 (12200), 336 (7600), 380 (5800), 395 (3800)
F4	253, 277, 291, 333, 355, 394	254, 273, 293, 333, 357, 395	252 (10100), 271 (8200), 288 (7000), 330 (6300), 354 (6000), 396 (3100)
F5	252, 281, 293, 341, 377, 395	254, 281, 296, 343, 380, 398	252 (11300), 281 (8200), 294 (8500), 339 (7800), 378 (5900), 396 (4200)
F6	251, 285, 339, 397	253, 286, 340, 400	252 (9200), 287 (7500), 340 (6700), 399 (3100)
F7	251, 287, 343, 399	251, 289, 345, 404	252 (10300), 288 (9400), 344 (9000), 400 (3400)

[a] Measured at 1 × 10^{-5} mol/L in CH, DCM and THF, respectively.

KF generated **5a**,**c** in 95%, and 93% yields, respectively. A similar Sonogashira coupling was performed between **4b** and **5a** to produce **6a**, which was directly desilylated into **6b** in a yield of 68%. **6c** and **7a** could be prepared by couplings between **3b** and **5a** as well as between **3b** and **5c** in 73% and 75% yields, respectively. **8a** was prepared from the coupling between **6b** and **7a** in 60% yield. 9,10-Bis(octyloxy)phenanthrene (**F1**) was directly synthesized in 49% yield by a procedure similar to that used to prepare **3a**,**b**. Finally, **F2**−**F7** were prepared via a Sonogashira coupling reaction. Thus, dropwise addition of **5a** into **3a** in the presence of Pd(0)/CuI/PPh_3 under N_2 afforded a white solid in 79% yield, which was demonstrated afterward to be **F2**.[23] **F3** was synthesized by a similar procedure in 72% yield after separation. Coupling between **6b** and **6c**, **5a** and **7a**, **8a** and **5a**, and **6b** and **7a** furnished **F4**−**F7** in yields of 65%, 61%, 56%, and 52%, respectively. The structures of oligomers **F1**−**F7** were characterized by ^{1}H and ^{13}C NMR spectroscopy and HRMS or MALDI-TOF MS.

Photophysical Properties of Oligomers. The synthesized oligomers **F1**−**F7** are soluble in common solvents such as acetone, dichloromethane, tetrahydrofuran, cyclohexane, and toluene but basically insoluble in polar solvents such as alcohols, acetonitrile, and water. The photophysical behavior of these compounds has been examined by measuring their absorption and fluorescence spectra in three different solvents, cyclohexane (CH), tetrahydrofuran (THF), and dichloromethane (DCM).

The absorption spectra of the oligomers in dilute CH, DCM, and THF are shown in Figure 1, while the absorption parameters are summarized in Table 1. Oligomers **F1**−**F7** absorbed strongly at about 250 nm with a weak maximum absorption band in the range of 300−400 nm. The maximum absorption band can be ascribed to a π−π* transition of the conjugated backbone. A trend of red-shifted absorption was exhibited in the absorption spectra of **F1**−**F7**. The maximum absorption wavelengths of **F1**−**F3** shifted regularly from 359 to 369 to 379 nm in CH, respectively, resulting from the significant elongation of the conjugated structure. For **F1**−**F3**, the accumulation of phenanthrene units extended the conjugated system as well as reduced the energy gap between the HOMO and LUMO, which was supported by theoretical calculations through the semi-empirical PM3 method of Gaussian 03 by simplification of octyloxy into methoxy (Table 2). Nevertheless, this trend was discontinuous. A nonlinear relationship was observed from **F4** to **F7**, as no significantly red-shifted absorption was recorded for **F4**−**F7** that was further confirmed by the calculated energy gaps between the HOMO and LUMO of **F4**−**F7** in either zigzag or helical structures (Table 2). However, an increasing trend in molar absorptivity at the maximum absorption bands of **F1**−**F7** appeared in dilute CH solution in comparison with the absorption bands at about 250 nm. A similar situation was observed for these oligomers in DCM and THF, respectively.

Emissive spectra of the oligomers in dilute CH, DCM, and THF are displayed in Figure 2, while the emissive data are summarized in Table 3. The vibrational emissions for **F1**−**F4** were assigned to the locally excited (LE) emissions of these oligomers. In dilute CH solutions (Figure 2, left), regular red-shifted emissions were observed from **F1** to **F4**. Emissive wavelengths of **F1** (382 nm), **F2** (395 nm), **F3** (419 nm), and **F4** (430 nm) indicated an effective elongation of conjugation through the accumulation of phenanthrene blocks. For **F5**−**F7**, the intensity of the LE emission became weaker and structureless emissions at lower energy appeared. The maximum emission wavelengths were recorded as 441, 446, and 450 nm for **F5**−**F7**, respectively (Figure 2, left). By changing CH to DCM, structureless emissions were observed for **F6** and **F7** only (Figure 2, middle). No structureless emission was seen for **F5**−**F7** in dilute THF solutions (Figure 2, right). According to the literature, the structureless emissions of **F5**−**F7** in CH and **F6** and **F7** in DCM could be assigned to the intramolecular excimer emission of two phenanthracene rings.[24]

The concentration effect of **F1**−**F7** on emission spectra was also investigated by fluorescence spectroscopy (Figures S54 and S55, Supporting Information). **F1** could not form an excimer even at 10^{-3} mol/L, while intermolecular excimers came into existence for **F2**−**F5** at 10^{-4} mol/L. **F6** and **F7** could form intramolecular excimers even at the 10^{-6} mol/L level in CH solutions.

All oligomers were highly fluorescent in both the solution and solid states. The PL quantum yields of the oligomers were measured in

Table 2. Calculated Data for F1−F7

	zigzag[a]				helical[a]			
	E, eV	HOMO, eV	LUMO, eV	E_g, eV	E, eV	HOMO, eV	LUMO, eV	E_g, eV
F1	−0.63	−8.69	−0.69	8.00				
F2	0.98	−8.45	−1.11	7.34				
F3	2.59	−8.39	−1.24	7.15				
F4	4.19	−8.37	−1.29	7.08	4.12	−8.42	−1.31	7.11
F5	5.80	−8.37	−1.32	7.05	5.58	−8.43	−1.36	7.07
F6	7.41	−8.36	−1.34	7.02	7.18	−8.35	−1.29	7.06
F7	9.02	−8.36	−1.35	7.01	8.73	−8.44	−1.42	7.02

[a] Calculated via the semiempirical PM3 method of Gaussian 03.

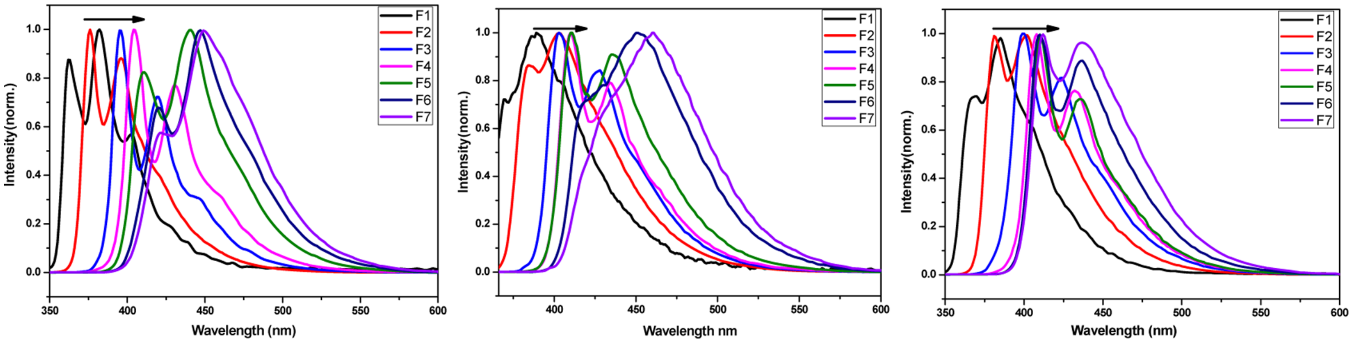


Figure 2. FL spectra of oligomers of **F1**−**F7** in CH (left), DCM (middle), and THF (right), measured at 1 × 10^{-5} mol/L and excited by the maximum excitation wavelength.

Table 3. Emission Data of Oligomers[a]

	CH		DCM		THF			film	
	λ_{ex}, nm	λ_{em}, nm	λ_{ex}, nm	λ_{em}, nm	λ_{ex}, nm	λ_{em}, nm	Φ^b	λ_{ex}, nm	λ_{em}, nm
F1	305	362, 382, 402	307	368, 389, 403	306	368, 386, 401	0.05	351	387, 406
F2	366	376, 395	370	384, 402	369	381, 404	0.41	375	406, 428
F3	368	396, 419	375	402, 428	371	400, 423	0.54	385	449
F4	354	405, 430	379	411, 434	376	408, 433	0.91	400	451
F5	342	409, 441	378	410, 435	376	410, 436	0.92	408	462
F6	345	420, 446	345	420, 452	378	410, 436	0.80	411	463
F7	344	421, 450	347	428, 461	349	411, 438	0.72	400	471

[a] Measured at 1 × 10^{-5} M in CH, DCM, and THF, respectively. [b] Measured in THF solutions using DPA as a standard.

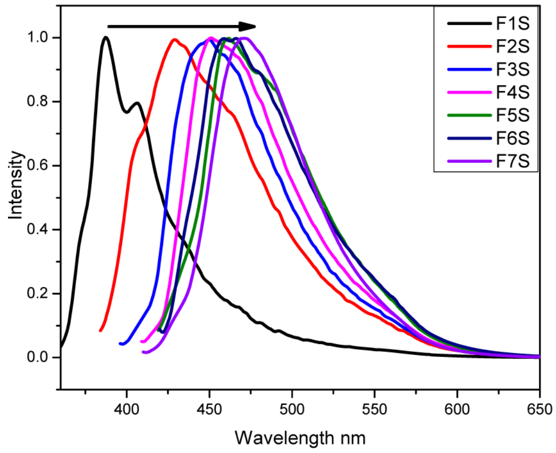


Figure 3. Emissive spectra of **F1**−**F7** in thin films, excited by its maximum excitation wavelength.

dilute THF solutions by using 9,10-bis(phenylehynyl)anthracene (DPA, Φ = 1.0 in cyclohexane[25]) as a standard. As shown in Table 3, the quantum yields of **F2**−**F7** (0.41−0.92) were much higher than that of **F1** (0.05) and gradually increased from 0.41 (**F2**) to 0.92 (**F5**) as increments of phenanthrene blocks. However, the quantum yields were determined to be 0.80 and 0.72 for **F6** and **F7**, respectively.

In thin films, **F1** and **F2** emitted light at 387 and 428 nm with shoulder peaks at lower energy bands (Figure 3). In contrast, **F3**−**F7** exhibited a broader red-shifted emission from 449 to 471 nm owing to the extension of phenanthrene blocks. The emissive wavelengths bathochromatically shifted about 10−20 nm in the solid state in comparison with those in dilute THF solutions, which was probably because they were prone to close, face-to-face $\pi-\pi$ stacking that led to aggregates and/or excimer formation of phenanthrene rings in the solid state.

In order to get a good insight into the absorption and emissive properties of these oligomers, theoretical calculations through the semiempirical PM3 method of Gaussian 03[26] by simplification of octoxy into methoxy were carried out, and the results are summarized in Table 2. Although the dispersion-corrected hybrid functionals should be used for precise calculations,[27] they is too expensive to allow calculation of these oligomers. Intramolecular excimer formation could be explained by the flexible backbone of the oligomers. The 120°

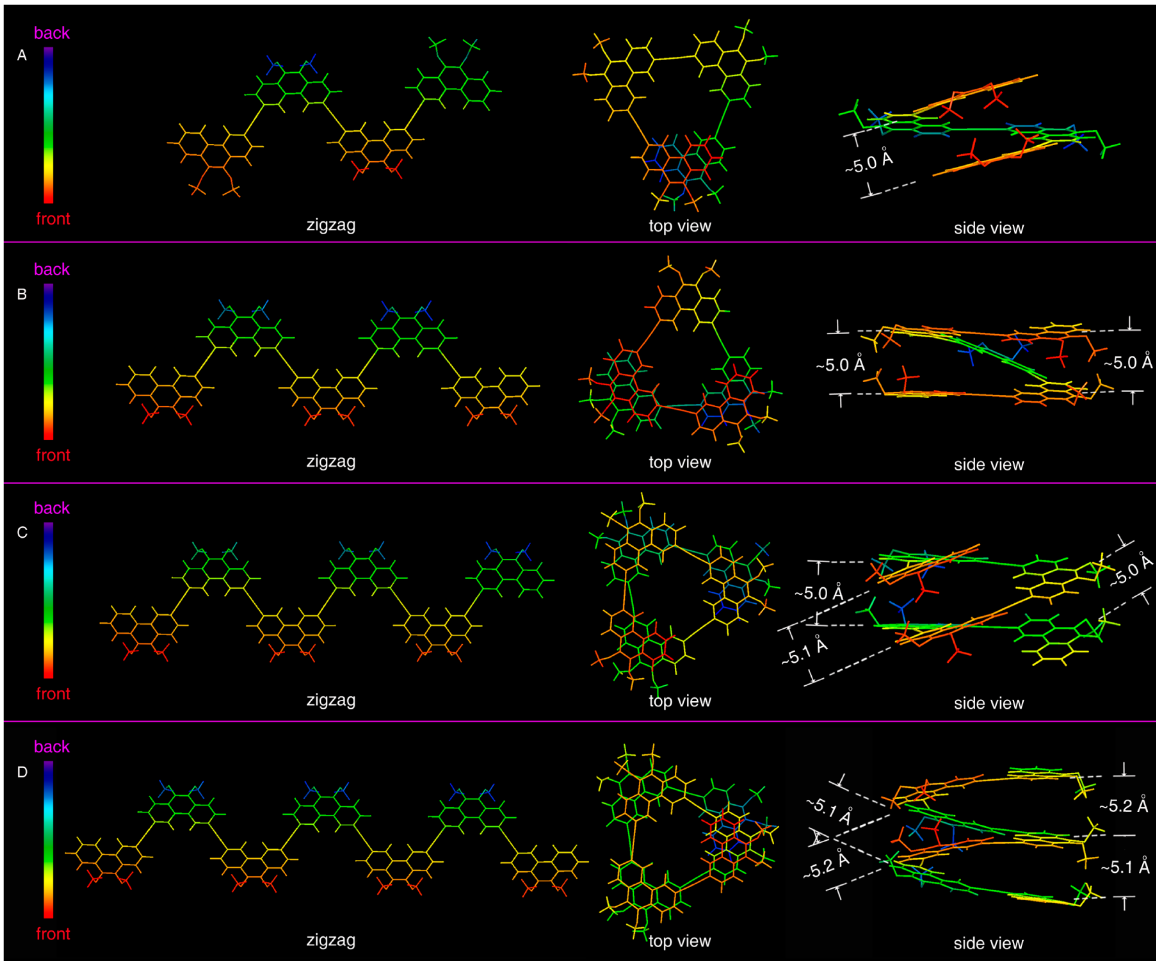


Figure 4. Conformations of **F4**−**F7**: zigzag vs helical.

bond angle at the 3- and 6-positions of phenanthrene was suitable to provide a cross-cover overlap, which led to the formation of intramolecular excimers and the resulting red-shifted emission. On the basis of theoretical calculations, **F4** should start to have excimer emission because it has a perfectly parallel stacking of the two terminal phenanthrenes (Figure 4). In comparison with the potential energy of **F4** in the zigzag conformer, intramolecular $\pi-\pi$ interactions arising from the stacking of phenanthrenes caused **F4** in the helical conformer to possess a lower potential energy with an energy difference of 0.07 eV. Similarly, **F5**−**F7** released their potential energies by the formation of helical conformers to the degree of 0.22, 0.23, and 0.29 eV, respectively. Meanwhile, the average screw pitch was determined to be about 5.0 Å.

In dilute solution, solvation existed. The insertion of solvent molecules into the middle of the two stacking phenanthrenes brought about a twisted helical conformation. Thus, the perfectly helical structure of **F4** was damaged even in dilute CH solution, which was the typical nonpolar solvent. As a result, the intramolecular excimer emission of **F4** in dilute CH solution could not be observed. As the solvent polarity increased, the degree of solvation increased. Excimer emission of **F5** in dilute DCM solution disappeared. When the solvent was changed to THF, no excimer emissions were detected, even for **F7**.

■ CONCLUSION

In summary, a series of well-defined oligo(3,6-phenanthrene ethynylenes) have been synthesized and fully characterized. The results, obtained through inspecting the absorption and emissive spectra of these pure oligomers in dilute solutions, demonstrated a certain fluorescent structure−property relationship of these oligomers. Red-shifted emissions and increased quantum yields were detected for **F1**−**F5**. Meanwhile, helical structures of **F4**−**F7** could be formed due to the inherent structural factor, which was supported by theoretical calculations. It was also evidenced by the intramolecular excimer emissions of **F5**−**F7** in dilute cyclohexane and **F6** and **F7** in dichloromethane. Further, these oligomers presented high quantum yields and could possibly be used as light-emitting materials in optoelectronic devices.

■ EXPERIMENTAL SECTION

General Methods. Unless otherwise stated, all chemicals were purchased from commercial suppliers and used without further purification. Tetrahydrofuran and toluene were distilled from sodium/benzophenone. Dichloromethane was distilled from calcium hydride. Cyclohexane was distilled under an N_2 atmosphere. Yields reported are isolated yields. NMR spectra were obtained at 400 or 500 MHz for ^{1}H NMR and 100 or 125 MHz for ^{13}C NMR in $CDCl_3$. Chemical shifts are reported in ppm using either tetramethylsilane or the residual $CDCl_3$ as standard. Flash column chromatography was performed employing 200−300 mesh silica gel. Thin-layer chromatography (TLC) was performed on silica with fluorescence at 254 nm.

3-Bromo-9,10-bis(octyloxy)phenanthrene (3a). To a solution of 3-bromophenanthrene-9,10-dione (**2a**; 5.72 g, 20 mmol) in THF (150 mL) were added $Na_2S_2O_8$ (11.5 g, 60 mmol) and H_2O (150 mL), and the resulting solution was stirred for 15 min. Then, K_2CO_3

(8.28 g, 60 mmol), TBAF (0.64 g, 2 mmol), and 1-bromooctane (11.5 g, 60 mmol) were sequentially added into the solution. After the solution was purged with nitrogen for 10 min, it was stirred under nitrogen for 48 h at room temperature. Then the solution was poured into H_2O and extracted with CH_2Cl_2 (4 × 30 mL). The organic layer was combined, dried over anhydrous $MgSO_4$, and filtered. The filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/dichloromethane as eluent) to give **3a** (4.60 g, 45% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 1.6 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.25 (dd, J = 7.6, 1.6 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.70 (dd, J = 8.8, 1.6 Hz, 1H), 7.67–7.59 (m, 2H), 4.21 (m, 4H), 1.94–1.88 (m, 4H), 1.63–1.52 (m, 4H), 1.39–1.33 (m, 16H), 0.94–0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 143.2, 135.6, 132.0, 130.7, 130.2, 129.1, 127.7, 127.6, 126.3, 124.4, 122.9, 122.7, 91.8, 74.0, 73.9, 32.2, 30.8, 29.9, 29.7, 26.6, 23.1, 14.5. HRMS (EI): calcd for $C_{30}H_{41}BrO_2$ 512.2290 (M^+), found 512.2302.

3,6-Dibromo-9,10-bis(octyloxy)phenanthrene (3b). The procedure was analogous to that described for **3a**, but 3,6-dibromophenanthrene-9,10-dione (**2b**; 7.26 g, 20 mmol) was used instead of **2a**. Thus, **3b** was obtained (5.43 g, 48% yield) as a white solid. Mp: 63–64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 1.6 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.71 (dd, J = 8.8, 1.6 Hz, 2H), 4.17 (t, J = 6.8 Hz, 4H), 1.92–1.85 (m, 4H), 1.57–1.53 (m, 4H), 1.31–1.28 (m, 16H), 0.92–0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 130.8, 129.2, 129.1, 125.7, 124.5, 120.6, 74.1, 32.2, 30.8, 29.8, 29.7, 26.6, 23.0, 14.4. HRMS (EI): calcd for $C_{30}H_{40}Br_2O_2$ 590.1395 (M^+), found 590.1413.

((9,10-Bis(octyloxy)phenanthren-3-yl)ethynyl)trimethylsilane (4a). To a solution of **3a** (1.02 g, 2 mmol), cuprous iodide (9 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.5 mg, 0.005 mmol), and triphenylphosphine (5.2 mg, 0.02 mmol) in dry triethylamine (100 mL) was added ethynyltrimethylsilane (0.22 g, 2.2 mmol). The mixture was refluxed under nitrogen for 8 h and then filtered. The filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/DCM as eluent) to give pure **4a** (0.95 g, 90% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.61 (dd, J = 7.6, 1.6 Hz, 1H), 8.24 (dd, J = 7.2, 2.0 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.67 (dd, J = 8.4, 1.2 Hz, 1H), 7.64–7.57 (m, 2H), 4.23–4.17 (m, 4H), 1.97–1.84 (m, 4H), 1.57–1.54 (m, 4H), 1.38–1.26 (m, 16H), 0.92–0.88 (m, 6H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 151.0, 142.3, 140.6, 131.5, 128.0, 127.2, 126.9, 123.2, 120.5, 120.4, 119.9, 85.1, 40.6, 32.1, 30.3, 29.6, 24.0, 22.9, 14.4. HRMS (EI): calcd for $C_{35}H_{50}O_2Si$ 530.3580 (M^+), found 530.3579.

((6-Bromo-9,10-bis(octyloxy)phenanthren-3-yl)ethynyl)-trimethylsilane (4b). When the ratio of **3b** to ethynyltrimethylsilane was changed to 1.1/1, **4b** was obtained (0.972 g, 80% yield) as a colorless oil. It could also be obtained as a byproduct in the synthesis of **4a,c** in a certain amount. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.66 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.71–7.67 (m, 2H), 4.21–4.16 (m, 4H), 1.91–1.87 (m, 4H), 1.57–1.53 (m, 4H), 1.36–1.31 (m, 16H), 0.90 (t, J = 6.4 Hz, 6H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 143.5, 130.6, 130.5, 130.2, 129.8, 128.9, 127.5, 127.0, 125.8, 124.5, 122.7, 120.9, 120.7, 105.8, 95.4, 74.1, 74.0, 32.2, 30.8, 29.8, 29.7, 26.6, 23.0, 14.5, 0.4. HRMS (EI): calcd for $C_{35}H_{49}BrO_2Si$ 608.2685 (M^+), found 608.2657.

(9,10-Bis(octyloxy)phenanthrene-3,6-diyl)bis(ethyne-2,1-diyl)bis(trimethylsilane) (4c). The procedure was analogous to that described for **4a**. Thus **4c** was obtained (1.10 g, 89% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 2H), 8.15 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 4.19 (t, J = 6.4 Hz, 4H), 1.93–1.86 (m, 4H), 1.57–1.51 (m, 4H), 1.37–1.31 (m, 16H), 0.92–0.88 (m, 6H), 0.33 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 130.4, 129.9, 128.0, 127.0, 122.6, 120.8, 105.9, 95.2, 74.1, 32.2, 30.8, 29.8, 29.7, 26.6, 23.0, 14.5, 0.4. HRMS (EI): calcd for $C_{40}H_{58}O_2Si_2$ 626.3975 (M^+), found 626.3973.

3-Ethynyl-9,10-bis(octyloxy)phenanthrene (5a). A solution of **4a** (1.06 g, 2 mmol) and KF (500 mg) in methanol (100 mL) was refluxed under nitrogen for 2 h. The solvent was then removed, and the crude product was purified by column chromatography (silica gel, hexane/DCM as eluent) to afford **5a** (0.87 g, 95% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.63–8.54 (m, 1H), 8.25 (dd, J = 7.8, 1.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.69 (dd, J = 8.4, 0.8 Hz, 1H), 7.67–7.55 (m, 2H), 4.24–4.17 (m, 4H), 3.20 (s, 1H), 1.97–1.84 (m, 4H), 1.58–1.53 (m, 4H), 1.38–1.31 (m, 16H), 0.92–0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 143.2, 130.2, 130.0, 128.8, 128.6, 128.4, 127.4, 127.3, 126.3, 122.9, 122.7, 84.7, 74.0, 32.2, 30.8, 29.9, 29.7, 26.6, 23.0, 14.5. HRMS (EI): calcd for $C_{32}H_{42}O_2$ 458.3185 (M^+), found 458.3168.

3,6-Diethynyl-9,10-bis(octyloxy)phenanthrene (5c). The procedure was analogous to that described for **5a**. **5c** was obtained (0.89 g, 93% yield) as a white solid. Mp: 77–78 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 2H), 8.17 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 4.18 (t, J = 6.6 Hz, 4H), 3.21 (s, 2H), 1.91–1.85 (m, 4H), 1.56–1.51 (m, 4H), 1.37–1.30 (m, 16H), 0.90 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 130.4, 130.2, 128.0, 127.3, 122.8, 119.9, 84.5, 78.1, 74.1, 32.2, 30.8, 29.8, 29.7, 26.6, 23.0, 14.4. HRMS (EI): calcd for $C_{34}H_{42}O_2$ 482.3185 (M^+), found 482.3183.

3-((9,10-Bis(octyloxy)phenanthren-3-yl)ethynyl)-6-ethynyl-9,10-bis(octyloxy)phenanthrene (6b). To a solution of **4b** (0.608 g, 1 mmol) in dry triethylamine (100 mL) were added tetrakis-(triphenylphosphine)palladium (3.5 mg, 0.005 mmol), cuprous iodide (10 mg, 0.05 mmol), and triphenylphosphine (5 mg, 0.02 mmol). After the solution was purged with nitrogen for 10 min, **5a** (0.456 g, 1.0 mmol) in 10 mL of triethylamine was added dropwise though a constant pressure dropping funnel in 10 min. Then the solution was refluxed under nitrogen for 8 h. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/DCM as eluent) to afford **6a**. After removal of TMS by KF, **6b** was obtained (0.670 g, 68% yield) as a slightly yellow solid. Mp: 79–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.86 (s, 1H), 8.83 (s, 1H), 8.70–8.68 (m, 1H), 8.27–8.21 (m, 3H), 8.18 (d, J = 8.4 Hz, 1H), 7.83–7.80 (m, 2H), 7.73 (dd, J = 8.4, 1.2 Hz, 1H), 7.64–7.62 (m, 2H), 4.24–4.18 (m, 8H), 3.21 (s, 1H), 1.92–1.89 (m, 8H), 1.57–1.54 (m, 8H), 1.3–1.31 (m, 32H), 0.92–0.89 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ144.5, 144.4, 144.1, 143.4, 132.5, 132.4, 130.3, 130.2, 130.1, 129.80, 129.75, 129.7, 128.9, 128.8, 127.4, 126.7, 126.6, 126.3, 122.9, 122.8, 91.4, 90.7, 84.6, 78.1, 74.1, 74.0, 32.2, 30.9, 30.8, 29.9, 29.7, 26.6, 23.0, 14.5. HRMS (EI): calcd for $C_{64}H_{82}O_4$ 914.6213 (M^+), found 914.6229.

3-((9,10-Bis(octyloxy)phenanthren-3-yl)ethynyl)-6-bromo-9,10-bis(octyloxy)phenanthrene (6c). **3b** (1.0 g, 1.7 mmol) and **5a** (0.458 g, 1.0 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **6c** (0.71 g, 73% yield) was obtained as a slightly yellow solid. Mp: 60–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (s, 1H), 8.94 (s, 1H), 8.81 (s, 1H), 8.72 (d, J = 8.8 Hz, 1H), 8.28–8.23 (m, 3H), 7.98 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.67–7.65 (m, 2H), 4.31–4.14 (m, 8H), 1.97–1.91 (m, 8H), 1.61–1.57 (m, 8H), 1.40–1.34 (m, 32H), 0.95–0.92 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 143.4, 138.2, 130.3, 130.1, 128.9, 128.6, 127.7, 127.5, 126.3, 124.3, 123.1, 122.9, 122.8, 119.2, 74.11, 74.07, 32.2, 30.89, 30.88, 29.90, 29.88, 29.71, 29.69, 26.65, 26.63, 23.1, 14.5. HRMS (EI): calcd for $C_{62}H_{81}BrO_4$ 968.5318 (M^+), found 968.5311.

6,6′-(9,10-Bis(octyloxy)phenanthrene-3,6-diyl)bis(ethyne-2,1-diyl)bis(3-bromo-9,10-bis(octyloxy)phenanthrene) (7a). **3b** (1.8 g, 3.05 mmol) and **5c** (0.482 g, 1.0 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **7a** (1.13 g, 75% yield) was obtained as a slightly yellow solid. Mp: 82–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (s, 2H), 8.82 (d, J = 4.4 Hz, 4H), 8.27–8.22 (m, 4H), 8.10 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 4H), 7.72 (d, J = 8.8 Hz, 2H), 4.26–4.21 (m, 12H), 1.96–1.92 (m, 12H), 1.62–1.58 (m, 12H), 1.48–1.35 (m, 48H), 0.97–0.92 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 144.1, 143.7, 132.5, 132.4, 132.3, 132.2, 130.5, 130.4, 130.2, 130.1, 130.0, 129.9, 128.93, 128.89, 128.8, 128.3, 127.7, 126.7, 126.7, 125.9, 124.5, 122.9, 121.1, 121.0, 120.8, 91.3, 91.0, 74.2, 74.1, 32.23, 32.21, 30.87, 30.83, 29.88, 29.87, 29.85, 29.70, 29.68, 29.67, 26.63, 26.60, 23.1, 23.0, 14.48, 14.47. HRMS (EI): calcd for $C_{94}H_{120}Br_2O_6$ 1502.7452 (M^+), found 1502.7450.

3-((9,10-Bis(octyloxy)phenanthren-3-yl)ethynyl)-6-((6-((6-((6-bromo-9,10-bis(octyloxy)phenanthren-3-yl)ethynyl)-9,10-bis(octyloxy)phenanthren-3-yl)ethynyl)-9,10-bis(octyloxy)-phenanthren-3-yl)ethynyl)-9,10-bis(octyloxy)phenanthrene (8a). **7a** (0.75 g, 0.5 mmol) and **6b** (0.44 g, 0.48 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **8a** (0.673 g, 60% yield) was obtained as a sticky oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.10 (s, 2H), 8.97−8.89 (m, 4H), 8.84 (s, 1H), 8.72 (s, 2H), 8.59 (d, J = 8.8 Hz, 1H), 8.29 (d, J = 8.4 Hz, 2H), 8.14−8.03 (m, 7H), 7.98 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.82−7.75 (m, 4H), 7.76 (dd, J = 8.8, 3.6 Hz, 2H), 7.70 (dd, J = 8.8, 3.6 Hz, 2H), 7.61 (dd, J = 8.8, 1.6 Hz, 1H), 7.50−7.45 (m, 2H), 4.29−4.07 (m, 20H), 2.00−1.88 (m, 20H), 1.64−1.56 (m, 20H), 1.43−1.37 (m, 80H), 0.97−0.94 (m, 30H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 144.3, 144.2, 144.1, 144.0, 143.5, 143.3, 130.4, 130.3, 130.2, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.4, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.5, 127.1, 126.9, 126.8, 126.60, 126.56, 126.4, 126.1, 125.8, 124.3, 122.9, 122.8, 122.7, 122.6, 122.4, 121.3, 121.2, 121.0, 120.9, 120.70, 120.66, 91.5, 91.3, 91.2, 91.0, 74.2, 74.0, 73.9, 32.3, 30.9, 29.9, 29.7, 26.7, 23.1, 14.5. MS (MALDI-TOF): m/z 2337.6 (M$^+$).

9,10-Bis(octyloxy)phenanthrene (F1). The procedure was analogous to that described for **3a**, but phenanthrene-9,10-dione (**1**; 0.416 g, 2 mmol) was used. After purification by column chromatography (silica gel, hexane/DCM as eluent), **F1** (0.43 g. 49% yield) was obtained as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.68 (d, J = 6.0 Hz, 2H), 8.32 (dd, J = 8.4, 1.2 Hz, 2H), 7.70−7.63 (m, 4H), 4.27 (t, J = 5.6 Hz, 4H), 2.03−1.97 (m, 4H), 1.68−1.62 (m, 4H), 1.50−1.39 (m, 16H), 1.00−0.97 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.6, 130.0, 129.0, 127.0, 126.0, 122.9, 122.6, 74.0, 32.2, 30.9, 29.9, 29.7, 26.7, 23.0, 14.5. HRMS: calcd for $C_{30}H_{42}O_2$ 434.3185 (M$^+$), found 434.3186.

1,2-Bis(9,10-bis(octyloxy)phenanthren-3-yl)ethyne (F2). **3a** (0.512 g, 1 mmol) and **5a** (0.241 g, 0.5 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **F2** (0.35 g, 79% yield) was obtained as a white solid. Mp: 60−61 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.91 (s, 2H), 8.71−8.68 (m, 2H), 8.28−8.24 (m, 4H), 7.82 (d, J = 8.8 Hz, 2H), 7.67−7.62 (m, 4H), 4.25−4.21 (m, 8H), 1.96−1.89 (m, 8H), 1.62−1.55 (m, 8H), 1.41−1.31 (m, 32H), 0.92−0.89 (m, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.5, 143.4, 130.3, 129.8, 129.7, 128.8, 128.5, 127.4, 126.7, 126.3, 123.1, 122.8, 122.8, 120.7, 91.0, 74.1, 32.2, 30.9, 29.9, 29.7, 26.6, 23.0, 14.5. HRMS: calcd for $C_{62}H_{84}O_4$ 890.6213 (M$^+$), found 890.6192.

3,3′-(9,10-Bis(octyloxy)phenanthrene-3,6-diyl)bis(ethyne-2,1-diyl)bis(9,10-bis(octyloxy)phenanthrene) (F3). **3a** (0.77 g, 1.5 mmol) and **5c** (0.241 g, 0.5 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **F3** (0.475 g, 72% yield) was obtained as a slightly yellow solid. Mp: 62−63 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.99 (s, 2H), 8.96 (s, 2H), 8.73 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 8.4 Hz, 6H), 7.82 (dd, J = 8.4, 1.2 Hz, 4H), 7.68−7.63 (m, 4H), 4.28−4.22 (m, 12H), 1.99−1.91 (m, 12H), 1.65−1.55 (m, 12H), 1.41−1.33 (m, 48H), 0.95−0.91 (m, 18H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.5, 144.3, 143.4, 130.2, 130.1, 129.9, 129.8, 129.7, 128.8, 128.5, 128.3, 127.4, 126.7, 126.3, 123.1, 122.9, 122.8, 122.7, 121.1, 120.6, 91.3, 90.8, 74.2, 74.1, 32.2, 30.9, 29.9, 29.7, 26.6, 23.0, 14.5. HRMS: calcd for $C_{94}H_{122}O_6$ 1346.9241 (M$^+$), found 1346.9246.

1,2-Bis(6-((9,10-bis(octyloxy)phenanthren-3-yl)ethynyl)-9,10-bis(octyloxy)phenanthren-3-yl)ethyne (F4). **6c** (0.300 g, 0.31 mmol) and **6b** (0.183 g, 0.2 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **F4** (0.234 g, 65% yield) was obtained as a white solid. Mp: 52−53 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.01 (d, J = 4.4 Hz, 4H), 8.90 (s, 2H), 8.67−8.64 (m, 2H), 8.29 (dd, J = 8.8, 3.2 Hz, 4H), 8.19 (dd, J = 8.8, 3.2 Hz, 4H), 7.88 (t, J = 8.8 Hz, 4H), 7.81 (d, J = 8.8 Hz, 2H), 7.57−7.54 (m, 4H), 4.28−4.13 (m, 16H), 2.00−1.86 (m, 16H), 1.63−1.53 (m, 16H), 1.41−1.32 (m, 64H), 0.95−0.90 (m, 24H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.5, 144.34, 144.29, 143.3, 137.6, 137.5, 134.2, 134.0, 132.5, 132.4, 130.2, 130.1, 130.0, 129.9, 129.7, 129.6, 129.0, 128.9, 128.8, 128.44, 128.36, 127.3, 126.8, 126.7, 126.3, 123.02, 122.96, 122.9, 122.8, 122.6, 121.2, 121.1, 120.6, 91.5, 91.2, 90.9, 74.1, 74.0, 32.2, 30.89, 30.85, 29.9, 29.7, 26.6, 14.5. MS (MALDI-TOF): m/z 1826.5 ([M + 23]$^+$).

6,6′-(9,10-Bis(octyloxy)phenanthrene-3,6-diyl)bis(ethyne-2,1-diyl)bis(3-((9,10-bis(octyloxy)phenanthren-3-yl)ethynyl)-9,10-bis(octyloxy)phenanthrene) (F5). **5a** (0.458 g, 1 mmol) and **7a** (0.600 g, 0.4 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **F5** (0.55 g, 61% yield) was obtained as a sticky oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.13 (s, 2H), 8.98 (s, 2H), 8.94 (s, 2H), 8.87 (s, 2H), 8.62 (d, J = 6.4 Hz, 2H), 8.32 (d, J = 8.4 Hz, 2H), 8.16−8.10 (m, 8H), 7.82 (d, J = 8.4 Hz, 2H), 7.83−7.77 (m, 4H), 7.73 (d, J = 8.8 Hz, 2H), 7.53−7.49 (m, 4H), 4.29−4.13 (m, 20H), 2.01−1.91 (m, 20H), 1.64−1.57 (m, 20H), 1.50−1.35 (m, 80H), 0.98−0.94 (m, 30H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 144.3, 144.2, 144.1, 143.2, 130.2, 130.0, 129.9, 129.73, 129.69, 129.6, 129.4, 128.6, 128.4, 128.3, 128.2, 128.1, 127.1, 126.8, 126.7, 126.6, 126.5, 126.1, 123.0, 122.8, 122.59, 122.56, 122.4, 121.2, 121.1, 120.9, 120.6, 91.5, 91.2, 91.0, 74.2, 74.0, 73.9, 32.3, 30.9, 29.9, 29.7, 26.6, 23.1, 14.5. MS (MALDI-TOF): m/z 2258.2.

1,2-Bis(6-((6-((9,10-bis(octyloxy)phenanthren-3-yl)ethynyl)-9,10-bis(octyloxy)phenanthren-3-yl)ethynyl)-9,10-bis-(octyloxy)phenanthren-3-yl)ethyne (F6). **8a** (0.234 g, 0.1 mmol) and **5a** (0.046 g, 0.1 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **F6** (0.152 g, 56% yield) was obtained as a sticky oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.01 (s, 2H), 8.90 (s, 2H), 8.87 (s, 2H), 8.79 (s, 4H), 8.54 (d, J = 6.4 Hz, 2H), 8.12 (d, J = 6.8 Hz, 2H), 8.02−7.95 (m, 8H), 7.91 (d, J = 6.4 Hz, 2H), 7.80 (d, J = 6.4 Hz, 2H), 7.71−7.69 (m, 4H), 7.53−7.51 (m, 4H), 7.36−7.31 (m, 4H), 4.17−4.09 (m, 24H), 1.93−1.87 (m, 24H), 1.61−1.55(m, 24H), 1.45−1.35 (m, 96H), 0.95−0.92 (m, 36H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 144.1, 144.0, 143.92, 143.88, 143.85, 143.1, 130.1, 129.9, 129.65, 129.60, 129.5, 129.3, 129.1, 129.0, 128.4, 128.2, 128.1, 127.93, 127.90, 126.8, 126.7, 126.5, 126.3, 126.1, 125.9, 122.8, 122.6, 122.3, 122.1, 121.0, 120.9, 120.8, 120.6, 91.5, 91.4, 90.9, 74.01, 73.96, 73.92, 73.86, 32.2, 30.9, 30.0, 29.8, 26.7, 23.2, 14.5. MS (MALDI-TOF): m/z 2712.9.

6,6′-(9,10-Bis(octyloxy)phenanthrene-3,6-diyl)bis(ethyne-2,1-diyl)bis(3-((6-((9,10-bis(octyloxy)phenanthren-3-yl)-ethynyl)-9,10-bis(octyloxy)phenanthren-3-yl)ethynyl)-9,10-bis(octyloxy)phenanthrene) (F7). **6c** (0.213 g, 0.22 mmol) and **7a** (0.150 g, 0.1 mmol) were used for coupling. After purification by column chromatography (silica gel, hexane/DCM as eluent), **F7** (0.165 g, 52% yield) was obtained as a sticky oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.96 (s, 2H), 8.86 (s, 2H), 8.75 (s, 2H), 8.72 (s, 4H), 8.57 (s, 2H), 8.42 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.81−7.74 (m, 8H), 7.68−7.63 (m 4H), 7.57 (d, J = 8.4 Hz, 2H), 7.43 (dd, J = 6.0, 3.6 Hz, 1H), 7.28 (d, J = 9.2 Hz, 2H), 7.22−7.18 (m, 3H), 7.16−7.12 (m, 2H), 7.07−7.04 (m, 2H), 4.22−4.13 (m, 16H), 4.06−3.95 (m, 12H), 1.96−1.80 (m, 28H), 1.70−1.56 (m, 28H), 1.52−1.37 (m, 112H), 0.97−0.90 (m, 42H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.94, 143.93, 143.88, 143.86, 143.7, 143.6, 143.0, 130.3, 129.7, 129.5, 129.4, 129.3, 129.2, 128.9, 128.8, 128.7, 128.4, 128.1, 128.0, 127.9, 127.7, 126.54, 126.49, 126.4, 126.3, 126.1, 125.9, 125.8, 122.6, 122.3, 122.2, 122.1, 122.1, 121.9, 121.8, 121.6, 121.3, 120.9, 120.79, 120.76, 120.5, 111.7, 92.0, 91.62, 91.59, 91.5, 91.4, 91.0, 74.0, 73.92, 73.86, 73.74, 73.68, 73.6, 32.4, 32.34, 32.29, 31.1, 31.0, 30.9, 30.2, 30.1, 30.0, 29.9, 29.8, 29.8, 26.8, 26.7, 23.11, 23.06, 14.5. MS (MALDI-TOF): m/z 3170.6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving general information, NMR and mass spectra of intermediates and oligomers, and the concentration effect of oligomers on excimer formation. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pinglu@zju.edu.cn (P.L.); orgwyg@zju.edu.cn (Y.W.). Fax: (+86) 571-87952543.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21272203; J1210042).

REFERENCES

(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−917.

(2) Xue, S.; Yao, L.; Shen, F.; Gu, C.; Wu, H.; Ma, Y. *Adv. Funct. Mater.* **2012**, *22*, 1092−1097.

(3) Cheng, G.; Li, F.; Duan, Y.; Feng, J.; Liu, S.; Qiu, S.; Lin, D.; Ma, Y.; Lee, S. T. *Appl. Phys. Lett.* **2003**, *82*, 4224−4226.

(4) Chen, C.-T. *Chem. Mater.* **2004**, *16*, 4389−4400.

(5) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539−541.

(6) Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. *Chem. Mater.* **2005**, *17*, 5032−5040.

(7) Kim, J.; Jin, Y.; Song, S.; Kim, S. H.; Park, S. H.; Lee, K.; Suh, H. *Macromolecules* **2008**, *41*, 8324−8331.

(8) Liddle, B. J.; Silva, R. M.; Morin, T. J.; Macedo, F. P.; Shukla, R.; Lindeman, S. V; Gardinier, J. R. *J. Org. Chem.* **2007**, *72*, 5637−5646.

(9) Hwang, G. T.; Son, H. S.; Ku, J. K.; Kim, B. H. *J. Am. Chem. Soc.* **2003**, *125*, 11241−11248.

(10) Ho, C.-L.; Chi, L.-C.; Hung, W.-Y.; Chen, W.-J.; Lin, Y.-C.; Wu, H.; Mondal, E.; Zhou, G.-J.; Wong, K.-T.; Wong, W.-Y. *J. Mater. Chem.* **2012**, *22*, 215−224.

(11) Park, S. H.; Jin, Y.; Kim, J. Y.; Kim, S. H.; Kim, J.; Suh, H.; Lee, K. *Adv. Funct. Mater.* **2007**, *17*, 3063−3068.

(12) Song, S.; Jin, Y.; Kim, K.; Kim, S. H.; Shim, Y. B.; Lee, K.; Suh, H. *Tetrahedron Lett.* **2008**, *49*, 3582−3587.

(13) Suh, H.; Jin, Y.; Park, S. H.; Kim, D.; Kim, J.; Kim, C.; Kim, J. Y.; Lee, K. *Macromolecules* **2005**, *38*, 6285−6289.

(14) Shi, J.; Wang, H.; Song, D.; Tian, H.; Geng, Y.; Yan, D. *Thin Solid Films* **2008**, *516*, 3270−3273.

(15) Hu, B.; Yao, C.; Huang, X. R. *Spectrosc. Lett.* **2012**, *45*, 17−21.

(16) Hung, H.-W.; Yokoyama, N.; Yahiro, M.; Adachi, C. *Thin Solid Films* **2008**, *516*, 8717−8720.

(17) Kwak, J.; Lyu, Y.-Y.; Noh, S.; Lee, H.; Park, M.; Choi, B.; Char, K.; Lee, C. *Thin Solid Films* **2012**, *520*, 7157−7163.

(18) Zhao, Z.; Li, J.-H.; Lu, P.; Yang, Y. *Adv. Funct. Mater.* **2007**, *17*, 2203−2210.

(19) Zhao, Z.; Li, J.-H.; Chen, X.; Wang, X.; Lu, P.; Yang, Y. *J. Org. Chem.* **2009**, *74*, 383−395.

(20) Zhao, Z.; Xu, X.; Wang, H.; Lu, P.; Yu, G.; Liu, Y. *J. Org. Chem.* **2008**, *73*, 594−602.

(21) Zhao, Z.; Zhao, Y.; Lu, P.; Tian, W. *J. Phys. Chem. C* **2007**, *111*, 6883−6888.

(22) Kim, H.-J.; Lee, E.; Park, H.; Lee, M. *J. Am. Chem. Soc.* **2007**, *129*, 10994−10995.

(23) Shirai, Y.; Osgood, A. J.; Zhao, Y.; Yao, Y.; Saudan, L.; Yang, H.; Yu-Hung, C.; Alemany, L. B.; Sasaki, T.; Morin, J.-F.; Guerrero, J. M.; Kelly, K. F.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 4854−4864.

(24) Nakamura, Y.; Yamazaki, T.; Nishimura, J. *Org. Lett.* **2005**, *7*, 3259−3262.

(25) MelHuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229−235.

(26) Miller, J. H. *Proc. Combust. Inst.* **2005**, *30*, 1381−1388.

(27) Wong, B. M.; Ye, S. H. *Phys. Rev. B* **2011**, *84*, 075115.