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Synthesis of Fluorescent C_2-Bridged Teraryls and Quateraryls for Blue, Sky-Blue, and Green Color Light-Emitting Devices

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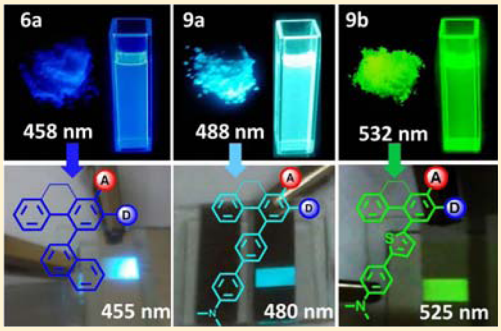
Supporting Information

ABSTRACT: A series of fluorescent teraryls and quateraryls were prepared from a ketene-*S*,*S*-acetal under mild conditions. These compounds exhibited blue, sky-blue and green color emissions both in the solid state and in a solution with good quantum yields, positive solvatochromic behavior, and reversible oxidation and reduction properties. The electronic characteristics of teraryl **6a** and quateraryls **9a**,**b** were examined by time-dependent density functional theory (TDDFT) calculations. Light-emitting devices were fabricated from teraryl **6a** and quateraryls **9a**,**b** as dyes and the configuration of ITO/PEDOT:PSS (40 nm)/NPB (20 nm)/ dye (50 nm)/BCP (7 nm)/ LiF (0.7 nm)/Al (200 nm), which exhibited electroluminescence maxima of 455, 480, and 525 nm, respectively. These devices operated at a substantially low turn-on voltage (3 and 4 V) and exhibited maximum luminance efficiencies of 0.62, 0.57, and 1.9 cd/A and brightnesses of 59, 160, and 1284 cd/m^2, respectively.



INTRODUCTION

Multicolor low-voltage-driven lighting devices have a huge market in the present high-tech society and help to meet the challenges of the energy crisis. Light-emitting devices (LEDs) operating at a low turn-on voltage are used for displays of mobile phones, mp3 players, car tracking, and signage. In this context, small polycyclic aromatic hydrocarbons (acenes) and oligomers have drawn much attention as fluorescent materials for use in next-generation flexible full-color flat-panel displays with excellent portability and lightweight organic electronics.[1,2] Acenes such as pyrene,[3] chrysene,[4] anthracene,[5−7] tetracene,[8] and pentacene[9] have been reported as fluorescent materials for use in organic light-emitting diodes (OLEDs). However, because of their flat architecture, they are prone to form excimers or aggregates through $\pi-\pi$ interactions sometimes leading to fluorescence quenching or photoluminescence with additional undesired long wavelength emission. Small molecule polyaromatic dendritic frameworks have been designed to inhibit aromatic−aromatic interactions and are reported in OLED applications.[10] We have also demonstrated how swapping of electron donor, acceptor, and chromophoric moieties onto the aromatic scaffold modulate the optical properties of fluorenes.[11] Recently, we have reported fluoranthenes,[12] pyrenylarenes,[13] and nonplanar benzo[*f*]-quinolines/acridines[14] as efficient light-emitting materials for OLED applications. Herein, we report the synthesis of a new series of teraryls and quateraryls that employ dihydrophenanthrene (DHP) as a core ring endowed with π-conjugated aryl moieties and demonstrate their photophysical, electrochemical, and optoelectronic properties.

RESULTS AND DISCUSSION

Numerous approaches have been reported for the synthesis of flexible or rigid teraryl derivatives.[15] Synthesis of two designed dimethylene C_2-bridged teraryls and quateraryls is depicted in Scheme 1 and Scheme 2. Typically, lactones **4a**−**e**, prepared using α-oxo-ketene-*S*,*S*-acetal (**2**), were reacted with 2-tetralone (**5**) in NaH-DMF for a few minutes to furnish DHPs in up to 85% yields.

To tune further the electronic properties of these DHPs, we incorporated aromatic substituents by exploiting the C−Br bond in **6d** and **6e** using "Nobel" Suzuki coupling.[16] Thus, a mixture of **6d** or **6e** and *N*,*N*-dimethylaminoarylboronic acid (**7**) or phenylboronic acid (**8**) in DMF under basic conditions afforded quateraryls **9a**−**c** in 75−78% yields (Scheme 2).

The photophysical properties of the compounds **6a**−**e**, and **9a**−**c** were examined via UV−vis absorption and photoluminescence (PL) spectra, and the data are shown in Table 1 and Figures S1−S8. Normalized UV−vis and PL spectra of selected compounds **6a**,**b**, and **9a**,**b** are given in Figure 1. The PL maxima of DHPs **6a**−**d** in THF showed blue fluorescence (λ_{max} = 465−474 nm) with quantum yields of up to 42%. π-Conjugated quateraryls **9a**−**c** exhibited green emission (λ_{max} = 497−537 nm) with good fluorescence (quantum yields of up to

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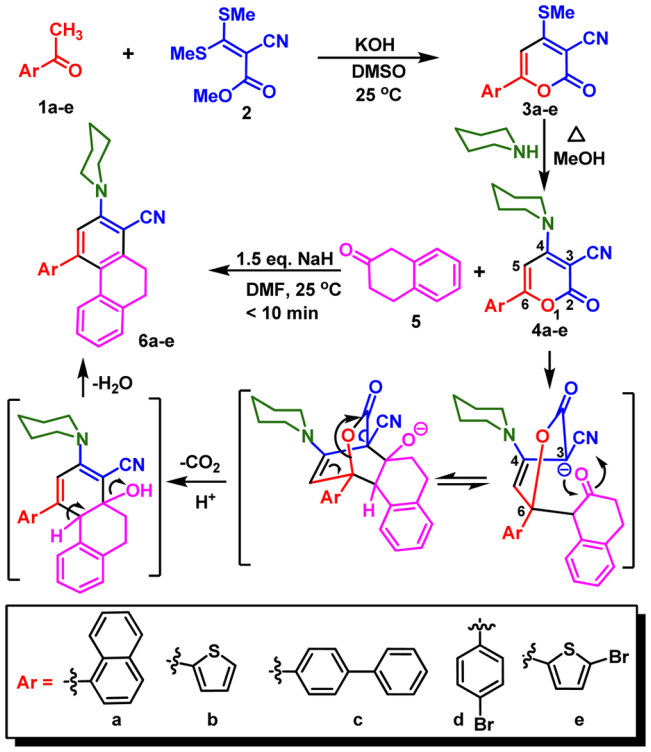
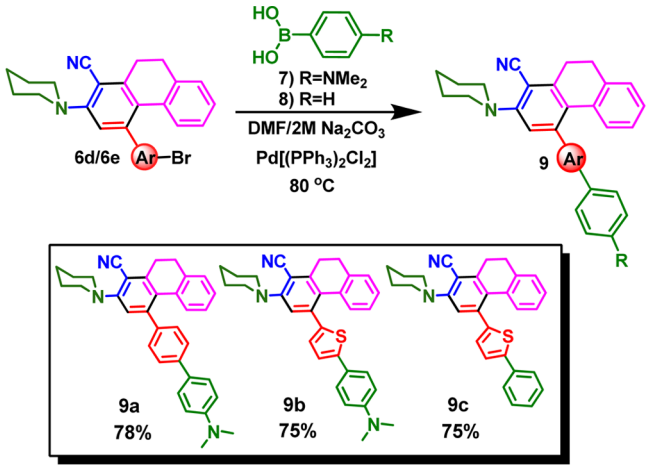
Scheme 1. Synthesis of Teraryls 6a−e



Scheme 2. Synthesis of Quateraryls 9a−c



85%). Thiophene moiety-containing **9b** showed a remarkable redshift of ∼40 nm in PL (solid as well as solution) when compared with the spectra of phenyl-substituted DHP **9a**.

To examine the nonaggregating behavior of the synthesized C_2-bridged teraryls and quateraryls, we evaluated the fluorescence of **6a−e** and **9a−c** in a solid state (powder, Figure 2); data are presented in Table 1. Powders of compounds **6a−e** and **9a** all showed blue emission characteristics with emission maxima in the range of 458−488 nm, whereas **9b,c** showed emission maxima at 503 and 530 nm, respectively. In comparison to the emission spectra of **6a−e** and **9a−c** in a dilute solution, the solid-state emission data indicated that there is no aggregation in the solid state. The nonaggregating properties of **6a** and **9a,b** were further confirmed using a thin film prepared by vacuum evaporation on a glass substrate. The PL spectra of the thin films of **6a** and

Table 1. Optical and Electrochemical Properties of 6a−e and 9a−c

entry	$\lambda_{max;\ abs}$ (nm)[a]	$\lambda_{max;\ em}$ (nm)[b]	$\lambda_{max;\ em}$ (nm)[c]	Φ_f (%)[d]	HOMO (eV)	LUMO (eV)	E_{op} (eV)[e]
6a	296, 353	465	462	42	−5.49	−2.51	2.97
6b	280, 330	474	465	21	−5.49	−2.56	2.93
6c	280, 332	462	460	38	−5.49	−2.40	3.09
6d	290, 356	468	458	20	−5.46	−2.70	2.76
6e	297, 364	493	482	18	−5.49	−2.79	2.70
9a	307, 342	497	488	68	−5.33	−2.66	2.67
9b	287, 350	537	532	85	−5.17	−2.60	2.57
9c	304, 345	515	503	23	−5.45	−2.69	2.76

[a]Longest-wavelength absorption maximum in THF. [b]Fluorescence emission maximum in THF. [c]Fluorescence emission maximum in the solid state. [d]Fluorescence quantum yield relative to harmine in 0.1 M H_2SO_4 as a standard (Φ = 45%).[17] [e]Optical band gap from CV.

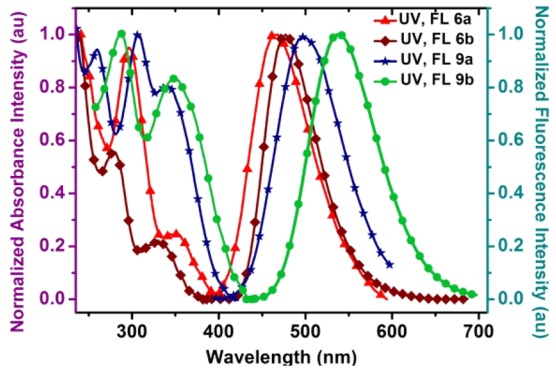


Figure 1. Normalized absorbance and fluorescence spectra of **6a,b** and **9a,b** in THF (∼10^{-6} M).

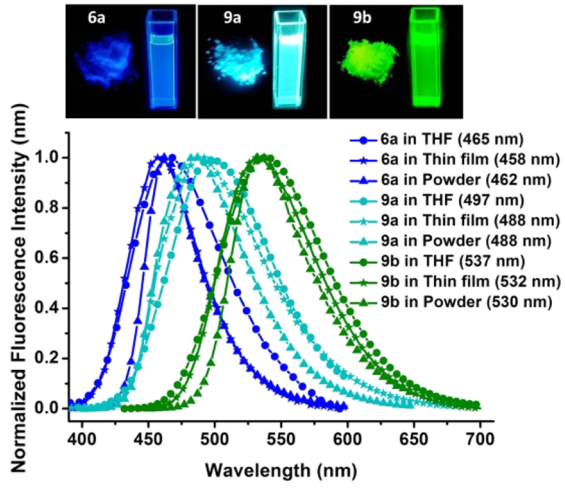


Figure 2. Fluorescence spectra of **6a** and **9a,b** in THF, thin film, and powder.

9a,b exhibited small hypsochromic shifts relative to those of the same compounds in solution, and exhibited blue (458 nm), sky-blue (488 nm), and green (532 nm) fluorescence, respectively. The absence of a redshift in the solid-state PL spectra and of an additional peak at a higher wavelength confirmed that these compounds do not form aggregates or excimers.

To investigate the characteristics of the newly developed DHPs in the solid state, we crystallized **6b** for X-ray structural analysis. Diffraction-quality crystals of **6b** were obtained by

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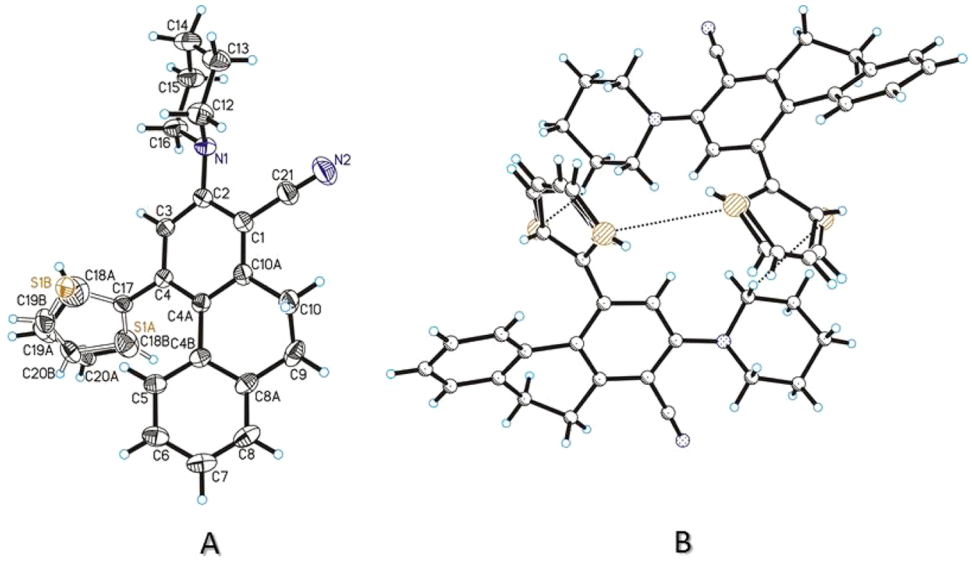

Figure 3. (A) ORTEP diagram of **6b** with 30% ellipsoid probability (CCDC no. 994833); (B) unit-cell packing diagram of **6b** showing noncovalent interactions.

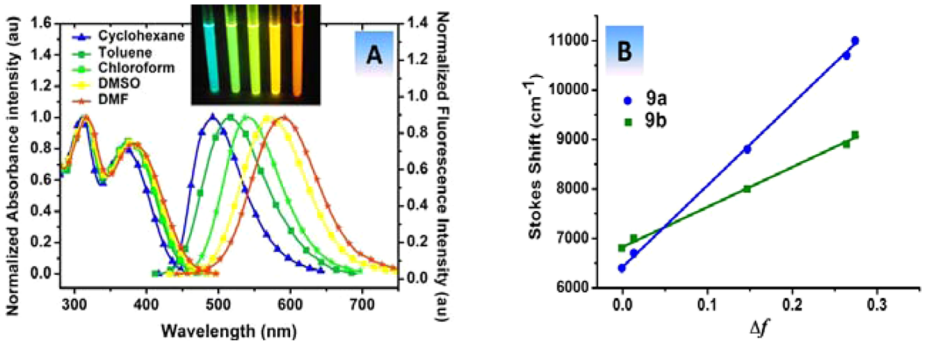

Figure 4. (A) Solvatochromism shown by **9b**; (B) Lippert−Mataga plots of **9a,b** in solvents of varying polarity.

recrystallization from ethyl acetate in hexane at room temperature. The conformation of compound **6b** is shown as an ORTEP diagram with arbitrary numbering (Figure 3A) that indicates a nonplanar conformation. The crystal structure of **6b** revealed that the thiophene ring is flipped in 50% of the packed molecules, as indicated in Figure 3A. The sulfur atom of the thiophene ring is denoted by S1A and S1B. The unit-cell packing diagram of **6b** showed dimerization due to intermolecular S·S and C−H·S interactions, but no $\pi-\pi$ interaction was observed in the crystal framework (Figure 3B).

Furthermore, the solvatochromic behavior of synthesized dyes **6a−e**, **9a−c** was investigated. Teraryls **6a−e** did not show any solvatochromic behavior, whereas an increase in the solvent polarity (from nonpolar cyclohexane to polar DMF) causes a bathochromic shift for **9a** ($\lambda_{em,max}$ shifted from 457 to 570 nm) and for **9b** ($\lambda_{em,max}$ shifted from 491 to 590 nm, Figure 4A and Table S1). This prominent shift in the emission wavelength clearly revealed that the dipole moment of the excited state is higher compared to that of the ground state. Further information regarding the solvent sensitivity of the emission spectra of **9a** and **9b** was obtained from evaluation of their Stokes' shifts in terms of Lippert−Mataga plots.[18] Table S1 reveals the changes in emission wavelength and Stokes' shifts with increasing solvent polarity. The correlation of the Stokes' shifts ($\Delta\nu$ in cm^{-1}) with the orientation polarizabilities (Δf) for **9a,b** is represented in Figure 4B. Linear correlation was found for phenanthrenes **9a,b** (r^2 = 0.98 and 0.99, respectively) after plotting a graph between their orientation polarizabilities (Δf) and Stokes' shifts. To examine the electronic properties of **6a** and **9a,b**, we carried out time-dependent density functional theory (TDDFT) calculations with Gaussian '09 software.[19] The geometries were optimized at a DFT/B3LYP level using a 6-31G(d,p) basis set. The TDDFT calculations were performed using the B3LYP/6-311++G(d,p) method. The energies of the HOMO and LUMO levels, HOMO−LUMO gap, main orbital transition, and oscillator strength (f) are listed in Table 2. Figure 5 shows the theoretically computed molecular orbitals in the ground states for the representative compounds **6a** and **9a,b**. The TDDFT calculations indicated that the charge density distribution for compound **6a** was spread over the DHP segment in HOMO and at the naphthyl moiety in LUMO . For compounds **9a,b**, the charge density was localized on the *N*,*N*-dimethylaminophenyl unit in the HOMO levels and on the DHP core in the LUMO levels.

The computational results for compound **6a** revealed that the longer-wavelength absorption originates from the HOMO − 1 to LUMO electronic excitation (Table 2). In the case of **9a,b**, longer-wavelength transitions occur from HOMO to LUMO, which involve a charge migration from the *N*,*N*-dimethylaminophenyl (donor) unit to the CN-containing DHP core segment (acceptor). The trends exhibited in the solution absorption wavelengths (in which the charge transfer bands are

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Table 2. Computed Values of Vertical Excitations, Oscillator Strength, Assignment, HOMO, LUMO, and Energy Band Gap

entry	λ_{max} (nm)	f	assignment	HOMO (eV)	LUMO (eV)	E_G(theo.)/ E_G (exp.) (eV)
6a	340	0.0475	HOMO − 1 → LUMO (75%)	−5.19	−2.07	3.12/2.97
	297	0.0061	HOMO − 2 → LUMO (48%)			
9a	335	0.0497	HOMO → LUMO (68%)	−4.97	−2.18	2.79/2.67
	322	0.0979	HOMO − 1 → LUMO (42%)			
9b	363	0.0001	HOMO → LUMO (97%)	−4.06	−1.40	2.66/2.57
	345	0.0017	HOMO − 1 → LUMO + 2 (74%)			
	308	0.0282	HOMO − 1 → LUMO (71%)			

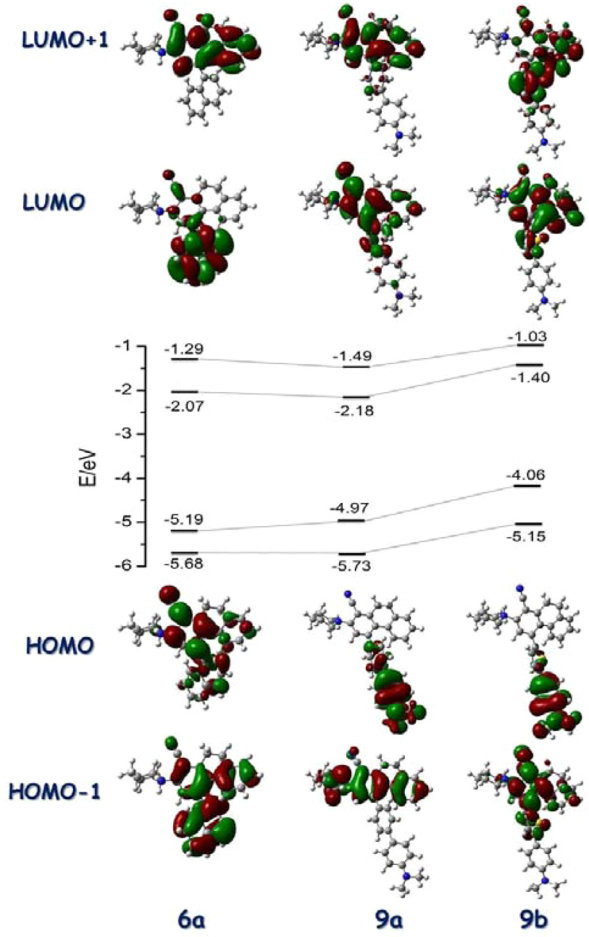

Figure 5. Computed molecular orbital energy diagrams and isodensity surface plots of HOMO − 1, HOMO, LUMO, and LUMO + 1 of **6a** and **9a**,**b**.

more intense for **9a**,**b** as compared to those of **6a**) are consistent with the theoretical predictions. All the dyes possess a low oscillator strength, as shown in Table 2.

Electrochemical studies were carried out to ascertain the redox behaviors of **6a**−**e** and **9a**−**c**. Cyclic voltammetric measurements were performed in a three-electrode cell setup using Ag/AgCl as the standard electrode and Pt disk as the working electrode, a 2 mM solution of the compound, and a 0.2 M solution of the electrolyte tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in DMF. All the potentials were calibrated with ferrocene (Fc/Fc^+). The HOMO and LUMO levels were readily estimated from onset oxidation (E_{ox}) and onset reduction potentials (E_{red}), using the equations $E_{HOMO} = -(E_{ox} + 4.8)$ eV and $E_{LUMO} = -(E_{red} + 4.8)$ eV. The data are summarized in Table 1.

Reversible oxidation and reduction peaks were observed for dyes **6a** and **9a**,**b** as shown in Figure 6, which indicates that

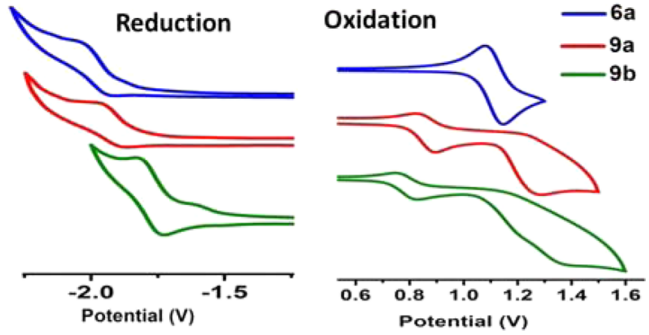

Figure 6. Cyclic voltammograms recorded for compounds **6a** and **9a**,**b** in DMF (scan rate = 100 mV/s).

both radical cations and radical anions are stable entities. These properties are useful for the fabrication of OLEDs. The HOMO values for compounds **6a**−**e** were found to be nearly the same (−5.46 to −5.49 eV), whereas the LUMO values were in the range of −2.40 to −2.79 eV (Figure S9−S16). In the case of quateraryls **9a**,**b**, the LUMO levels were nearly the same; however, the HOMO level of **9b** was greater than that of **9a**, possibly due to the introduction of the electron-rich thiophene moiety. The experimental band gaps of dyes **9a**,**b** were 2.67 and 2.57 eV, respectively, which is in good agreement with the theoretical calculations (Table 2). The thermal properties of **6a** and **9a**,**b** were gauged by thermogravimetric analysis (TGA) and DSC experiments under an argon atmosphere. The melting temperatures obtained by DSC experiments for dyes **6a** and **9a**,**b** were 190, 175, and 196 °C respectively. Teraryl **6a** and quateraryls **9a**,**b** were thermally stable up to 248, 165, and 350 °C, respectively (5% weight loss temperature) as shown in Table 3 and Figure S17.

On the basis of photophysical and electrochemical studies, compounds **6a** and **9a**,**b** were selected for further studies to demonstrate their application in OLEDs. Multilayer devices were fabricated with the device configuration of ITO/poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) (40 nm)/NPB (20 nm)/dye **6a** or **9a** or **9b** (50 nm)/BCP (7 nm)/ LiF (0.7 nm)/Al (200 nm). The patterned ITO glass plate was cleaned in 6:1:1 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 following ozone treatment, the first layer of PEDOT:PSS was spin-coated at 2400 rpm on the patterned ITO surface to form a hole-injection layer. The PEDOT:PSS layer was vacuum-dried at 120 °C for 1 h. All other organic layers and metal layers were sublimed in high vacuum ($\sim 1^{-5} \times 10^{-6}$ mbar). A bilayer metal cathode of composed of LiF (0.7 nm) and Al (200 nm) was deposited in a separate vacuum chamber. Then, the devices were sealed with a glass cover plate using UV epoxy. The *I*−*L*−*V* characteristics for the sealed OLEDs were obtained using a

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Table 3. OLED Performance of ITO/PEDOT:PSS (40 nm)/NPB (20 nm)/[6a or 9a or 9b (50 nm)]/BCP (7 nm)/LiF (0.7 nm)/Al (200 nm)

entry	$\lambda_{max;\ em}$ [a] (nm)	EL (nm) (λ_{max})	T_d [b]/T_m [c] (°C)	turn-on voltage (V)	max. brightness (cd/m^2)	max. current eff. (Cd/A)	CIE 1931
6a	458	455	248/190	3	59 (±5)	0.62 (±0.03)	0.19, 0.25
9a	488	480	165/175	4	160 (±8)	0.57 (±0.028)	0.20, 0.34
9b	530	525	350/195	4	1284 (±60)	1.9 (±0.1)	0.35, 0.58

[a]Fluorescence emission maximum in film. [b]Decomposition temperature (5% weight loss) under nitrogen atmosphere in the TGA measurements. [c]Melting temperature gauged by DSC.

Keithley source-measure unit. Electroluminescence (EL) spectra were recorded using a fiber optic spectrometer. Device performance data and Commission Internationale de L'Eclairage (CIE) color coordinates of the OLEDs containing **6a** or **9a,b** are depicted in Table 3. EL spectra of OLED-**6a** showed a λ_{max} peak at 455 nm (blue) with CIE coordinates (0.19, 0.25), EL spectra of OLED-**9a** exhibited a λ_{max} peak at 480 nm (sky-blue) with CIE coordinates (0.20, 0.34), and EL spectra of OLED-**9b** exhibited a λ_{max} peak at 525 nm (green) with CIE coordinates (0.35, 0.58). Pictures of the actual fabricated multilayered devices, chromaticity diagrams, and EL spectra of the OLEDs containing **6a** and **9a,b** are shown in Figure 7A,B, and C, respectively.

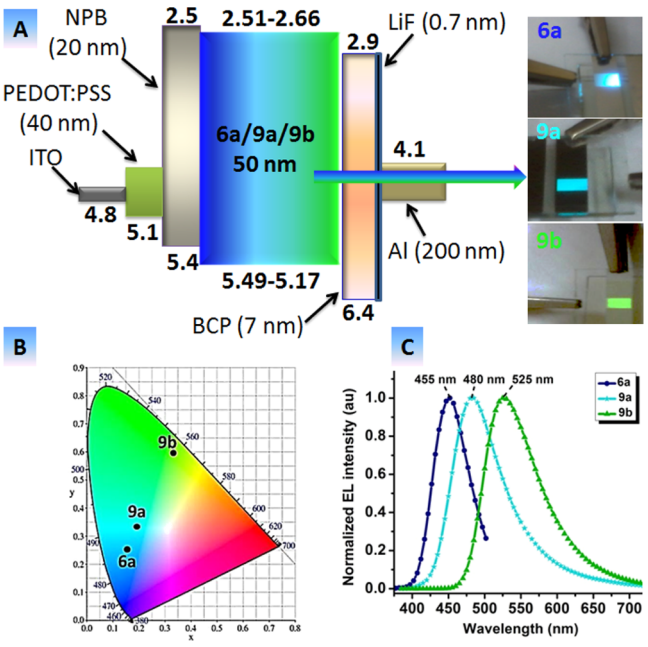

Figure 7. (A) Device structure and actual OLEDs with **6a** and **9a,b**; (B) CIE coordinates; (C) EL spectra of **6a** and **9a,b**.

The *I*–*L*–*V* characteristics of **6a** and **9a,b** are shown in Figure 8A. All the devices were operated at a low turn-on voltage (3 V for **6a**, 4 V for **9a,b**) and were found to be stable. The OLEDs exhibited good luminance efficiencies (0.62, 0.57, and 1.9 cd/A for **6a** and **9a,b**, respectively, Figure 8B) and brightnesses (59, 160, and 1284 cd/m^2 for **6a** and **9a,b**, respectively, Figure 8C). It is worth mentioning that the presence of the thiophene ring in **9b** significantly enhanced its brightness as compared to that of **9a**, which contains a phenyl moiety. The dependence of the devices' stability on the applied voltage was investigated by increasing the voltage in intervals of 1 V (Figure 8D). Interestingly, these OLEDs were found to be stable under bias voltage of up to 10 V, which revealed that the devices are electro-optically stable. Further studies to optimize the configuration for improving the efficiency of the devices using these dyes are under way.

CONCLUSIONS

We have synthesized a new series of teraryls and quateraryls that employ dihydrophenanthrene (DHP) as a core ring substituted with aryl moieties and have demonstrated their photophysical, electrochemical, and optoelectronic properties. These compounds exhibited blue, sky-blue, or green photoluminescence with good quantum yields both in a solid state and in a solution. They showed positive solvatochromic and nonaggregating behavior. The computational studies using Gaussian software showed that the longer-wavelength transitions of **9a,b** occur from HOMO to LUMO, which involve a charge transfer from the *N*,*N*-dimethylaminophenyl (donor) segment to the nitrile-containing DHP unit (acceptor). The cyclic voltammetry analysis of dyes **6a** and **9a,b** revealed both reversible oxidation and reversible reduction potentials, indicating that both cations and anions are stable entities. OLEDs containing **6a** and **9a,b** were successfully fabricated and exhibited blue, sky-blue, and green electroluminescence, respectively, with maximum brightnesses of 59, 160, and 1284 cd/m^2, respectively, and low turn-on voltages of 3 or 4 V. Of the three devices (using **6a** or **9a,b**), the one containing thiophene ring-substituted DHP **9b** exhibited good current efficiency and brightness. On the basis of their interesting photophysical properties, these compounds may also find application as blue and green fluorescent probes in live cell imaging.

EXPERIMENTAL SECTION

General. ^{1}H and ^{13}C NMR spectra were measured with 300 and 400 MHz spectrotometers. $CDCl_3$ and DMSO-d_6 were used as solvents. Chemical shifts are reported in parts per million shift (δ) from Me_4Si (δ 0 ppm for ^{1}H) or based on the middle peak of the solvent ($CDCl_3$) (δ 77.00 ppm for ^{13}C NMR) as an internal standard. Signal patterns are indicated as s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet. Coupling constants (*J*) are given in hertz. Infrared (IR) spectra were recorded in KBr discs and are reported in wavenumber (cm^{-1}). An ESIMS spectrometer was used for mass spectra analysis. High-resolution mass spectra were taken with a Q-ToF analyzer. The cyclic voltammograms were obtained on a CV analyzer and were employed to evaluate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels. All the reactions were monitored by TLC, and visualization was done by UV light (254 nm).

General Procedure for the Synthesis of 3a–e and 4a–e. A mixture of methyl 2-cyano-3,3-dimethylsulfanyl acrylate **2** (2.03 g, 10 mmol), substituted acetophenones **1a–e** (11 mmol), and powdered KOH (12 mmol) in dry DMSO (50 mL) was stirred at room temperature for 10–14h. 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

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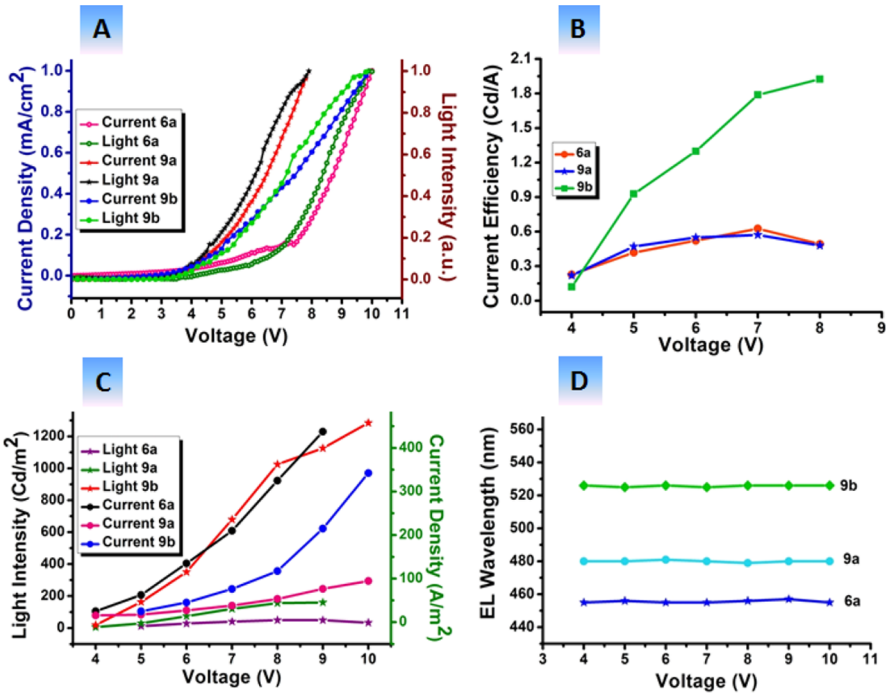

Figure 8. (A) *I*–*L*–*V* characteristics; (B) current efficiency; (C) light intensity and current density; (D) EL stability characteristics of **6a** and **9a**,**b**.

chloroform as the eluent to yield 6-aryl-2-oxo-4-methylsulfanyl-2*H*-pyran-3-carbonitriles **3a**–**e**. Compounds **3a**–**e** (1 mmol) were refluxed in methanol with piperidine (120 μL, 1.2 mmol) for 6–7 h. The reaction mixture was cooled to room temperature, and the solid obtained was filtered to furnish 6-aryl-2-oxo-4-piperidin-1-yl-2*H*-pyran-3-carbonitriles **4a**–**e** in good yields. 2*H*-Pyran-2-ones **3a**,**b**,**d**, and **4d** were synthesized according to a procedure described previously.[20]

*6-(Biphenyl-4-yl)-4-(methylsulfanyl)-2-oxo-2H-pyran-3-carbonitrile (**3c**).* Yellow solid (1.98 g, 62% yield); R_f = 0.55 (chloroform/methanol, 99:1, v/v); mp (chloroform/methanol) > 250 °C; MS (ESI) 320 $[M + H]^+$; IR (KBr) ν = 1708, 2211; ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.87 (s, 3H), 7.30 (s, 1H), 7.41–7.56 (m, 3H), 7.80 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 14.8, 89.9, 105.3, 114.7, 124.5, 125.3, 126.8, 127.1, 127.4, 127.6, 128.3, 129.9, 130.1, 130.5, 131.1, 133.6, 158.2, 163.8, 171.8; HRMS (ESI) calculated for $C_{19}H_{14}NO_2S$, 320.074 5 $[M + H^+]$, found, 320.074 2.

*6-(5-Bromothiophen-2-yl)-4-(methylthio)-2-oxo-2H-pyran-3-carbonitrile (**3e**).* Brown solid (2.44 g, 75% yield); R_f = 0.53 (chloroform/methanol, 99:1, v/v); mp (chloroform/methanol) > 250 °C; MS (ESI) 327 $[M + H]^+$, 329 $[M + 2 + H]^+$; IR (KBr) ν = 1703, 2209; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.76 (s, 3H), 7.12 (s, 1H), 7.47 (d, J = 4.2 Hz, 1H), 7.99 (d, J = 4.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 14.9, 88.7, 98.7, 114.7, 120.5, 132.7, 133.5, 135.1, 156.1, 156.9, 171.8; HRMS (ESI) calculated for $C_{11}H_6BrNO_2S_2$, 327.910 1 $[M + H^+]$, found, 327.909 9.

*6-(Naphthalen-1-yl)-2-oxo-4-(piperidin-1-yl)-2H-pyran-3-carbonitrile (**4a**).* White solid (280 mg, 85% yield); R_f = 0.57 (chloroform/methanol, 49:1, v/v); mp (chloroform/methanol) 193–195 °C; MS (ESI) 331 $[M + H]^+$; IR (KBr) ν = 1700, 2210; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.65–1.70 (m, 6H), 3.81–3.88 (m, 4H), 6.87 (s, 1H), 7.57–7.65 (m, 3H), 7.78 (d, J = 7.0 Hz, 1H), 7.98–8.31 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7, 26.6, 50.8, 70.6, 101.2, 118.2, 125.3, 125.7, 127.1, 128.0, 128.8, 129.1, 130.1, 130.2, 131.9, 133.6, 160.3, 161.7, 162.8; HRMS (ESI) calculated for $C_{21}H_{18}N_2O_2$, 331.114 6 $[M + H^+]$, found, 331.115 9.

*2-Oxo-4-(piperidin-1-yl)-6-(thiophen-2-yl)-2H-pyran-3-carbonitrile (**4b**).* Yellow solid (228 mg, 80% yield); R_f = 0.55 (chloroform/methanol, 99:1, v/v); mp (chloroform/methanol) 199–201 °C; MS (ESI) 287 $[M + H]^+$; IR (KBr) ν = 1682, 2208; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.67–1.70 (m, 6H), 3.83–3.89 (m, 4H), 7.00 (s, 1H), 7.24–7.31 (m, 1H) 7.93 (dd, J = 0.84, 3.72 Hz, 1H), 8.06 (dd, J = 0.88, 4.92 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 23.8, 26.6, 50.9,69.9, 94.2, 118.2, 129.4, 130.0, 132.2, 134.4, 155.7, 160.2, 161.9; HRMS (ESI) calculated for $C_{15}H_{14}N_2O_2S$, 287.084 5 $[M + H^+]$, found, 287.086 2.

*6-(Biphenyl-4-yl)-2-oxo-4-(piperidin-1-yl)-2H-pyran-3-carbonitrile (**4c**).* White solid (292 mg, 82% yield); R_f = 0.53 (chloroform/methanol, 49:1, v/v); mp (chloroform/methanol) 214–216 °C; MS (ESI) 357 $[M + H]^+$; IR (KBr) ν = 1686, 2205; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69–1.93 (m, 6H), 3.72–3.95 (m, 4H), 6.50 (s, 1H), 7.28–7.52 (m, 3H), 7.63 (d, J = 7.11 Hz, 4H), 7.69 (d, J = 8.22 Hz, 1H), 7.89 (d, J = 8.28 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.7, 26.2, 50.8, 71.9, 94.5, 117.4, 126.5, 126.9, 127.3, 128.1, 128.8, 129.2, 139.2, 144.2, 160.2, 160.3, 162.5; HRMS calculated for $C_{23}H_{20}N_2O_2$, 357.160 3 $[M + H^+]$, found, 357.159 5.

*6-(5-Bromothiophen-2-yl)-2-oxo-4-(piperidin-1-yl)-2H-pyran-3-carbonitrile (**4e**).* Yellow solid (290 mg, 80% yield); R_f = 0.51 (chloroform/methanol, 99:1, v/v); mp (chloroform/methanol) > 250 °C; MS (ESI) 365 $[M + H]^+$, 367 $[M + 2 + H]^+$; IR (KBr) ν = 1682, 2204; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.76 (s, 3H), 7.12 (s, 1H), 7.47 (d, J = 4.2 Hz, 1H), 7.99 (d, J = 4.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 23.8, 26.7, 51.0, 70.0, 94.7, 117.9, 118.2, 130.7, 132.9, 135.9, 154.3, 160.1, 161.8; HRMS (ESI) calculated for $C_{15}H_{13}BrN_2O_2S$, 364.995 9 $[M + H^+]$, found, 364.995 4.

Synthesis of 4-(Naphthalen-1-yl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (6a). A mixture of 6-(naphthalen-1-yl)-2-oxo-4-(piperidin-1-yl)-2*H*-pyran-3-carbonitrile (**4a**, 330 mg, 1 mmol), 3,4-dihydronaphthalen-2(1*H*)-one (**5**, 161 μL, 1.2 mmol), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol) in dry DMF (5 mL) was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC; on 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 silica-gel column with 2% ethyl acetate in hexane as the eluent to afford 352 mg (80%) of **6a** as a white solid. R_f = 0.51 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 188–190 °C; MS (ESI) 415 $[M + H]^+$; IR (KBr) ν = 2212 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50–1.60 (m, 2H), 1.75–1.83 (m, 4H), 2.85–2.96 (m, 2H), 3.09–3.26 (m, 6H), 6.42–6.57 (m, 2H), 6.92–6.97 (m, 2H), 7.15 (d, J = 7.2 Hz, 1H), 7.29–7.40 (m, 2H), 7.45 (t, J =

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7.6 Hz, 2H) 7.63 (d, J = 8.4 Hz, 1H) 7.87 (t, J = 7.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 26.2, 29.0, 29.3, 53.3, 105.1, 117.7, 121.2, 125.6, 126.0, 126.4, 126.6, 127.1, 127.3, 127.7, 128.1, 128.4, 131.2, 132.8, 133.8, 138.0, 140.2, 142.9, 145.6, 155.1; HRMS (ESI) calculated for $C_{30}H_{27}N_2$, 415.217 4 [M + H$^+$], found, 415.214 9; anal. calcd for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.76; found: C, 86.89; H, 6.49; N, 6.62.

Synthesis of 2-(Piperidin-1-yl)-4-(thiophen-2-yl)-9,10-dihydrophenanthrene-1-carbonitrile (6b). A mixture of 2-oxo-4-(piperidin-1-yl)-6-(thiophen-2-yl)-2*H*-pyran-3-carbonitrile (**4b**, 286 mg, 1 mmol), 3,4-dihydronaphthalen-2(1*H*)-one (**5**, 161 μL, 1.2 mmol), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol) in dry DMF (5 mL) was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC; on 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 silica-gel column with 2% ethyl acetate in hexane as the eluent to afford 298 mg (81%) of **6b** as a white solid. R_f = 0.49 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 170−172 °C; MS (ESI) 371 [M + H]$^+$; IR (KBr) ν = 2215 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60−1.69 (m, 2H), 1.83−1.87 (m, 4H), 2.85−2.93 (m, 2H), 3.06−3.12 (m, 2H), 3.23−3.28 (m, 4H), 6.84−7.04 (m, 5H), 7.05−7.14 (m, 1H), 7.24−7.25 (m, 1H) 7.35−7.37 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.0, 26.0, 28.7, 29.2, 53.1, 105.1, 117.4, 120.6, 125.6, 126.2, 126.8, 127.1, 127.3, 127.5, 127.9, 128.4, 132.4, 136.9, 138.3, 143.6, 145.9, 155.2; HRMS (ESI) calculated for $C_{24}H_{23}N_2S$, 371.158 2 [M + H$^+$], found, 371.156 7.

Synthesis of 4-(Biphenyl-4-yl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (6c). A mixture of 6-(biphenyl-4-yl)-2-oxo-4-(piperidin-1-yl)-2*H*-pyran-3-carbonitrile (**4c**, 356 mg, 1 mmol), 3,4-dihydronaphthalen-2(1*H*)-one (**5**, 161 μL, 1.2 mmol), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol) in dry DMF (5 mL) was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC; on 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 silica-gel column with 2% ethyl acetate in hexane as the eluent to afford 350 mg (80%) of **6c** as a white solid. R_f = 0.50 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 166−168 °C; MS (ESI) 441 [M + H]$^+$; IR (KBr) ν = 2216 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59−1.68 (m, 2H), 1.76−1.85 (m, 4H), 2.84−2.95 (m, 2H), 3.02−3.12 (m, 2H), 3.18−3.28 (m, 4H), 6.73−6.86 (m, 2H), 6.84 (s, 1H), 7.05 (t, J = 7.2 Hz, 1H) 7.19−7.25 (m, 1H) 7.30−7.41 (m, 3H) 7.46 (t, J = 7.5 Hz, 2H) 7.55−7.69 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.2, 26.2, 29.0, 29.3, 53.3, 104.8, 117.7, 120.1, 125.7, 126.7, 127.0, 127.3, 127.6, 128.9, 129.3, 129.6, 132.8, 138.3, 140.4, 141.4, 144.4, 145.9, 155.6; HRMS (ESI) calculated for $C_{32}H_{29}N_2$, 441.233 0 [M + H$^+$], found, 441.226 9.

Synthesis of 4-(4-Bromophenyl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (6d). A mixture of 6-(4-bromophenyl)-2-oxo-4-(piperidin-1-yl)-2*H*-pyran-3-carbonitrile (**4e**, 356 mg, 1 mmol), 3,4-dihydronaphthalen-2(1*H*)-one (**5**, 161 μL, 1.2 mmol), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol) in dry DMF (5 mL) was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC; on 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 silica-gel column with 2% ethyl acetate in hexane as the eluent to afford 372 mg (84%) of **6d** as a white solid. R_f = 0.49 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 166−168 °C; MS (ESI) 443 [M + H]$^+$, 445 [M + 2 + H$^+$]; IR (KBr) ν = 2216 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60−1.66 (m, 2H), 1.71−1.88 (m, 4H), 2.81−2.90 (m, 2H), 3.00−3.09 (m, 2H), 3.17−3.25 (m, 4H), 6.67 (d, J = 7.7 Hz, 1H), 6.76−6.89 (m, 2H), 7.02−7.25 (m, 4H) 7.47 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 26.1, 28.9, 29.2, 53.2, 104.9, 117.5, 119.9, 121.9, 125.7, 126.8, 127.1, 127.5, 129.1, 130.8, 131.9, 132.4, 138.4, 141.3, 143.3, 146.1, 155.6; HRMS (ESI) calculated for $C_{26}H_{24}BrN_2$, 443.112 3 [M + H$^+$], found, 443.110 9.

Synthesis of 4-(5-Bromothiophen-2-yl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (6e). A mixture of 6-(5-bromothiophen-2-yl)-2-oxo-4-(piperidin-1-yl)-2*H*-pyran-3-carbonitrile (**4e**, 365 mg, 1 mmol), 3,4-dihydronaphthalen-2(1*H*)-one (**5**, 161 μL, 1.2 mmol), and NaH (60% dispersion in oil, 60 mg, 1.5 mmol) in dry DMF (5 mL) was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC; on 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 silica-gel column with 2% ethyl acetate in hexane as the eluent to afford 384 mg (85%) of **6e** as a greenish-white solid. R_f = 0.48 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 168−170 °C; MS (ESI) 449 [M + H]$^+$, 451 [M + 2 + H]$^+$; IR (KBr) ν = 2217 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60−1.67 (m, 2H), 1.75−1.84 (m, 4H), 2.79−2.88 (m, 2H), 2.98−3.07 (m, 2H), 3.17−3.26 (m, 4H), 6.69 (d, J = 4.0 Hz, 1H), 6.86 (s, 1H), 6.92−7.17 (m, 4H) 7.20−7.25 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.0, 26.1, 28.7, 29.2, 53.1, 105.5, 112.7, 117.2, 120.3, 125.8, 127.1, 127.4, 127.4, 128.4, 130.3, 132.1, 135.8, 138.3, 145.3, 146.2, 155.4; HRMS (ESI) calculated for $C_{24}H_{22}BrN_2S$, 449.068 7 [M + H$^+$], found, 449.064 2.

Synthesis of 4-(4′-(Dimethylamino)biphenyl-4-yl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (9a). A solution of 4-(4-bromophenyl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (**6d**, 442 mg, 1 mmol) and *N*,*N*-dimethylaminophenylboronic acid (198 mg, 1.2 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min followed by the addition of Na_2CO_3 (1.5 mL, 2M) under a continuous flow of nitrogen. $PdCl_2(PPh_3)_2$ (190 mg, 0.20 mmol) was added to the reaction mixture under a nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 50 min. After completion, the reaction mixture was diluted with H_2O (10 mL) and then extracted four times with ethyl acetate (15 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under high vacuum. The crude product was purified on a silica-gel column with 5% ethyl acetate in hexane as the eluent to afford 378 mg (78%) of **9a** as a greenish-white solid. R_f = 0.48 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 172−174 °C; MS (ESI) 484 [M + H]$^+$; IR (KBr) ν = 2213 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61−1.69 (m, 2H), 1.79−1.88 (m, 4H), 2.85−2.95 (m, 2H), 3.00−3.14 (m, 8H), 3.20−3.27 (m, 4H), 6.80−6.94 (m, 5H), 7.02−7.12 (m, 1H), 7.22−7.35 (m, 3H), 7.57 (d, J = 7.7 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 26.2, 29.0, 29.3, 40.7, 53.3, 104.5, 112.8, 117.7, 120.1, 125.6, 126.2, 126.6, 127.3, 127.5, 128.3, 129.3, 129.5, 132.9, 138.2, 139.9, 140.3, 144.7, 145.8, 150.1, 155.6; HRMS (ESI) calculated for $C_{34}H_{34}N_3$, 484.275 3 [M + H$^+$], found, 484.274 1; anal. calcd for $C_{34}H_{33}N_3$: C, 84.43; H, 6.88; N, 8.69; found: C, 84.36; H, 6.78; N, 8.81.

Synthesis of 4-(5-(4-(Dimethylamino)phenyl)thiophen-2-yl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (9b). A solution of 4-(5-bromothiophen-2-yl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (**6e**, 449 mg, 1 mmol) and *N*,*N*-dimethylaminophenylboronic acid (198 mg, 1.2 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min followed by the addition of Na_2CO_3 (1.5 mL, 2 M) under a continuous flow of nitrogen. $PdCl_2(PPh_3)_2$ (190 mg, 0.20 mmol) was added to the reaction mixture under a nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 50 min. After completion, the reaction mixture was diluted with H_2O (10 mL), and then extracted four times with ethyl acetate (15 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under high vacuum. The crude product was purified on a silica-gel column with 5% ethyl acetate in hexane as the eluent to afford 390 mg (80%) of **9b** as a greenish-yellow solid. R_f = 0.47 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 198−200 °C; MS (ESI) 490 [M + H]$^+$; IR (KBr) ν = 2214 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60−1.67 (m, 2H), 1.76−1.87 (m, 4H), 2.80−3.09 (m, 10H), 3.18−3.26 (m, 4H), 6.80−6.99 (m, 4H), 7.01−7.20 (m, 3H), 7.19−7.25 (m, 2H), 7.47−7.61 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 26.1, 28.8, 29.3, 40.4, 53.1, 104.8, 112.5, 117.5, 120.3, 121.1, 122.4, 125.7, 126.6, 126.8, 127.2, 127.7, 128.2, 128.6, 132.6, 137.2, 138.1, 140.5, 145.9, 146.3, 150.1, 155.4;

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HRMS (ESI) calculated for $C_{32}H_{32}N_3S$, 490.231 7 [M + H$^+$], found, 490.230 6; anal. calcd for $C_{32}H_{31}N_3S$: C, 78.49; H, 6.38; N, 8.58; found: C, 78.54; H, 6.47; N, 8.49.

Synthesis of 4-(5-Phenylthiophen-2-yl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (9c). A solution of 4-(5-bromothiophen-2-yl)-2-(piperidin-1-yl)-9,10-dihydrophenanthrene-1-carbonitrile (**6e**, 449 mg, 1 mmol) and phenylboronic acid (146 mg, 1.2 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min followed by the addition of Na_2CO_3 (1.5 mL, 2 M) under a continuous flow of nitrogen. $PdCl_2(PPh_3)_2$ (190 mg, 0.20 mmol) was added to the reaction mixture under a nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 50 min. After completion, the reaction mixture was diluted with H_2O (10 mL) and then extracted four times with ethyl acetate (15 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under high vacuum. The crude product was purified on a silica-gel column with 5% ethyl acetate in hexane as the eluent to afford 335 mg (75%) of **9c** as a green solid. R_f = 0.50 (*n*-hexane/ethyl acetate, 9:1, v/v); mp (*n*-hexane/ethyl acetate) 170−172 °C; MS (ESI) 447 [M + H]$^+$; IR (KBr) ν = 2216 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60−1.68 (m, 2H), 1.77−1.87 (m, 4H), 2.82−2.90 (m, 2H), 2.99−3.02 (m, 2H), 3.19−3.26 (m, 4H), 6.85−6.99 (m, 3H), 7.05−7.18 (m, 2H), 7.18−7.29 (m, 3H), 7.38 (t, J = 7.5, 2H), 7.59 (d, J = 6.8, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 26.1, 28.8, 29.3, 53.1, 105.1, 117.4, 120.4, 123.4, 125.6, 125.8, 126.9, 127.3, 127.7, 127.8, 128.2, 128.5, 128.9, 132.5, 134.0, 136.8, 138.2, 142.9, 145.2, 146.0, 155.4; HRMS (ESI) calculated for $C_{30}H_{27}N_2S$, 447.189 5 [M + H$^+$], found, 447.184 7.

■ ASSOCIATED CONTENT

Supporting Information

UV−vis, fluorescence spectra, and cyclic voltammograms of **6a−e** and **9a−c**; atom coordinates and absolute energies and TGA plots of **6a**, and **9a,b**; X-ray data of **6b**; NMR spectra of **3c,e**, **4a−c**, **4e**, **6a−e**, and **9a−c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Professor Dr. Ganesh Pandey on the occasion of his 60th birthday.

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