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Synthesis, Electrochemical and Optical Properties of Stable Yellow Fluorescent Fluoranthenes†

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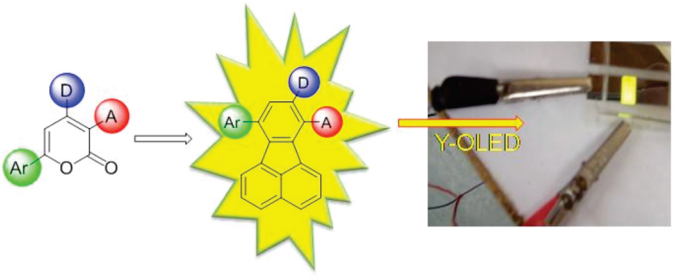

A novel series of thermally stable yellow light emitting fluoranthenes with an amine donor and a nitrile acceptor was prepared from a ketene-*S*,*S*-acetal under mild conditions without using an organometal catalyst. The organic light emitting device of yellow fluoranthene **10b** exhibited substantially low turn-on voltage (2.6 V) and maximum brightness of 470 Cd/m^2 with luminance efficiency of 2.0 Cd/A without using any dopant.

Introduction

Considering the growing importance of energy conservation, modernization, and miniaturization requirements, polymer light emitting diodes (PLEDs) and small molecule organic light emitting diodes (OLEDs) have generated amazing enthusiasm toward developing next generation electroluminescent (EL) material.[1] These multicolored illuminants have wide application ranging from flat surface displays to leading edge lighting technology, automobile industry, home appliances, and cell phone business.

To achieve high EL quantum efficiency, a doping approach is commonly employed. For example, in a typical yellow OLED configuration, the yellow-emitting layer is often fabricated by doping a yellow fluorophore such as rubrene.[2] However, the success of the doping technology requires selection of appropriate dopant and/or dopant concentration to avoid phase separation in a host−dopant system leading to ineffective energy transfer.[3] Therefore, novel nondoped illuminants with efficient electroluminescence are essentially in great demand.

Intense research has been focused on examining optical and electronic properties of 9,9-disubstituted fluorenes and polyfluorenes for developing OLEDs[4,5] (Figure 1, **I**−**III**); however, comparatively very little attention has been devoted to the closely related scaffold, fluoranthene (**IV**).

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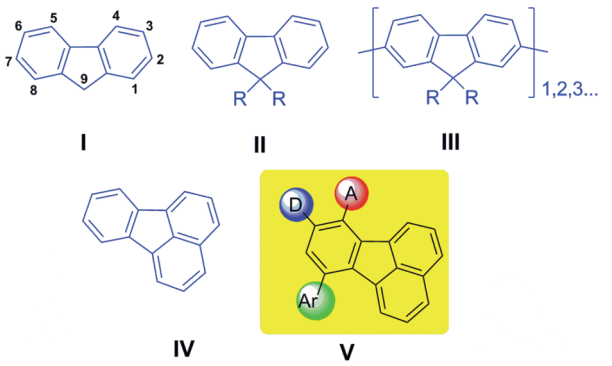

FIGURE 1. Fluorenes **I**−**III** and fluoranthenes **IV**−**V**.

Fluoranthenes possess interesting electronic and thermal properties[6] similar to those of fluorene with an advantage of having an oxidatively labile 9-methylene moiety of fluorene blocked by a 1,9-fused benzene ring. Recent reports on fluoranthene scaffold include fabrication of highly efficient blue OLEDs,[7,8] green OLEDs,[9] and fluoranthene-based matrix material[10] to improve charge-carrier transport. In this paper, we report a highly rapid novel approach for the synthesis of thermally stable donor−acceptor fluoranthenes (**V**) and their potential use in preparing economical, efficient non-doped yellow-OLED devices.

Few synthetic methodologies are available for the synthesis of fluoranthene derivatives, which mainly include the cycloaddition reaction of cyclopentadienone derivatives and alkynes or alkenes,[11,12] Suzuki−Heck reaction of 1-bromonaphthalene and 2-bromophenyl boronic acid,[13] reaction involving two triple bonds in 1,8-bis(phenylethynyl)naphthalene under thermal or photochemical conditions[14] or in the presence of metal catalysts[15] such as $RhCl_3$−Aliquat 336,[16] 1,4-palladium migration from 2-iodo-1-phenylnaphthalene,[17] reaction of propargylic alcohol bearing a fluorene moiety with diphenyl phosphine oxide,[18] or benzoannulation reactions of α-oxoketene dithioacetals with various Grignard reagents[19] or Pd-catalyzed electrocyclic reaction of a substituted acenaphthene.[20]

Recently we have shown that appropriately functionalized donor−acceptor quateraryls[21] and 9-unsubstituted fluorenes[22a] and fluorenones exhibited efficient, stable blue emission and demonstrated their potential application in developing blue OLEDs. We have demonstrated how the positioning of donor−acceptor groups onto the fluorene−fluorenone backbone transforms the green emission to blue emission.[22a] To investigate photophysical properties of fluoranthenes, a simple, general, and efficient synthetic route that could offer flexibility of diverse functional groups in their molecular framework was desirable. However, there is a paucity of literature protocols that could generate fluoranthene derivatives with donor−acceptor and various chromophoric functionalities in a rapid manner. Although numerous Diels−Alder reactions[23] of 2*H*-pyran-2-ones with electron-deficient and electron-rich dienophiles do provide annulated benzene derivatives, to the best of our knowledge, none has utilized the chemistry of 2*H*-pyran-2-ones for preparing fluoranthene scaffold. On the basis of retro-synthesis, we envisaged that the reaction of 2*H*-pyran-2-ones (**3** and **9**) with 2*H*-acenaphthylen-1-one (**4**) may furnish fluoranthene derivatives under mild conditions.

Results and Discussion

The reaction of methyl 2-carbomethoxy-3,3-bis(methylsulfanyl)acrylate[22] **1** with substituted acetophenones (**2a**−**e**) under alkaline conditions furnished substituted 2*H*-pyran-2-ones (**3a**−**e**) in excellent yields. Our approach to prepare substituted fluoranthenes **5a**−**e** involved stirring an equimolar mixture of **3a**−**e**, 2*H*-acenaphthylen-1-one (**4**) in the presence of NaH, and dry THF at room temperature for 35−90 min as shown in Scheme 1. The plausible reaction mechanism for the ring transformation of 2*H*-pyran-3-carboxylic acid methyl esters **3a**−**e** into fluoranthenes **5a**−**e** showed that the reaction is possibly initiated by Michael addition of a conjugate base of 2*H*-acenaphthylen-1-one (**4**) at position C6 of lactone **3**, followed by intramolecular cyclization involving the carbonyl functionality of **4** and C3 of the pyranone ring followed by elimination of carbon dioxide to yield **5a**−**e**.

To demonstrate the synthetic utility and scope of this methodology for regiospecific introduction of electron donor or acceptor functionalities, we explored the synthesis of fluoranthene derivatives with an amine donor and a nitrile acceptor substituent. An independent reaction of methyl 2-cyano-3,3-bis(dimethylsulfanyl)acrylate (**6**) with 1-acetylnaphthalene or

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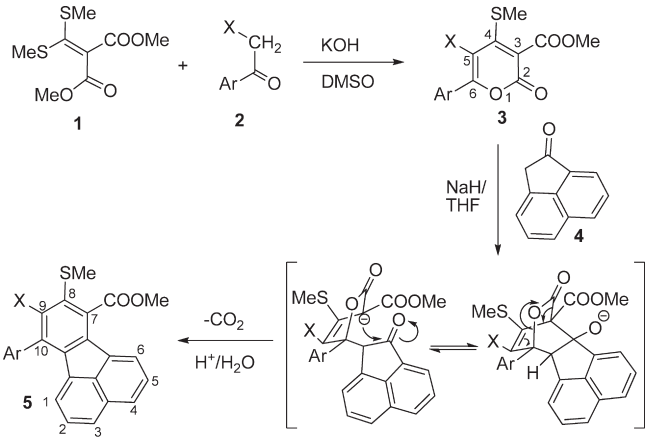
SCHEME 1. Synthesis of Fluoranthenes 5a−e



entry	Ar	X	reaction time (min)	yield (%)
5a	phenyl	H	45	70
5b	4-bromophenyl	H	40	65
5c	2-furyl	H	35	70
5d	2-thienyl	H	40	68
5e	phenyl	phenyl	90	60

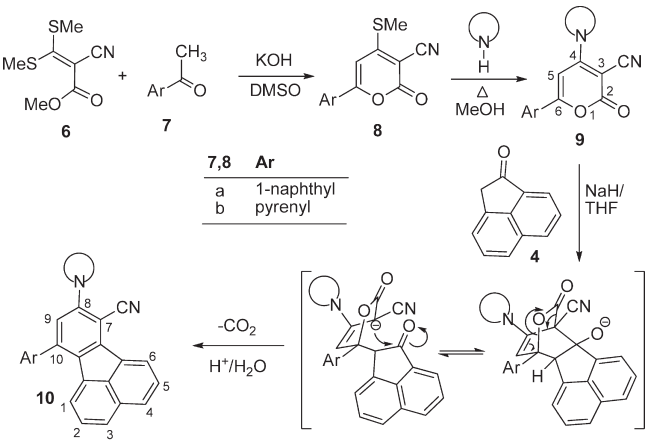
with 1-acetylpyrene was carried out to afford 6-aryl-3-cyano-4-methylsulfanyl-2*H*-pyran-2-ones (**8a**,**b**) in 80−90% yields. To prepare compounds with different donor functionalities, the methylsulfanyl group of lactones (**8a**,**b**) was replaced with various secondary amines such as piperidine or pyrrolidine to furnish 6-aryl-2-oxo-4-amin-1-yl-2*H*-pyran-3-carbonitriles (**9a**−**c**) in good yields. Further stirring an equimolar mixture of **9** and 2*H*-acenaphthylen-1-one (**4**) in the presence of NaH in THF for 12−15 min at room temperature yielded 10-aryl-8-(amin-1-yl)fluoranthene-7-carbonitriles **10a**−**c** in 82−85% yields (Scheme 2).

To generalize our methodology, an attempt was made to prepare 8-methylsulfanylacenaphtho[1,2-*j*]fluoranthene-7-carbonitrile (**12**). The parent precursor 10-methylsulfanyl-8-oxo-8*H*-7-oxa-fluoranthene-9-carbonitrile (**11**) was prepared by the reaction of **6** with 2*H*-acenaphthylen-1-one (**4**) at 0−5 °C under alkaline conditions in 70% yield (Scheme 3). The cyclic lactone **11** was reacted with 2*H*-acenaphthylen-1-one (**4**) in the presence of NaH in THF for 25 min and afforded 5-methylsulfanylacenaphtho[1,2-*j*]fluoranthene-4-carbonitrile (**12**) in 54% yield. It is worth mentioning that these polycyclic systems are not easy to synthesize by classical approaches.

Table 1 shows the λ_{max} of their UV and fluorescence spectral data, fluorescence quantum yield, HOMO/LUMO energy levels, and electrochemical band gap (Eop) of fluoranthenes **5a**−**e**, **10a**−**c**, and **12**. Figure 2 shows the UV−vis and PL spectra of fluoranthenes (**5a**, **5c**, and **10a**−**c**), respectively.

Unsubstituted fluoranthene exhibits PL maxima at two wavelengths (431 and 455 nm).[24] Fluoranthenes **5a**−**e** containing SMe and COOMe groups show PL in the range of 481−487 nm; however, when these groups were replaced

SCHEME 2. Synthesis of Fluoranthenes10a−c



entry	Ar	*sec*.amine	reaction time(min)	yield (%)
10a	1-naphthyl	pyrrolidine	12	82
10b	1-naphthyl	piperidine	13	85
10c	1-pyrenyl	piperidine	15	82

with an amine donor (piperidine/pyrrolidine) and a nitrile acceptor group respectively as in the case of fluoranthenes **10a**−**c** (λ_{PL} 549−552 nm), a remarkable red shift of nearly 70 nm was observed. These findings match the results demonstrated by Yamaguchi−Yoshida and co-workers.[25] By the modification of the donor groups at the terminal position of polycyano-oligo(phenyleneethylene) fluorophores, they found that the PL is more red-shifted in the presence of an amine functionality compared to the fluorophore having a methylsulfanyl group. Unsubstituted fluoranthene showed the quantum efficiency of about 20% in cyclohexane.[24] The quantum yields of synthesized fluoranthenes **5a**−**e** and **10a**−**c** are shown in Table 1, which revealed that the presence of the methylsulfanyl donor group at position 8 and the carbomethoxy acceptor group at position 9 of fluoranthenes **5a**−**e** showed low quantum efficiency (Φ = 1.8−5.1%) while fluoranthenes **10a**−**c** substituted with an amine donor and a nitrile acceptor group showed better quantum yields (Φ = 36−56%) compare to those of unsubstituted fluoranthene.

The electrochemical studies were carried out to ascertain the redox behavior of the fluoranthenes (**5a**−**e**, **10a**−**c**, and **12**). Cyclic voltammetric measurements were performed in a three-electrode cell setup with Ag/AgCl as the standard electrode and Pt disk as the working electrode, 2 mM of fluoranthenes, and 0.2 M of electrolyte tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in DMF. All the potentials were calibrated taking ferrocene as standard and the data are summarized in Table 1.

One irreversible oxidation and one reversible reduction peak were observed for all fluoranthenes as shown in Figure 3 (see the Supporting Information), which indicates that radical anions are stable entities but the radical cations (oxidized species) may react with the solvent DMF or supporting electrolyte. On close examination of CV graphs,

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SCHEME 3. Synthesis of Acenaphtho[1,2-*j*]fluoranthene-7-carbonitrile 12

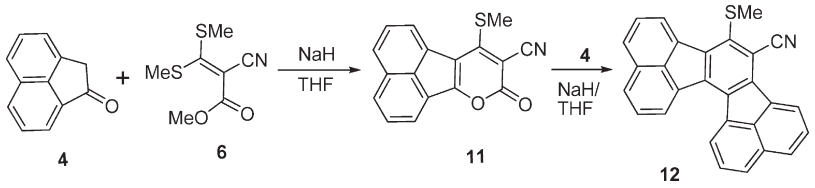

TABLE 1. Photophysical and Electrochemical Properties of Fluoranthenes 5a−e, 10a−c, and 12

entry	$\lambda_{max;abs}$[a] (nm)	$\lambda_{max;em}$[b] (nm)	Φ_f[c] (%)	HOMO (eV)	LUMO (eV)	E_{op}[d] (eV)
5a	319, 370	482	5.1	−5.69	−2.85	2.84
5b	314, 365	481	3.2	−5.72	−2.82	2.90
5c	313, 375	483	4.9	−5.72	−2.84	2.88
5d	311, 375	481	4.7	−5.70	−2.85	2.85
5e	298, 368	487	1.8	−5.67	−2.83	2.84
10a	338, 357*, 440	550	56	−5.27	−2.77	2.50
10b	331	552	36	−5.34	−2.85	2.49
10c	332	549	51	−5.51	−2.85	2.46
12	357	483	8.9	−5.77	−3.10	2.67

[a]Longest wavelength absorption maximum in THF (the asterisk indicates the shoulder peak). [b]Fluorescence emission maximum in THF. [c]Fluorescence quantum yield relative to harmine in 0.1 M H_2SO_4 as a standard (Φ = 0.45). [d]Optical band gap from CV.

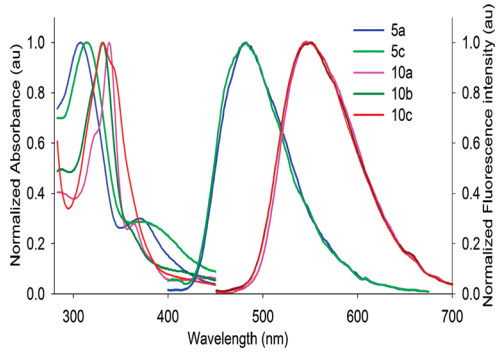

FIGURE 2. Absorbance and fluorescence spectra of fluoranthenes **5a**, **5c**, and **10a−c** in THF (~10^{-6} M).

we observed that incorporation of an amine donor and nitrile acceptor moieties decreases the oxidation potential of fluoranthenes (**10a−c**) with respect to fluoranthenes (**5a−e**). However, no change was observed in reduction potentials and hence the bandgap of fluoranthenes **10a−c** was found lower than that of fluoranthenes **5a−e**.

The thermal properties of fluoranthenes **10a−c** were gauged by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (see the Supporting Information). The TGA and DSC traces of **10b** are shown in Figure 4. Fluoranthenes **10a−c** exhibited good thermal stability. The TG thermogram of **10b** exhibited high thermal stability as evidenced by its TGA, with its 5% weight loss temperature under nitrogen atmosphere being up to 300 °C. The temperature corresponding to the complete weight loss of **10a**, **10b**, and **10c** was 600, 435, and 470 °C, respectively. DSC was performed in the temperature range from 30 to 340 °C under nitrogen atmosphere at the rate of 10 deg/min. Fluoranthenes **10a** and **10b** melted at 239 and

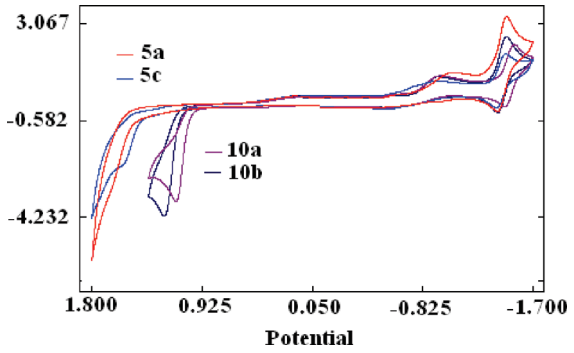

FIGURE 3. Cyclic voltammograms of **5a**, **5c** and **10a** and **10b** (in DMF).

206 °C respectively, while **10c** with a bulky pyrene group showed a higher melting temperature of 330 °C (see the Supporting Information).

On the basis of the above studies, fluoranthenes **10a−c** having an amine donor and a nitrile acceptor group were selected for further electroluminescent studies. Multilayer devices were fabricated to investigate the performance of yellow light-emitting fluoranthenes (**10a−c**) with the device configuration of ITO/PEDOT:PSS (40 nm)/NPB(20 nm) / fluoranthenes (60 nm)/BCP (8 nm)/Ca(3.2 nm)/Al (200 nm). The relative energy-level alignment of the fabricated multilayered OLEDs and actual device picture of **10b** are shown in Figure 5.

Figure 6 shows the ILV characteristics of **10a−c**. The "turn-on" voltage and luminances of the devices **10a**, **10b** (Figure 7), and **10c** were found to be 3 V (17.91 Cd/m^2), 2.6 V (5.0 Cd/m^2), and 3 V (7.65 Cd/m^2), respectively. The low "turn on" voltage suggests efficient charge injection into the emitting layer. The turn-on voltage of 2.6 V in the case of device **10b** is quite impressive. One of the important objectives of developing OLEDs is to reduce the operating voltage and current to drive these OLED displays with commercially available drivers of 5 V outputs. The low information content displays like 7-segment and general displays for signage have a large market. Luminance intensity of 381 Cd/m^2 at 5 V for compound **10b** is good enough for such applications (Figure 7). The devices of fluoranthenes **10a−c** exhibited maximum luminance of 410, 470, and 420 Cd/m^2, respectively.

The similarity of the photoluminescence (λ_{PL} 549−552 nm) and the electroluminescence (λ_{EL} 554−559 nm) spectra suggests that the EL was attributed to emission from the radiation decay of the excited state of fluoranthenes **10a−c**. To further evaluate the electrochemical stability of fluoranthenes (**10a−c**), the EL spectra of these fluoranthenes were recorded with an increase in applied voltage at an interval of 1 V (Figure 8). All the devices were found to be stable even

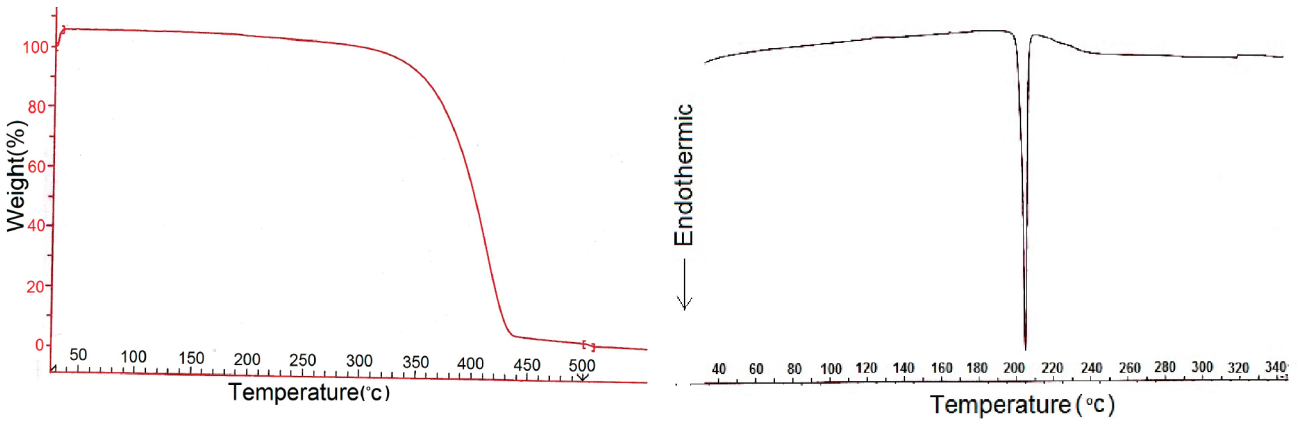

FIGURE 4. TGA and DSC plots of **10b** under N_2 atmosphere.

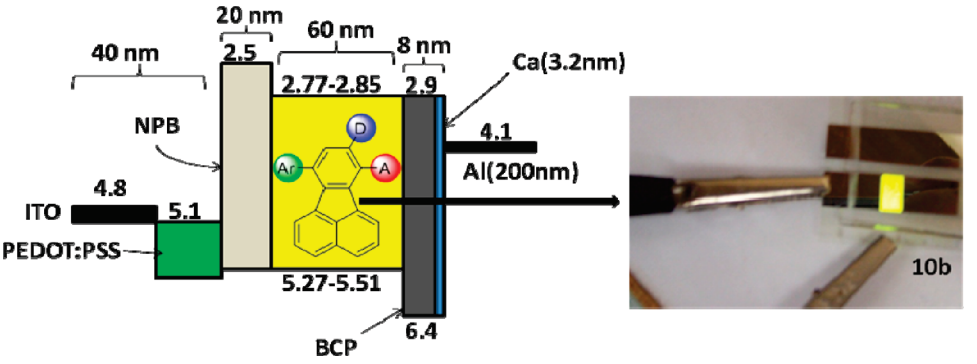

FIGURE 5. Relative energy-level alignment and layer thickness of **10a**−**c** OLEDs and actual device picture of fluoranthene **10b**.

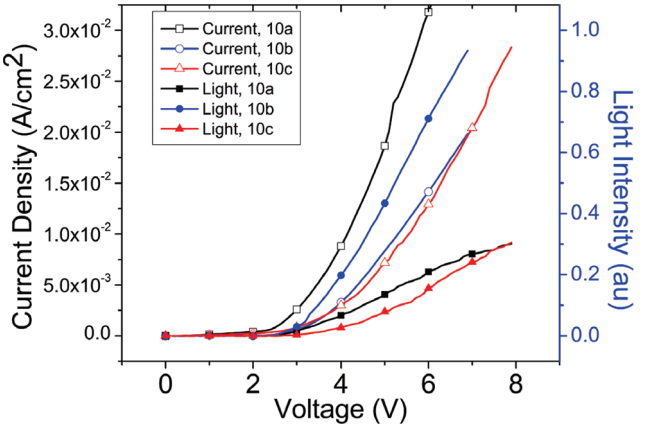

FIGURE 6. ILV characteristics of device of **10a**, **10b**, and **10c** respectively.

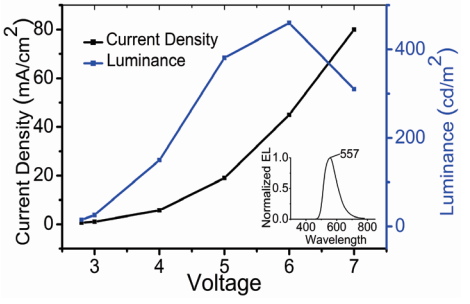

FIGURE 7. ILV characteristics (current density and luminance) of **10b** (insert: the EL spectrum).

under bias stress up to 9 V. Out of three OLEDs (**10a**−**c**), the device of **10b** was quite efficient with low turn-on voltage (2.6 V) and giving good luminance efficiency of 2.0 Cd/A (at 5 V) with a maximum luminance of 470 Cd/m^2.

In summary, we have demonstrated a novel approach for the synthesis of D/A fluoranthenes and acenaphtho[1,2-*j*]fluoranthene from ketene-*S*,*S*-acetals in excellent yields through carbanion-induced ring transformation of 2*H*-pyran-2-ones as a key step. Our methodology is simple and convenient and does not require any specialized organometal catalyst or reagents. We have successfully fabricated highly efficient nondoped fluoranthene-based yellow OLEDs, which exhibited bright yellow fluorescence, high quantum efficiency, and good thermal stability. One of the Y-OLEDs showed bright yellow emission with low turn-on voltage of 2.6 V and maximum brightness of 470 Cd/m^2 with luminance efficiency of 2.0 Cd/A (at 5 V) without using any dopant. The series of fluoranthenes **10a**−**c** demonstrating emission in the yellow region may solve the problem of dopant aggregation to a large extent. Owing to interesting photophysical, electrochemical, and thermal properties, these compounds may also find application for developing new yellow fluorescent molecular probes.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were taken at 200, 300, and 400 MHz, respectively. $CDCl_3$ was taken as the solvent.

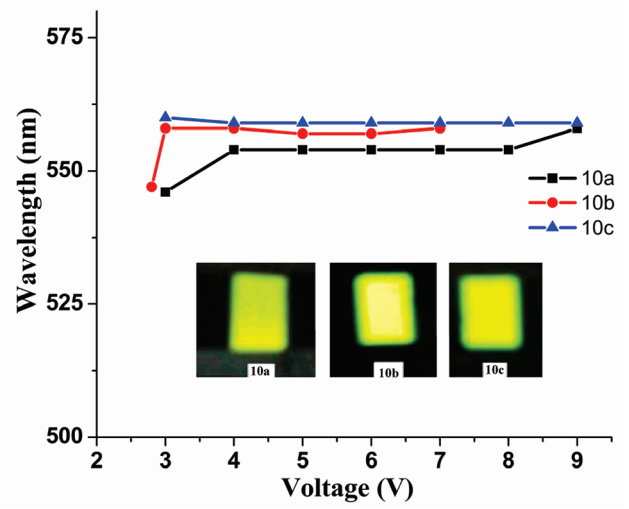

FIGURE 8. Electrochemical stability vs voltage curves and yellow OLEDs pictures of **10a**−**c**.

Chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^1H) or based on the middle peak of the solvent ($CDCl_3$) (δ 77.00 ppm for ^{13}C NMR) as an internal standard. Signal pattern are indicate as follows: s, singlet; d, doublet; dd, double doublet; t, triplet; and m, multiplet. Coupling constants (J) are given in hertz. Infrared (IR) spectra were recorded in KBr disk and reported in wavenumber (cm^{-1}). An ESIMS, EI spectrometer was used for mass spectra analysis. UV/vis spectra were obtained with THF as solvent of choice having a concentration of about 10^{-6} M. Fluorescence spectra were obtained with THF as solvent of choice, having a concentration of about 10^{-6} M. Melting points were measured with a melting point apparatus. Cyclic voltammetry was done with Ag/AgCl as the reference electrode. All the reactions were carried out under anhydrous conditions and were monitored by TLC; visualization was done with UV light (254 nm).

Synthesis of Methyl 8-(Methylsulfanyl)-10-phenylfluoranthene-7-carboxylate (5a). A mixture of **3a** (276 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (5 mL) was stirred at room temperature for 45 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 40% chloroform in hexane as the eluent to afford 267 mg (70%) of **5a** as a yellow solid. R_f 0.52 (1:1 chloroform−hexane); mp 210−212 °C; MS (EI) 382 (M^+); IR (KBr) 2922, 2853, 1724, 1595 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.55 (s, 3H), 4.15 (s, 3H), 7.14 (d, J = 6.9 Hz, 1H), 7.25 (s, 1H), 7.32−7.38 (m, 1H), 7.51−7.65 (m, 6H), 7.77 (d, J = 8.1 Hz, 1H), 7.83−7.89 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 18.1, 52.6, 122.6, 127.0, 127.7, 127.8, 128.2, 128.5, 128.7, 128.8, 129.0, 129.8, 132.9, 134.0, 134.4, 135.1, 136.7, 140.0, 140.2, 168.8; HRMS calcd for $C_{25}H_{18}O_2S$ 382.1028, found 382.1031.

Synthesis of Methyl 10-(4-Bromophenyl)-8-(methylsulfanyl)-fluoranthene-7-carboxylate (5b). A mixture of **3b** (355 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (5 mL) was stirred at room temperature for 40 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 40% chloroform in hexane as the eluent to afford 299 mg (65%) of **5b** as a yellow solid. R_f 0.54 (1:1 chloroform−hexane); mp 208−210 °C; MS (ESI) 461 (M^+ + 1), 463 (M^+ + 3); IR (KBr) 3060, 2942, 1724, 1656, 1586 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.55 (s, 3H), 4.15 (s, 3H), 7.15−7.20 (m, 2H), 7.36−7.49 (m, 3H), 7.59−7.72 (m, 3H), 7.79 (d, J = 8.1 Hz, 1H), 7.83−7.90 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 18.1, 52.7, 122.4, 122.7, 123.0, 127.2, 127.7, 127.9, 128.0, 128.7, 129.9, 130.6, 131.9, 132.8, 133.8, 134.6, 134.8, 134.9, 136.8, 138.7, 138.8, 168.7; HRMS (DART) calcd for $C_{25}H_{18}BrO_2S$ 461.01958, found 461.02109.

Synthesis of Methyl 10-(Furan-2-yl)-8-(methylsulfanyl)-fluoranthene-7-carboxylate (5c). A mixture of **3c** (266 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (5 mL) was stirred at room temperature for 35 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 45% chloroform in hexane as the eluent to afford 260 mg (70%) of **5c** as a yellow solid. R_f 0.48 (1:1 chloroform−hexane); mp 140−142 °C; MS (EI) 372 (M^+), 341 (M^+ − 31); IR (KBr) 3108, 3058, 2946, 1725, 1652, 1572 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 4.14 (s, 3H), 6.64−6.68 (m, 1H), 6.79−6.83 (m, 1H), 7.48 (s, 1H), 7.55 (t, J = 5.72 Hz, 1H), 7.62 (t, J = 5.72 Hz, 1H), 7.67−7.72 (m, 1H), 7.82−7.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 52.7, 109.5, 111.7, 122.5, 123.7, 127.4, 127.8, 127.9, 128.0, 128.4, 128.7, 129.5, 129.9, 132.9, 133.8, 134.4, 134.7, 135.2, 137.3, 142.5, 152.4, 168.7; HRMS calcd for $C_{23}H_{16}O_3S$ 372.0820, found 372.0817.

Synthesis of Methyl 8-(Methylsulfanyl)-10-(thiophen-2-yl)-fluoranthene-7-carboxylate (5d). A mixture of **3d** (282 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (5 mL) was stirred at room temperature for 40 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 40% chloroform in hexane as the eluent to afford 264 mg (68%) of **5d** as a yellow solid. R_f 0.51 (1:1 chloroform−hexane); mp 152−154 °C; MS (ESI) 388 (M^+), 357 (M^+ − 31); IR (KBr) 2941, 1724, 1658, 1631, 1574 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.56 (s, 3H), 4.15 (s, 3H), 7.21−7.25 (m, 1H), 7.31−7.36 (m, 2H), 7.38−7.46 (m, 2H), 7.50−7.54 (m, 1H), 7.58−7.66 (m, 1H), 7.79−7.91 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 18.1, 52.7, 122.7, 123.1, 126.3, 127.1, 127.3, 127.4, 127.8, 128.0, 129.1, 129.8, 130.0, 132.4, 132.8, 133.7, 134.4, 134.8, 136.3, 136.8, 140.4, 168.6; HRMS calcd for $C_{23}H_{16}O_2S_2$ 388.05917, found 388.06130.

Synthesis of Methyl 8-(Methylsulfanyl)-9,10-diphenylfluoranthene-7-carboxylate (5e). A mixture of **3e** (352 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (5 mL) was stirred at room temperature for 90 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 35% chloroform in hexane as the eluent to afford 275 mg (60%) of **5e** as a white solid. R_f 0.55 (1:1 chloroform−hexane); mp 254−256 °C; MS (EI) 458 (M^+); IR (KBr) 3054, 2997, 1728, 1635, 1555 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 3H), 4.18 (s, 3H), 6.51 (d, J = 7.1 Hz, 1H), 7.11−7.21 (m, 7H), 7.25−7.32 (m, 4H), 7.61−7.67 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.81−7.89 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.6, 52.7, 121.9, 123.9, 126.7, 127.1, 127.2, 127.3, 127.7, 127.9, 128.2, 129.6, 129.8, 130.4, 130.5, 133.0, 133.8, 134.3, 134.7, 135.5,

138.5, 138.8, 138.9, 139.6, 146.3, 169.1; HRMS calcd for $C_{31}H_{22}O_2S$ 458.1341, found 458.1337.

Synthesis of 10-(Naphthalen-1-yl)-8-(pyrrolidin-1-yl)fluoranthene-7-carbonitrile (10a). A mixture of **9a** (316 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (5 mL) was stirred at room temperature for 12 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 30% chloroform in hexane as the eluent to afford 346 mg (82%) of **10a** as a yellow solid. R_f 0.61 (1:1 chloroform−hexane); mp 236−238 °C; MS (ESI) 423 ($M^+ + 1$); IR (KBr) 2924, 2199, 1632, 1580 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.98−2.12 (m, 4H), 3.68−3.82 (m, 4H), 6.16 (d, J = 7.0 Hz, 1H), 6.61 (s, 1H), 7.02−7.09 (m, 1H), 7.27−7.33 (m, 1H), 7.45−7.71 (m, 6H), 7.86 (d, J = 8.1 Hz, 1H), 7.96−8.04 (m, 2H), 8.75 (d, J = 7.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.8, 50.6, 89.1, 114.9, 120.3, 121.2, 123.9, 125.2, 125.5, 126.0, 126.1, 126.2, 126.4, 127.4, 127.8, 127.9, 128.2, 128.4, 129.4, 131.4, 132.4, 133.5, 134.7, 134.8, 137.9, 141.3, 143.5, 150.2; HRMS calcd for $C_{31}H_{22}N_2$ 422.1783, found 422.1796.

Synthesis of 10-(Naphthalen-1-yl)-8-(piperidin-1-yl)fluoranthene-7-carbonitrile (10b). A mixture of **9b** (330 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (5 mL) was stirred at room temperature for 13 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 32% chloroform in hexane as the eluent to afford 370 mg (85%) of **10b** as a yellow solid. R_f 0.62 (1:1 chloroform−hexane); mp 206−208 °C; MS (ESI) 437 ($M^+ + 1$); IR (KBr) 2931, 2848, 2214, 1642, 1578 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.62−1.67 (m, 2H), 1.81−1.89 (m, 4H), 3.24−3.35 (m, 4H), 6.33 (d, J = 7.1 Hz, 1H), 6.95 (s, 1H), 7.10−7.15 (m, 1H), 7.26−7.34 (m, 1H), 7.48−7.76 (m, 6H), 7.91 (d, J = 8.1 Hz, 1H), 7.98−8.05 (m, 2H), 8.70 (d, J = 7.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 24.1, 26.2, 53.8, 99.4, 117.8, 119.6, 122.4, 123.6, 123.7, 125.5, 125.8, 126.1, 126.3, 126.5, 127.9, 128.0, 128.4, 128.6, 128.7, 129.6, 131.3, 131.8, 132.8, 133.6, 134.1, 134.5, 137.5, 141.1, 143.0, 156.3; HRMS calcd for $C_{32}H_{24}N_2$ 436.1940, found 436.1943.

Synthesis of 8-(Piperidin-1-yl)-10-(pyren-1-yl)fluoranthene-7-carbonitrile (10c). A mixture of **9c** (406 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (5 mL) was stirred at room temperature for 15 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 30% chloroform in hexane as the eluent to afford 420 mg (82%) of **10c** as a yellow solid. R_f 0.62 (1:1 chloroform−hexane); mp >250 °C; MS (ESI) 513 ($M^+ + 1$); IR (KBr) 2936, 2850, 2215, 1632, 1581 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.61−1.68 (m, 2H), 1.83−1.91 (m, 4H), 3.25−3.35 (m, 4H), 6.15 (d, J = 7.1 Hz, 1H), 6.95−7.01 (m, 1H), 7.04 (s, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.71−7.77 (m, 1H), 7.84−7.93 (m, 3H), 8.03−8.28 (m, 6H), 8.34 (d, J = 7.8 Hz, 1H), 8.74 (d, J = 7.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 24.1, 26.2, 53.8, 99.4, 117.9, 120.0, 122.4, 123.7, 124.7, 124.8, 124.9, 125.0, 125.4, 125.5, 126.2, 126.3, 126.7, 127.4, 127.9, 127.9, 128.0, 128.1, 128.7, 129.6, 131.0, 131.4, 132.0, 132.8, 134.1, 134.5, 134.8, 141.5, 143.1, 156.3.

Synthesis of 10-(Methylsulfanyl)-8-oxo-8*H*-7-oxa-fluoranthene-9-carbonitrile (11). A mixture of methyl 2-cyano-3,3-bis-(methylsulfanyl)acrylate **6** (203 mg, 1 mmol, 1 equiv), 2*H*-acenaphthylen-1-one **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil, 48 mg, 1.2 mmol, 1.2 equiv) in dry THF (6 mL) was stirred at 0−5 °C for 30−35 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring. The precipitate obtained was filtered and purified on silica gel column with chloroform as the eluent to afford 203 mg (70%) of **11** as an orange solid. R_f 0.35 (chloroform); mp 220−222 °C; MS (EI^+) 291 (M^+); IR (KBr) 2817, 2217, 1695, 1595, 1528 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.14 (s, 3H), 7.67−7.79 (m, 2H), 7.94 (d, J = 8.3 Hz, 1H), 8.11−8.13 (m, 2H), 8.26 (d, J = 7.08 Hz, 1H); HRMS calcd for $C_{17}H_9NO_2S$ 291.0354, found 291.0354.

Synthesis of 8-(Methylsulfany)acenaphtho[1,2-*j*]fluoranthene-7-carbonitrile (12). A mixture of **11** (291 mg, 1 mmol, 1 equiv), compound **4** (168 mg, 1 mmol, 1 equiv), and NaH (60% dispersion in oil 60 mg, 1.5 mmol, 1.5 equiv) in dry THF (6 mL) was stirred at room temperature for 25 min. The progress of the reaction was monitored by TLC and on completion solvent was evaporated and the reaction mixture was poured onto crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column with 20% chloroform in hexane as the eluent to afford 214 mg (54%) of **12** as a yellow solid. R_f 0.71 (1:1 chloroform−hexane); mp > 250 °C; MS (ESI) 398 ($M^+ + 1$); IR (KBr) 2964, 2229, 1633, 1426 cm^{-1}; ^1H NMR (300 Hz, $CDCl_3$) δ 2.62 (s, 3H), 7.67−7.79 (m, 4H), 7.89−7.99 (m, 4H), 8.55−8.61 (m, 2H), 8.65 (d, J = 7.2 Hz, 1H), 8.95 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.9, 111.4, 117.9, 124.0, 125.2, 125.6, 126.2, 128.1, 128.3, 128.6, 128.7, 128.8, 129.1, 130.3, 133.6, 133.7, 133.9, 134.1, 134.6, 135.2, 135.8, 136.0, 139.1, 141.9; HRMS calcd for $C_{28}H_{15}NS$ 397.0925, found 397.0919.

Experimental Device. Multilayer devices were fabricated to investigate the performance of yellow light-emitting materials (**10a**, **10b**, and **10c**) with the device configuration of ITO/PEDOT:PSS (40 nm)/NPB(20 nm)/fluoranthenes (60 nm)/BCP (8 nm)/Ca(3.2 nm)/Al (200 nm). The patterned ITO glass plate was cleaned in 6:1:1 in RCA-I solution, rinsed in DI water a number of times, and then dried. The ITO surface was treated in ozone for 15 min. Immediately, the first layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) was spin-coated on patterned ITO to form a hole injection layer. The PEDOT-PSS was vacuum dried at 120 °C for 1 h. All other organic layers and metal layers were sublimed in high vacuum (~$1-5 \times 10^{-6}$ mbar). Then devices were sealed with a covering glass plate with UV epoxy. The ILV characteristics of sealed OLED devices were obtained by using Keithley source-measure unit. EL spectra were recorded with an optic spectrometer.

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Supporting Information Available: ^1H and ^{13}C NMR spectra, UV−vis and fluorescence spectra, DSC, TGA, cyclic voltammograms and device efficiency graph for the compounds **5a−e**, **10a−c**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.