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Thermally Stable Nonaggregating Pyrenylarenes for Blue Organic Light-Emitting Devices[†,⊥]

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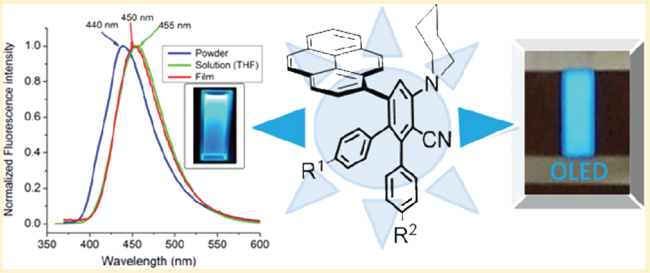
Supporting Information

ABSTRACT: A new series of thermally stable blue light-emitting nonplanar pyrenylarenes having an amine donor and a nitrile acceptor group was prepared from a ketene-*S*,*S*-acetal under conventional heating and/or microwave irradiation. The photophysical, electrochemical, and optical behavior of donor−acceptor pyrenylarenes are demonstrated. The performance of blue light-emitting pyrenylarenes was investigated by fabricating a multilayer device with the device configuration of ITO/PEDOT:PSS (40 nm)/NPB (30 nm)/pyrenylarene (55 nm)/BCP (8 nm)/LiF (0.6 nm)/Al (200 nm), which exhibited low turn-on voltage (5 V) with luminance efficiency of 0.8 Cd/A with nonaggregation behavior in both solution and solid state.



INTRODUCTION

Pyrene belongs to the class of polycyclic aromatic hydrocarbons (PAHs), which by virtue of their interesting photophysical[1] and electrochemical[2] properties have been widely used in many applications such as molecular probes,[3] fluorescent sensors,[4] liquid crystalline materials,[5] and supramolecular self-assembly[6] and in carbon nanotube functionalization.[7] Pyrene-containing receptors for transition metal ions were also reported as a versatile class of photoactive supramolecular systems.[8] Recently, pyrene derivatives have been developed as hole-transporting materials or host blue-emitting materials in organic light-emitting diodes (OLEDs).[9] However, the use of pyrenes as emitters in OLEDs is limited because pyrenes easily form π-aggregates, leading to excimer emission with low quantum efficiency.[10] Thus, there is substantial interest[10d] in design and synthesis of new pyrene-based blue light-emitting molecules which have no aggregating behavior in the solid state.

In order to prevent aggregation, we designed a new series of thermally stable pyrenylarenes as blue emissive materials, in which the pyrene ring is attached with a nonplanar teraryl moiety having a donor and an acceptor group to tune the electron−hole combination efficiency. We surmised that the sterically congested teraryl ring at position 1 of pyrene would lie perpendicular to the plane of the core pyrene ring to prevent undesirable face-to-face π-stacking, so that self-quenching may be prevented to permit efficient emission in solution and the solid state.

The most common procedure for aryl/aryl couplings at position 1 of pyrene is the Gomberg reaction of diazonium arenes with pyrene.[11] The products obtained in low yields are accompanied by regioisomers. Suzuki cross-coupling reactions,[12] being presently the most efficient and widely applicable aryl/aryl bond-forming reactions, have been employed as the key reaction for the coupling of pyrene with substituted aryl partners in low yields.[13]

Over the past decade, our group is involved in developing new methodologies for preparing arenes and heteroarenes of biological and material importance. We recently developed a new methodology[14] for the synthesis of functionalized fluoranthenes and demonstrated that donor−acceptor fluoranthenes are potential candidates for developing yellow organic light-emitting diodes. We have also shown that appropriately functionalized donor−acceptor quateraryls[15] and 9-unsubstituted fluorenes and fluorenones exhibited efficient, stable blue emission and demonstrated their potential application in developing efficient blue OLEDs.[16] We have revealed how the positioning of donor−acceptor groups onto the fluorene-fluorenone backbone transforms the green emission to blue emission.[16] In order to investigate photophysical and optical properties of pyrenylarenes, a simple, general, and efficient synthetic route that could offer flexibility of substituent variations in their molecular framework was desirable. Herein, we report a suitable protocol for generating a variety of pyrenylarene derivatives with donor−acceptor and various chromophoric functionalities in a

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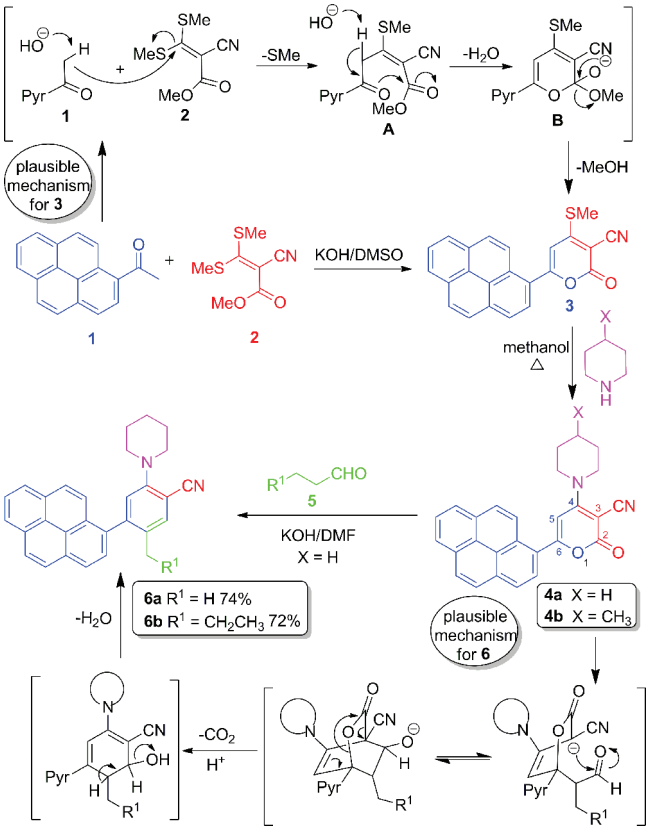
rapid manner and further explore their nonaggregating behavior for potential use in blue OLEDs.

RESULTS AND DISCUSSION

Synthesis. The designed pyrenylarene compounds for blue light-emitting applications were synthesized by preparing a key intermediate α-oxo-ketene-*S*,*S*-acetal[17] **2** from easily accessible precursors methyl cyanoacetate, carbon disulfide, and methyl iodide, following the Tominaga protocol.[18] Substrate **2**, upon Michael addition−cyclization reaction with 1-(pyren-1-yl)ethanone **1** under alkaline conditions, furnished 4-(methylthio)-2-oxo-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile **3** in excellent yield (Scheme 1). In order to prepare compounds with a donor (*N*,*N*-dialkylamine) functionality, a good leaving methylsulfanyl group of lactone **3** was replaced with an amine (piperidine/4-methylpiperidine) to furnish 2-oxo-4-(piperidin-1-yl/4-methylpiperidin-1-yl)-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (**4a**,**b**) in quantitative yields. To prepare pyrenylarenes with substituents particularly at the ortho position around the biaryl axis to inhibit $\pi-\pi$ overlapping, an equimolar mixture of **4a** was reacted with aliphatic aldehydes **5a**,**b** in the presence of KOH and DMF at room temperature for 12−14 h to furnish pyrenylarenes **6a**,**b** as shown in Scheme 1.

Scheme 1. Synthesis of Pyrenes 6a,b



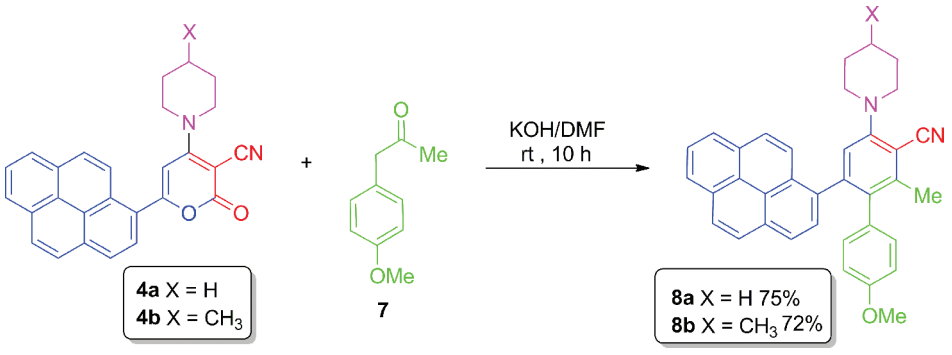
To demonstrate the synthetic utility and scope of this methodology for preparing functionally hindered pyrenylarenes, a reaction of 2-oxo-4-(piperidin-1-yl/4-methylpiperidin-1-yl)-6-(pyren-1-yl)-2*H*-pyran-3-carbonitriles (**4a**,**b**) with 1-(4-methoxyphenyl)propan-2-one **7** was carried out, which afforded substituted pyrenes **8a**,**b** in good yields (Scheme 2).

To generalize this methodology further for furnishing functionally congested pyrenes, an independent reaction of **4a** with functionalized deoxybenzoin **9a**−**d** was carried out to afford **10a**−**d** at room temperature (Scheme 3). The ring transformation reaction proceeded slowly, yielding 65−76% of desired product after 15−17 h (Table 1). In order to optimize the reaction conditions, these reactions were performed under conventional heating as well as under microwave irradiation at 100 °C using an internal probe.

When the reactions were carried out under conventional heating at 100 °C, the reaction time was reduced from 17 to 1 h and yields were comparable to that obtained at room temperature (Table 2). Longer reaction time or higher temperature did not show any further improvement. Therefore, microwave-assisted methodology was attempted and compared with the conventional heating protocol using the same reagents and solvent (Table 2). Notably, the reaction time was significantly reduced from 17 h (at room temperature condition) to 1 h (under conventional heating) and further to 10 min (under microwave irradiation) without compromising the yields. The cycloaddition reactions between 2*H*-pyran-2-ones as a diene and alkene or alkyne as a dienophile under microwave conditions generally lead to a mixture of endo/exo products or a mixture of product with unreacted starting material. However for the first time, we report the reaction of 2*H*-pyran-2-one with a methylene carbonyl compound under microwave condition to afford a single aromatic compound in good yield.

Studies of Photophysical, Optical, and Electrochemical Properties. The optical, thermal, and electrochemical properties of these pyrenylarenes in dilute solutions and in the solid state

Scheme 2. Synthesis of Pyrenes 8a,b



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Scheme 3. Synthesis of Pyrenes 10a−d

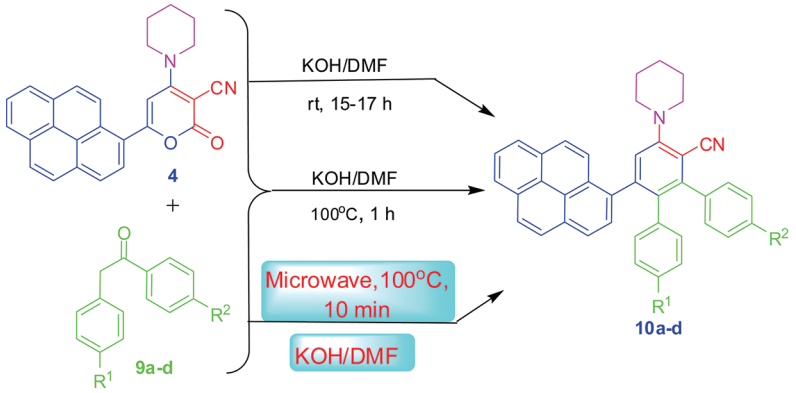

Table 1. Synthesis of 10a−d at Room Temperature

entry	R^1	R^2	reaction time (h)	yield (%)
10a	H	H	16	70
10b	H	OMe	15	72
10c	OMe	OMe	15	74
10d	phenyl	OMe	17	68

Table 2. Synthesis of 10a−d under Conventional Heating or Microwave Irradiation

			reaction time (min)		yield (%)	
entry	R^1	R^2	Δ	μW	Δ	μW
10a	H	H	60	10	72	70
10b	H	OMe	60	10	75	74
10c	OMe	OMe	60	10	76	75
10d	phenyl	OMe	60	10	68	65

were investigated. The electronic absorbance maxima (λ_{max}), emission maxima (λ_{max}), the fluorescence quantum yield, HOMO/LUMO energy levels, and electrochemical band gap (E_{op}) for all pyrene derivatives **6a,b**, **8a,b**, and **10a−d** are summarized in Table 3.

The UV−vis absorption and photoluminance (PL) spectra of some of the representative pyrenylarenes **6b**, **8a**, and **10c** are shown in Figure 1. The absorption spectra of all pyrenylarenes revealed a vibronic feature that was characteristic for unsubstituted parent pyrene with a short wavelength absorption maximum at 277−279 nm.[1] The long wavelength absorption maxima for all pyrenylarenes (**6a,b**, **8a,b**, and **10a−d**) occur at 344−347 nm. Upon excitation at 350 nm, all pyrenylarenes showed blue emission characteristics with the emission maxima in the range of 445−456 nm with quantum yields up to 76% as shown in Table 3. The full-width at half-maximum (fwhm) for each individual emission was observed in the range from 62 to 70 nm.

Unsubstituted pyrene shows PL_{max} at 393 nm,[10c] while the donor−acceptor pyrenylarenes **6a,b**, **8a,b**, and **10a−d** showed a PL emission maximum in the range of 445−456 nm. At a concentration of 10^{-4} M and above, unsubstituted pyrene shows excimer emission with stable steric configuration leading to

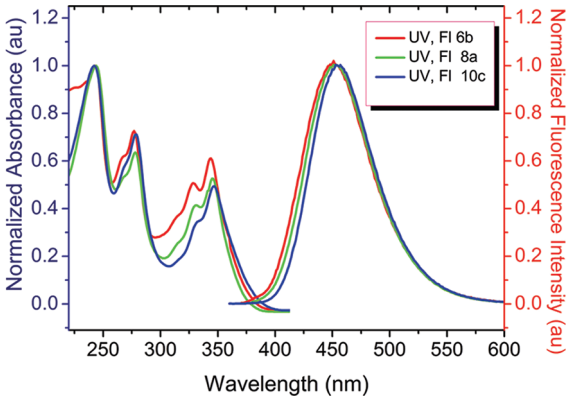

Figure 1. Absorbance and fluorescence spectra of pyrenes **6b**, **8a**, and **10c** in THF (~10^{-6} M).

an additional low intensity broad band in the vicinity of 470 nm.[19] In order to evaluate the behavior of synthesized pyrenylarenes (**6a,b**, **8a,b**, and **10a−d**) at different concentrations, we examined the concentration effect of **10c** with respect to fluorescence emission in dry THF. By increasing the concentration from 10^{-6} M to 10^{-3} M (Figure 2), the intensity of PL band increased gradually up to the concentration of 10^{-4} M and then reduced at 10^{-3} M. Importantly, in all concentrations, the emission corresponded only to the monomer at 454−456 nm (Figure 2). No red shift or additional peak of excimer formation was observed in pyrenylarene **10c**.

The solid-state fluorescence of **10c** was further examined using both powder and a thin film prepared by vacuum evaporation on glass substrate (Figure 3). The thin film on the glass substrate was continuous and exhibited emission at 450 nm. The powder of **10c** exhibited strong blue emission with a maximum peak at 440 nm as shown in Figure 3 (for other compounds, see the Supporting Information), which was 10 nm blue-shifted from the emission maxima of the thin film (Figure 3). In comparison to the emission spectra in the dilute solution, the solid-state emission was slightly blue-shifted, which confirmed that indeed there is no excimer formation in the solid state.

The electrochemical studies were carried out to ascertain the redox behavior of the pyrenes (**6a,b**, **8a,b**, and **10a−d**). Cyclic voltammetric measurements were performed in a three-electrode cell setup using Ag/AgCl as standard electrode and Pt disk as the

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Table 3. Optical and Electrochemical Properties of Pyrenes 6a,b, 8a,b, and 10a−d

entry	$\lambda_{max;\ abs}$ [a] (nm)	$\lambda_{max;\ em}$ [b] (nm)	Φ_f [d] (%)	HOMO (eV)	LUMO (eV)	E_{op} [e] (eV)
6a	277, 344	456 (70)[c]	68	−5.50	−2.68	2.82
6b	277, 344	448 (68)[c]	65	−5.49	−2.64	2.85
8a	278, 345	451 (67)[c]	71	−5.51	−2.70	2.81
8b	278, 345	452 (65)[c]	69	−5.53	−2.74	2.79
10a	279, 346	445 (62)[c]	70	−5.54	−2.72	2.82
10b	279, 346	446 (63)[c]	72	−5.56	−2.70	2.86
10c	279, 347	455 (65)[c]	76	−5.50	−2.68	2.82
10d	278, 347	450 (62)[c]	73	−5.50	−2.74	2.76

[a] Longest wavelength absorption maximum in THF. [b] Fluorescence emission maximum in THF. [c] Full-width at half-maximum (fwhm). [d] Fluorescence quantum yield relative to harmine in 0.1 M H_2SO_4 as a standard (Φ = 0.45). [e] Optical band gap from CV.

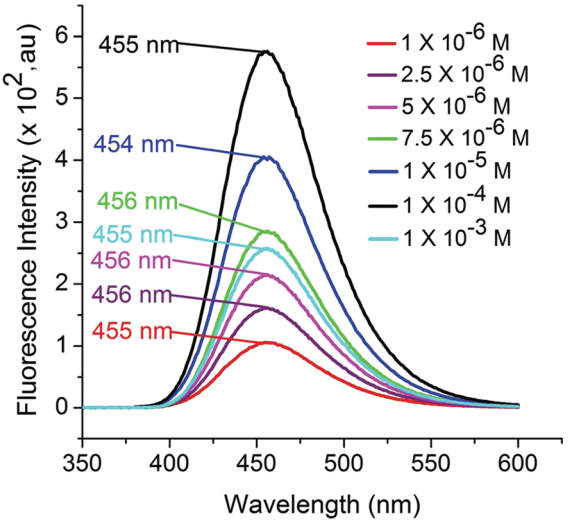

Figure 2. Effect of concentration on the fluorescence emission spectrum of **10c** in THF.

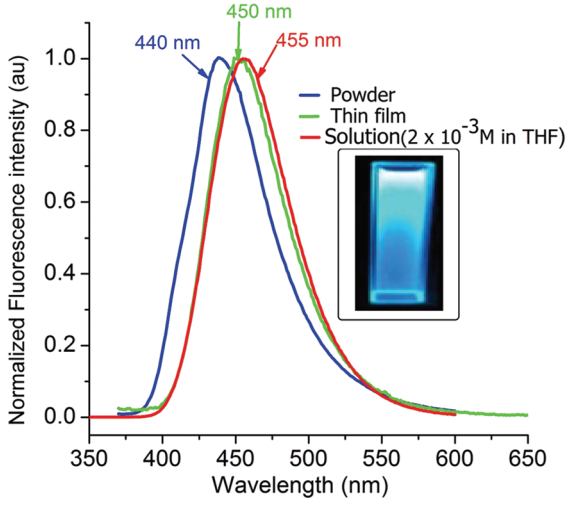

Figure 3. PL spectrum of compound **10c** in solution (in THF) and in solid-state (powder and the thin film). The inset shows photograph of the blue emission from **10c** in THF.

working electrode, using 2 mM pyrenylarene and 0.2 M electrolyte tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved

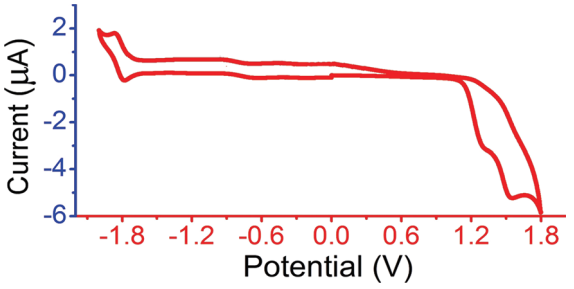

Figure 4. Cyclic voltammogram of **10c** in DMF under N_2 atmosphere.

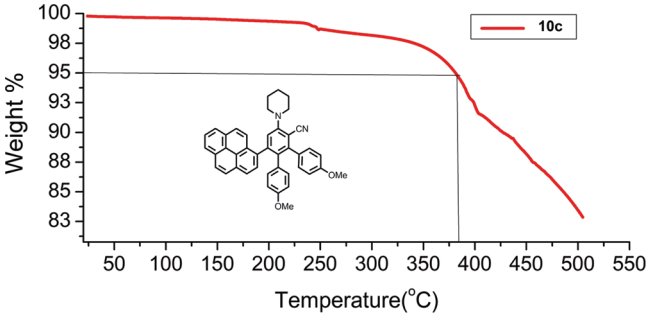

Figure 5. TGA plot of **10c** under N_2 atmosphere.

in DMF. All the potentials were calibrated with ferrocene, and the data are summarized in Table 3.

Two irreversible oxidation and one reversible reduction peak were observed for pyrenylarenes **10a**−**d** as exemplary shown for **10c** in Figure 4 (for **10a**,**b**,**d**, see Supporting Information), which indicates that radical anions are stable entities but the radical cations (oxidized species) may react with the solvent DMF or the supporting electrolyte. The HOMO and LUMO levels were calculated by using onset of first oxidation and reduction peak. The results are presented in Table 3. The calculated HOMO values are in the range of −5.49 to −5.56 eV, indicating that these materials are suitable for application in OLEDs.

The thermal properties of selected pyrenylarenes **6b**, **8a**, and **10c** were gauged by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (see Supporting Information). Pyrenylarene **10c** exhibited high thermal stability as demonstrated by its TGA (Figure 5), with its 5% weight loss temperature under nitrogen atmosphere being up to 370 °C. The DSC results of **6b**, **8a**, and **10c** are shown in Figure 6. DSC was

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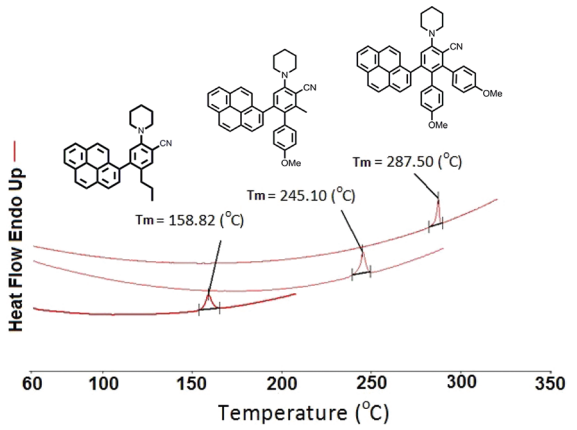

Figure 6. DSC plots of **6b**, **8a**, and **10c** under N_2 atmosphere.

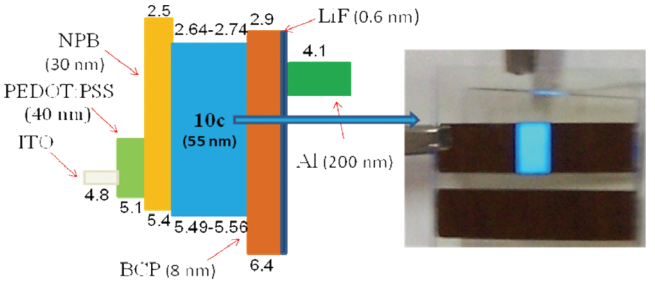

Figure 7. Relative energy-level alignment and layer thickness of OLED **10c** and actual device picture of **10c**.

performed in the temperature range from 50 °C to 350 °C. DSC analysis indicates that there was no phase transformation of **6b**, **8a**, and **10c** before the samples completely melted. Figure 6 display the DSC curve of **6b**, **8a**, and **10c**. Pyrene **6b** and **8b** melted at 159 °C and 245 °C, respectively, while **10c** with a higher molecular weight showed a higher melting temperature of 287 °C.

OLED Device Performance. On the basis of photophysical, optical, and electrochemical studies, pyrenylarene **10c** was selected for further studies to demonstrate the application in preparing a organic light-emitting device. A multilayer device was fabricated to investigate the performance of blue light-emitting pyrene **10c** with the device configuration of ITO/PEDOT:PSS (40 nm)/NPB (30 nm)/pyrenylarene (55 nm)/BCP (8 nm)/LiF (0.6 nm)/Al (200 nm). The relative energy-level alignment of the fabricated multilayered OLED and actual device picture of **10c** are shown in Figure 7.

Figure 8 shows the *I*−*L*−*V* characteristics and EL spectrum of **10c** as inset. The EL spectrum of device **10c** showed a band at 465 nm, which was slightly red-shifted relative to PL in solution (455 nm). To further evaluate the electrochemical stability of pyrenylarene **10c**, the EL characteristics of **10c** was recorded with an increase in applied voltage at an interval of 1 V (Figure 9). The device of **10c** was found to be stable even under bias stress up to 9 V. The device of **10c** was quite efficient with low turn-on voltage (5 V) and exhibiting good luminance efficiency of 0.8 Cd/A (Figure 9).

In conclusion, we have developed an efficient method for the preparation of pyrenylarenes with a variety of donor−acceptor and chromophoric substituents from easily accessible ketene-*S*,

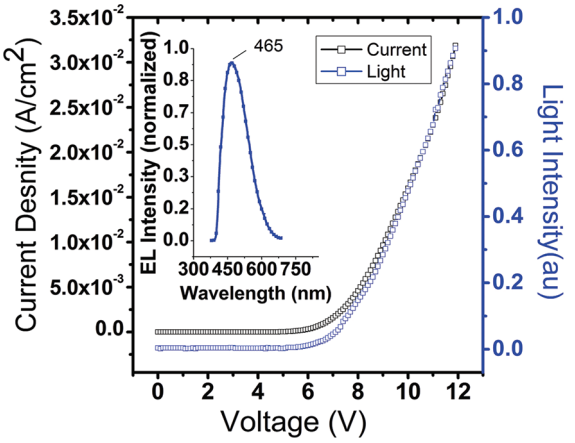

Figure 8. *I*−*L*−*V* characteristics of device of **10c** (insert shows the EL spectrum).

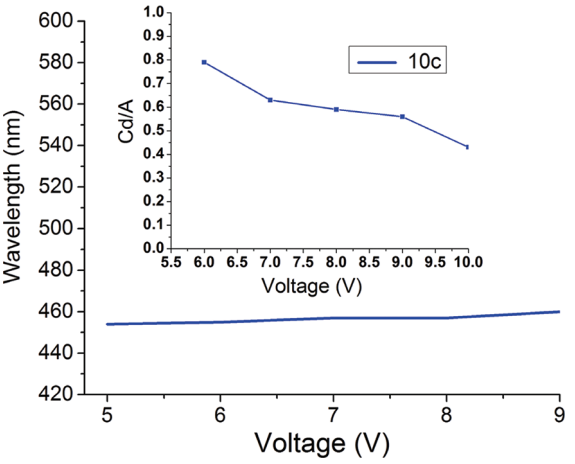

Figure 9. Electrochemical stability vs voltage curves of **10c**. Insert shows the luminance efficiency vs voltage curve of **10c**.

S-acetals in good yields. For the first time, we successfully demonstrated microwave-assisted carbanion-induced ring transformation of 2*H*-pyran-2-ones into a benzene ring under mild reaction conditions in a short time. Our methodology is operationally simple and convenient and does not require any specialized organometal catalyst or reagents. In addition, we have uncovered the photophysical, optical, and electrochemical properties of these interesting nonaggregating and thermally stable blue pyrenylarenes and demonstrated their potential use in preparing high demanding blue OLEDs.

EXPERIMENTAL SECTION

Synthesis of 4-(Methylsulfanyl)-2-oxo-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (3). A mixture of methyl 2-cyano-3,3-dimethylsulfanylacrylate (**2**, 203 mg, 1 mmol), 1-(pyren-1-yl)ethanone (**1**, 293 mg, 1.2 mmol), and powdered KOH (67 mg, 1.2 mmol) in dry DMSO (6 mL) was stirred at room temperature for 12 h. After completion, the reaction mixture was poured into ice−water with constant stirring. The precipitate thus obtained was filtered and purified on a silica gel column using chloroform as the eluent to afford **3** (323 mg, 88%) as a yellow solid: R_f = 0.55 (*n*-hexane/ethyl acetate, 6:4, v/v); mp (chloroform) > 250 °C; MS (ESI^+) 368 [M + H^+]; IR (KBr) ν = 2223 (s), 1723 (s),

1589 (s) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6 at 50 °C): δ = 2.84 (s, 3H), 7.21 (s, 1H), 8.17 (t, J = 7.6 Hz, 1H), 8.28 (d, J = 8.7 Hz, 1H), 8.34−8.44 (m, 6H), 8.58 (d, J = 9.6 Hz, 1H) ppm; HRMS calculated for $C_{23}H_{14}NO_2S$ (M^+ + H) 368.07452, found: 368.07367.

General Procedure for the Synthesis of 4a,b. A mixture of 4-(methylsulfanyl)-2-oxo-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (**3**, 367 mg, 1 mmol) and piperidine or 4-methylpiperidine (1.2 mmol) in methanol was refluxed for 6−7 h, the reaction mixture was cooled to room temperature, and the solid obtained was filtered to furnish 2-oxo-4-(piperidin-1-yl/4-methylpiperidin-1-yl)-6-(pyren-1-yl)-2*H*-pyran-3-carbonitriles **4a,b** in 92−94% yields, respectively.

Synthesis of 4-(Piperidin-1-yl)-2-oxo-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (4a). White solid; R_f = 0.40 (*n*-hexane/ethyl acetate, 6:4, v/v); mp (chloroform/methanol) 256−258 °C; MS (FAB) 405 (M^+ + 1); IR (KBr) ν = 2198 (s), 1690 (s), 1628 (s), 1531 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 1.79−1.83 (m, 6H), 3.85−3.88 (m, 4H), 6.48 (s, 1H), 8.00−8.10 (m, 2H), 8.11−8.19 (m, 4H), 8.21−8.27 (m, 2H), 8.39 (d, J = 9.3 Hz, 1H) ppm; HRMS calculated for $C_{27}H_{21}N_2O_2$ (M^+ + H) 405.16030, found: 405.16133.

Synthesis of 4-(4-Methylpiperidin-1-yl)-2-oxo-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (4b). White solid; R_f = 0.42 (*n*-hexane/ethyl acetate, 6:4, v/v); mp (chloroform/methanol) > 250 °C; MS (ESI^+) 419 [M + H^+]; IR (KBr) ν = 2201 (s), 1690 (s), 1631 (s), 1529 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 (d, J = 6.06 Hz, 3H), 1.32−1.48 (m, 2H), 1.74−1.96 (m, 3H), 3.21−3.36 (m, 2H), 4.36−4.48 (m, 2H), 6.46 (s, 1H), 7.98−8.28 (m, 8H), 8.40 (d, J = 9.3 Hz, 1H) ppm; ^{13}C NMR (75 MHz, DMSO d_6): δ = 21.1, 29.7, 34.1, 49.6, 70.2, 101.3, 117.8, 123.4, 123.7, 123.9, 124.7, 126.1, 126.4, 126.5, 126.8, 127.1, 127.4, 128.3, 129.0, 129.1, 130.0, 130.6, 132.5, 159.8, 161.3, 162.4 ppm; HRMS calculated for $C_{28}H_{23}N_2O_2$ (M^+ + H) 419.17595, found: 419.17578.

Synthesis of 5-Methyl-2-(piperidin-1-yl)-4-(pyren-1-yl)-benzonitrile (6a). A mixture of 2-oxo-4-(piperidin-1-yl)-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (**4a**, 404 mg, 1 mmol, 1 equiv), propionaldehyde (**5a**, 86 μL, 1.2 mmol, 1.2 equiv), and KOH (67 mg, 1.2 mmol, 1.2 equiv) in dry DMF (5 mL) was stirred at room temperature for 10 h. The progress of reaction was monitored by TLC and upon completion, 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 neutral alumina column using 2% ethyl acetate in *n*-hexane as the eluent to afford **6a** (296 mg, 74%) as a white solid: R_f = 0.56 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 158−160 °C; MS (ESI) 401 [M + H^+]; IR (KBr) ν = 3038 (m), 2932 (s), 2857 (w), 2807 (s), 2214 (s),1597 (s), 1489 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.59−1.65 (m, 2H), 1.74−1.84 (m, 4H), 1.97 (s, 3H), 3.09−3.25 (m, 4H), 7.01 (s, 1H), 7.57 (s, 1H), 7.64−7.67 (m, 1H), 7.81−7.83 (m, 1H), 7.92−8.26 (m, 7H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1, 24.0, 26.1, 53.2, 105.1, 118.7, 121.1, 124.5, 124.7, 125.2, 125.4, 126.2,126.5, 127.3, 127.7, 128.0, 128.4, 130.2, 130.8, 130.9, 131.3, 135.2, 135.7, 146.4, 154.6 ppm; HRMS calculated for $C_{29}H_{25}N_2$ (M^+ + H) 401.2018, found: 401.2010.

Synthesis of 2-(Piperidin-1-yl)-5-propyl-4-(pyren-1-yl)-benzonitrile (6b). A mixture of 2-oxo-4-(piperidin-1-yl)-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (**4a**, 404 mg, 1 mmol, 1 equiv), valeraldehyde (**5b**, 128 μL, 1.2 mmol, 1.2 equiv), and KOH (67 mg, 1.2 mmol, 1.2 equiv) in dry DMF (5 mL) was stirred at room temperature for 12 h. The progress of reaction was monitored by TLC, and upon completion, 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 neutral alumina column using 2% ethyl acetate in *n*-hexane as the eluent to afford **6b** (308 mg, 72%) as a white solid: R_f = 0.58 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 152−154 °C; MS (ESI) 429 [M + H^+]; IR (KBr) ν = 3037 (m), 2931 (s), 2856 (w), 2806 (s), 2213 (s), 1598 (s), cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 0.46−0.56 (m, 3H), 1.16−1.27 (m, 2H), 1.46−1.55 (m, 2H), 1.62−1.72 (m, 4H), 2.12−2.38 (m, 2H), 3.08−3.16 (m, 4H), 7.01 (s, 1H), 7.61 (d, J = 9.2 Hz, 1H), 7.77 (s, 1H), 7.93 (d, J = 7.8 Hz, 1H), 8.08−8.18 (m, 2H), 8.22−8.42 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 23.6, 24.0, 26.1, 29.7, 34.2, 53.2, 105.1, 118.9, 121.3, 124.3, 124.6, 124.8, 125.2, 125.4, 126.2, 126.8, 127.3, 127.6, 127.8, 128.7, 130.8, 131.3, 134.5, 134.7, 135.6, 146.1, 154.3 ppm; HRMS calculated for $C_{31}H_{29}N_2$ (M^+ + H) 429.2331, found: 429.2340.

Synthesis of 4′-Methoxy-2-methyl-4-(piperidin-1-yl)-6-(pyren-1-yl)biphenyl-3-carbonitrile (8a). A mixture of 2-oxo-4-(piperidin-1-yl)-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (**4a**, 404 mg, 1 mmol, 1 equiv), 1-(4-methoxyphenyl)propan-2-one (**7**, 185 μL, 1.2 mmol, 1.2 equiv), and KOH (67 mg, 1.2 mmol, 1.2 equiv) in dry DMF (5 mL) was stirred at room temperature for 10 h. The progress of reaction was monitored by TLC, and upon completion, 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 neutral alumina column using 3% ethyl acetate in *n*-hexane as the eluent to afford **8a** (380 mg, 75%) as a white solid: R_f = 0.52 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 242−244 °C; MS (ESI) 507 [M + H^+]; IR (KBr) ν = 3041 (m), 2931 (s), 2852 (w), 2208 (s), 1578 (s), 1513 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.58−1.61 (m, 2H), 1.75−1.84 (m, 4H), 2.41 (s, 3H), 3.15−3.21 (m, 4H), 3.51 (s, 3H), 6.24−6.29 (m, 1H), 6.58−6.68 (m, 2H), 6.94 (s, 1H), 6.97−7.02 (m, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.92−8.05 (m, 5H), 8.12−8.18 (m, 2H), ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1, 24.0, 26.2, 53.4, 54.7, 106.9, 112.9, 113.1, 118.1, 119.3, 123.8, 124.4, 124.5, 124.9, 125.2, 125.9, 127.3, 127.4, 127.6, 128.6, 130.2, 130.5, 130.7, 131.2, 135.7, 136.5, 142.6, 145.7, 155.6, 157.9 ppm; HRMS calculated for $C_{36}H_{31}N_2O$ (M^+ + H) 507.2436, found: 507.2584.

Synthesis of 4′-Methoxy-2-methyl-4-(4-methylpiperidin-1-yl)-6-(pyren-1-yl)biphenyl-3-carbonitrile (8b). A mixture of 4-(4-methylpiperidin-1-yl)-2-oxo-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (**4b**, 418 mg, 1 mmol, 1 equiv), 1-(4-methoxyphenyl)propan-2-one (**7**, 185 μL, 1.2 mmol, 1.2 equiv), and KOH (67 mg, 1.2 mmol, 1.2 equiv) in dry DMF (5 mL) was stirred at room temperature for 10 h. The progress of reaction was monitored by TLC, and upon completion, 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 neutral alumina column using 3% ethyl acetate in *n*-hexane as the eluent to afford **8b** (375 mg, 72%) as a white solid: R_f = 0.54 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 218−220 °C; MS (ESI) 521 [M + H^+]; IR (KBr) ν = 3040 (w), 2927 (s), 2814 (w), 2210 (s), 1580 (s), 1514 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.0 (d, J = 5.5 Hz, 3H), 1.45−1.62 (m, 3H), 1.72−1.82 (m, 2H), 2.42 (s, 3H), 2.71−2.84 (m, 2H), 3.53 (s, 3H), 3.58−3.72 (m, 2H), 6.26−6.32 (m, 1H), 6.58−6.72 (m, 2H), 6.96 (s, 1H), 6.98−7.05 (m, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.92−8.08 (m, 5H), 8.12−8.18 (m, 2H), ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1, 21.8, 30.6, 34.5, 52.5, 53.1, 54.8, 107.0, 113.0, 113.2, 118.1, 119.4, 123.9, 124.5, 124.7, 125.0, 125.2, 126.0, 127.3, 127.4, 127.5, 127.6, 128.7, 130.3, 130.6, 130.9, 131.3, 135.7, 136.6, 142.7, 145.8, 155.5, 158.0 ppm; HRMS calculated for $C_{37}H_{33}N_2O$ (M^+ + H) 521.2593, found: 521.2573.

General Procedure for the Synthesis of 10a−d at Room Temperature or Conventional Heating. A mixture of 2-oxo-4-(piperidin-1-yl)-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (**4a**, 404 mg, 1 mmol), deoxybenzoins (**9a**−**d**, 1.2 mmol), and KOH (67 mg, 1.2 mmol, 1.2 equiv) in dry DMF (5 mL) was stirred at room temperature or at 100 °C. The progress of reaction was monitored by TLC, and upon completion, 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 neutral alumina column using 3% ethyl acetate in *n*-hexane as the eluent to afford **10a**−**d**.

General Procedure for the Microwave-Assisted Synthesis of 10a−**d.** A mixture of 2-oxo-4-(piperidin-1-yl)-6-(pyren-1-yl)-2*H*-pyran-3-carbonitrile (**4a**, 101 mg, 0.25 mmol), deoxybenzoin (**9a**−**d**, 0.3 mmol), and KOH (17 mg, 0.3 mmol) in dry DMF (5 mL) was placed in a microwave vial. The solution was heated at 100 °C for 10 min using internal probe in microwave (Biotage). The reaction mixture was cooled to room temperature, poured onto crushed ice with vigorous stirring, and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a neutral alumina column using 3% ethyl acetate in *n*-hexane as the eluent to afford **10a**−**d**.

Synthesis of 2,3-Diphenyl-6-(piperidin-1-yl)-4-(pyren-1-yl)benzonitrile (10a). White solid; R_f = 0.45 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 188−190 °C; MS (ESI) 539 [M + H$^+$]; IR (KBr) ν = 3034 (m), 2932 (s), 2811 (w), 2217 (s), 1567 (s) cm^{-1}; ^{1}H NMR (300 MHz, DMSO d_6): δ = 1.52−1.58 (m, 2H), 1.65−1.76 (m, 4H), 3.18−3.26 (m, 4H), 6.48−6.90 (m, 5H), 7.18−7.28 (m, 6H), 7.80 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 8.02−8.18 (m, 5H), 8.22−8.30 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 26.2, 53.4, 106.8, 117.8, 121.2, 123.9, 124.5, 124.6, 125.0, 125.1, 125.3, 125.9, 126.0, 126.9, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.8, 130.2, 130.4, 130.8, 131.3, 135.2, 136.2, 138.0, 138.3, 145.7, 147.5, 155.8 ppm; HRMS calculated for $C_{40}H_{31}N_2$ (M$^+$ + H) 539.2487, found: 539.2457.

Synthesis of 2-(4-Methoxyphenyl)-6-(piperidin-1-yl)-3-phenyl-4-(pyren-1-yl)benzonitrile (10b). White solid; R_f = 0.42 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 198−200 °C; MS (ESI) 569 [M + H$^+$]; IR (KBr) ν = 3044 (m), 2932 (s), 2848 (w), 2214 (s), 1574 (s), 1509 (s), 1444 (s) cm^{-1}; ^{1}H NMR (300 MHz, DMSO d_6): δ = 1.48−1.58 (m, 2H), 1.65−1.74 (m, 4H), 3.15−3.24 (m, 4H), 3.69 (s, 3H), 6.52−6.92 (m, 7H), 7.12−7.17 (m, 3H), 7.76 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 8.02−8.15 (m, 5H), 8.23−8.28 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 26.2, 53.5, 55.0, 107.0, 113.2, 118.1, 121.0, 123.9, 124.5, 124.6, 125.0, 125.2, 125.3, 125.8, 126.0, 126.9, 127.3, 127.4, 127.6, 127.8, 128.8, 130.3, 130.6, 130.8, 131.3, 131.5, 135.4, 136.3, 138.2, 145.7, 147.2, 155.9, 158.9 ppm; HRMS calculated for $C_{41}H_{33}N_2O$ (M$^+$ + H) 569.2593, found: 569.2582.

Synthesis of 2,3-Bis(4-methoxyphenyl)-6-(piperidin-1-yl)-4-(pyren-1-yl)benzonitrile (10c). White solid; R_f = 0.40 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 286−288 °C; MS (ESI) 599 [M + H$^+$]; IR (KBr) ν = 3023 (s), 2934 (w), 2848 (w), 2212 (s), 1574 (s), 1518 (s), 1432 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52−1.60 (m, 2H), 1.74−1.86 (m, 4H), 3.18−3.32 (m, 4H), 3.43 (s, 3H), 3.77 (s, 3H), 6.10−6.28 (m, 2H), 6.52−6.84 (m, 4H), 6.96−7.15 (m, 2H), 7.36 (s, 1H), 7.58 (d, J = 7.9, 1H), 7.94−8.08 (m, 6H), 8.12−8.18 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 26.2, 53.5, 54.7, 55.1, 107.1, 112.5, 113.3, 118.1, 121.0, 124.0, 124.5, 124.7, 125.0, 125.1, 125.2, 126.0, 127.3, 127.6, 127.8, 128.8, 130.3, 130.5, 130.7, 130.8, 131.3, 131.5, 131.9, 135.0, 136.6, 145.9, 147.4, 155.7, 157.3, 158.8 ppm; HRMS calculated for $C_{42}H_{35}N_2O_2$ (M$^+$ + H) 599.2699, found: 599.2692.

Synthesis of 3-(Biphenyl-4-yl)-2-(4-methoxyphenyl)-6-(piperidin-1-yl)-4-(pyren-1-yl)benzonitrile (10d). White solid; R_f = 0.38 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 234−236 °C; MS (ESI) 645 [M + H$^+$]; IR (KBr) ν = 3035 (w), 2926 (s), 2859 (s), 2213 (s), 1577 (m), 1508 (m), 1454 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54−1.65 (m, 2H), 1.72−1.88 (m, 4H), 3.16−3.36 (m, 4H), 3.74 (s, 3H), 6.62−7.30 (m, 14H), 7.58−7.62 (m, 1H), 7.88−8.08 (m, 6H), 8.12−8.22 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 26.2, 53.4, 55.0, 107.0, 113.3, 118.1, 121.1, 124.0, 124.5, 124.6, 125.0, 125.1, 125.3, 125.4, 126.0, 126.5, 126.9, 127.3, 127.4, 127.7, 127.8, 128.4, 128.8, 130.3, 130.5, 130.8, 131.3, 131.5, 134.9, 136.3, 137.3, 137.9, 140.1, 145.7, 147.3, 155.9, 158.9 ppm; HRMS calculated for $C_{47}H_{37}N_2O$ (M$^+$ + H) 645.2906, found: 645.3248.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra, UV−vis and fluorescence spectra, DSC, TGA, cyclic voltammograms for compounds **6a**,**b**, **8a**,**b**, and **10a**−**d** and a device efficiency graph for compound **10c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

[⊥]Dedicated to Prof. Dr. Dr. h. c. Gerhard Bringmann on the occasion of his 60th birthday.

■ REFERENCES

(1) (a) Marsitzky, D.; Mullen, K. In *Advances in Synthetic Metals, Twenty Years of Progress in Science and Technology*; Bernier, P., Lefrant, S., Bidan, G., Eds.; Elsevier: New York, 1999; p 1. (b) Figueira-Duarte, T. M.; Müllen, K. *Chem. Rev.* **2011**, in press, dx.doi.org/10.1021/cr100428a. (c) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897. (d) Miyata, S.; Nalwa, H. S. *Organic Electroluminescent Materials and Devices*; Gordon and Breach Publishers: Amsterdam, 1997. (e) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.

(2) (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405. (c) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350. (d) Berresheim, A. J.; Muller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747. (e) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124. (f) Fujitsuka, M.; Luo, H.; Murata, Y.; Kato, N.; Ito, O.; Komatsu, K. *Chem. Lett.* **2002**, 968.

(3) (a) Okamoto, A.; Kanatani, K.; Saito, I. *J. Am. Chem. Soc.* **2004**, *126*, 4820. (b) Fujimoto, K.; Shimizu, H.; Inouye, M. *J. Org. Chem.* **2004**, *69*, 3271. (c) Han, M. K.; Lin, P.; Paek, D.; Harvey, J. J.; Fuior, E.; Knutson, J. R. *Biochemistry* **2002**, *41*, 3468. (d) Langenegger, S. M.; Häner, R. *Chem. Commun.* **2004**, 2792.

(4) (a) Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419. (b) Yuasa, H.; Miyagawa, N.; Izumi, T.; Nakatani, M.; Izumi, M.; Hashimoto, H. *Org. Lett.* **2004**, *6*, 1489. (c) Abe, H.; Mawatari, Y.; Teraoka, H.; Fujimoto, K.; Inouye, M. *J. Org. Chem.* **2004**, *69*, 495. (d) Kim, S. K.; Bok, J. H.; Bartsch, R. A.; Lee, J. Y.; Kim, J. S. *Org. Lett.* **2005**, *7*, 4839. (e) Chou, T.-C.; Hwa, C.-L.; Lin, J.-J.; Liao, K.-C.; Tseng, J.-C. *J. Org. Chem.* **2005**, *70*, 9717.

(5) (a) De Halleux, V.; Calbert, J.-P.; Brocorens, P.; Cornil, J.; Declercq, J.-P.; Brédas, J.-L.; Geerts, Y. *Adv. Funct. Mater.* **2004**, *14*, 649. (b) Hassheider, T.; Benning, S. A.; Kitzerow, H.-S.; Achard, M.-F.; Bock, H. *Angew, Chem. Int. Ed.* **2001**, *40*, 2060–2063.

(6) Barboiu, M.; Prodi, L.; Montalti, M.; Zaccheroni, N.; Kyritsakas, N.; Lehn, J.-M. *Chem.—Eur. J.* **2004**, *10*, 2953.

(7) Martin, R. B.; Qu, L.; Harruff, B. A.; Bunker, C. E.; Gord, J. R.; Allard, L. F.; Sun, Y.-P. *J. Phys. Chem. B* **2004**, *108*, 11447.

(8) (a) Bodenant, B.; Fages, F.; Delville, M.-H. *J. Am. Chem. Soc.* **1998**, *120*, 7511. (b) Maubert, B.; McClenaghan, N. D.; Indelli, M. T.; Campagna, S. *J. Phys. Chem. A* **2003**, *107*, 447. (c) Tyson, D. S.; Henbest, K. B.; Bialecki, J. F.; Castellano, N. *J. Phys. Chem. A* **2001**, *105*, 8154.

(9) (a) Wu, K.-C.; Ku, P.-J.; Lin, C.-S.; Shih, H.-T.; Wu, F.-I.; Huang, M.-J.; Lin, J.-J.; Chen, I.-C.; Cheng, C.-H. *Adv. Funct. Mater.* **2008**, *18*, 67. (b) Moorthy, J. N.; Natarajan, P.; Venkatkrishnan, P.; Huang, D. F.; Chow, T. J. *Org. Lett.* **2007**, *9*, 5215. (c) Liu, F.; Lai, W. Y.; Tang, C.; Wu, H. B.; Chen, Q. Q.; Peng, B.; Wei, W.; Huang, W.; Cao, Y. *Macromol. Rapid Commun.* **2008**, *29*, 659. (d) Jia, W.-L.; McCormick, T.; Liu, Q.-D.; Fukutani, H.; Motala, M.; Wang, R.-Y.; Tao, Y.; Wang, S. *J. Mater. Chem.* **2004**, *14*, 3344.

(10) (a) Mikroyannidis, J. A.; Fenenko, L.; Adachi, C. *J. Phys. Chem. B* **2006**, *110*, 20317. (b) Oyamada, T.; Uchiuzou, H.; Akiyama, S.; Oku, Y.; Shimoji, N.; Matsushige, K.; Sasabe, H.; Adachi, C. *J. Appl. Phys.* **2005**, *98*, 074506. (c) Venkataramana, G.; Sankaraman, S. *Eur. J. Org. Chem.* **2005**, 4162. (d) Figueira-Duarte, T. M.; Del Rosso, P. G.; Trattnig, R.; Sax, S.; List, E. J. W.; Müllen, K. *Adv. Mater.* **2010**, *22*, 990.

(11) (a) Hagopian, S.; Singer, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 1874. (b) Rice, J. E.; LaVoie, E. J.; McCarstland, D. J.; Fischer, D. L.; Wiley, J. C., Jr. *J. Org. Chem.* **1986**, *51*, 2428.

(12) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

(13) (a) Beinhoff, M.; Weigel, W.; Jurczok, M.; Rettig, W.; Modrakowski, C.; Brüdgam, I.; Hartl, H.; Schlüter, A. D. *Eur. J. Org. Chem.* **2001**, 3819.

(14) Goel, A.; Kumar, V.; Chaurasia, S.; Rawat, M.; Prasad, R.; Anand, R. S. *J. Org. Chem.* **2010**, *75*, 3656.

(15) Goel, A.; Dixit, M.; Chaurasia, S.; Kumar, A.; Raghunandan, R.; Maulik, P. R.; Anand, R. S. *Org. Lett.* **2008**, *10*, 2553.

(16) Goel, A.; Chaurasia, S.; Dixit, M.; Kumar, V.; Prakash, S.; Jena, B.; Verma, J. K.; Jain, M.; Anand, R. S.; Manoharan, S. S. *Org. Lett.* **2009**, *11*, 1289.

(17) (a) Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029. (b) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron* **1990**, *46*, 5423. (c) Goel, A.; Ram, V. J. *Tetrahedron* **2009**, *65*, 7865.

(18) (a) Tominaga, Y.; Ushirogouchi, A.; Matsuda, Y. *J. Heterocycl. Chem.* **1987**, *24*, 1557. (b) Tominaga, Y. *Trends Heterocycl. Chem.* **1991**, *2*, 43.

(19) (a) Zachariasse, K. A. *Trends Photochem. Photobiol.* **1994**, *3*, 211. (b) Birks, J. B.; Dyson, D. J.; Munro, I. H. *Proc. R. Soc. London, Ser. A* **1963**, *275*, 575. (c) Birks, J. B.; Lumb, M. D.; Munro, I. H. *Proc. R. Soc. London, Ser. A* **1964**, *280*, 289. (d) Honda, C.; Katsumata, Y.; Yasutome, R.; Yamazaki, S.; Ishii, S.; Matsuoka, K.; Endo, K. *J. Photochem. Photobiol., A* **2006**, *182*, 151.