New Fluorescent Columnar Mesogens Derived from Phenanthrene-Cyanopyridone Hybrids for OLED Application

D. R. Vinayakumara, ^{*a*} Hidayath Ulla, ^{*b*} Sandeep Kumar, ^{*c*} M. N. Satyanarayan, ^{*d*} Airody Vasudeva Adhikari * ^{*a*}

Supporting information

Table of contents

SL NO.	Contents	Page numbers
1	Materials and methods	S2-S4
2	Synthesis scheme	S4
3	Experimental methods	S5-S7
4	FTIR Characterization	S8-S9
5	NMR Characterization	S9-S17
6	HRMS Characterization	S17-S18
7	XRD Characterization	S18
8	Optical Characterization	S19
9	Electrochemical Characterization	S19-S21

6. Material and methods

General: All the chemicals, reagents and solvents were procured from local companies (Sigma-Aldrich, Loba chemi, Merck, S D Fine) and used without further purification. The high quality solvents were used after drying by means of standard procedures. In the chromatographic separations, silica gel (100-200 and 230-400 mesh, Merck made) or neutral aluminium oxide (Merck made) was used as stationary phase. Aluminium sheets coated with silica gel were used for thin layer chromatography (TLC) to monitor the reactions and column purifications. FTIR spectra were measured on Bruker alpha Fourier Transform IR spectrophotometer using ATR method at room temperature and only major peaks are reported in cm⁻¹. ¹H NMR were recorded on Bruker machine at 500 MHz and ¹³C NMR at 125 MHz using CDCl₃ solvent (Sigma-Aldrich made) and chemical shifts were reported in δ related to TMS internal standard. Elemental analysis was performed on a Carlo-Erba Flash 1112 analyser. Mass spectrometric analysis was carried out using MALDI-TOF mass spectrometer.

The optical textures of mesogenic materials were acquired by employing Olympus BX51 Polarized Optical Microscope (POM) connected with a Mettler FP82HT hot stage and FP90 central processor attached with a digital camera (Olympus, Tokyo, Japan). DSC traces were obtained on METTLER TOLEDO DSC 3 STAR^e system with PC system operating on STAR^e software. Prior to the use, the instrument was calibrated using pure indium and zinc. All thermograms were recorded at a scan rate of 5 °C min⁻¹ under a continuous flow of nitrogen gas. The temperature dependent X-ray diffraction (XRD) measurements were performed on unoriented samples filled in a Lindemann capillary of the diameter of 1 mm (Hampton Research) with Cu K_{α} ($\lambda = 1.54060$ Å) radiation using DY 1042-Empyrean X-ray diffractometer comprising a programmable divergence slit and PIXcel 3D detector.

The steady-state UV-visible and fluorescence spectra were recorded using SPECORD S 600 UV-visible spectrophotometer and Fluoromax 4 HORIBA spectrofluorometer, respectively. Absolute quantum yields were determined by using an integrated sphere set-up EDINBURGH (UK) and FLS 980 TCSPC instrument. Fluorescence life time was estimated by employing the Time-Correlated Single Photon Counting (TCSPC) technique using a nano-LED with a spectral width of 1.2 nm as an excitation source and their decay profiles were best fitted using DAS6 software. Electrochemical properties of LC materials were studied by using CH-instrument connected to CHI660E software. The CV experiments were carried out by

employing Ag/AgCl as a reference electrode, calibrated with ferrocene/ferrocenium (Fc/Fc⁺) redox couple which has the absolute energy 4.8 eV to vacuum, glassy carbon as a working electrode, platinum wire as a counter electrode, tetrabutyl ammonium perchlorate (0.1 M) as the supporting electrolyte in dry dichloromethane solvent.

Device Fabrication and Measurement:

The OLED devices were fabricated using patterned indium tin oxide (ITO, Kintec, Hong Kong) coated glass substrates with a sheet resistance of 15 Ω square⁻¹ and ITO thickness of 120 nm were used as transparent anodes. Prior to the deposition of organic materials, the ITO substrates were treated by the UV-Ozone after a careful series of chemical cleaning process.^[1] All the organic and cathode materials were purchased from Sigma-Aldrich and used as received without further purification. A hole injection material poly(3,4-ethylenedioxythiophene)/poly(styrene-sulfonate) (PEDOT: PSS) was spin-coated on the ITO substrates of 50 nm thick from aqueous dispersion and baked at 120 °C for 30 min. Then, Py-2 (device I) or a mixture of CPO-2 (10 wt.%) and the Poly(9-vinylcarbazole) (PVK) host (device II/III) was spin-coated onto the hole injection layer. The thickness of emissive layer was controlled as 80 nm by adjusting the solution concentration and the spin rate. After coating the emission layer, the substrates was annealed at 135 °C for 2 hrs and slowly cooled at a rate of 1 °C/min. In the device II, PVK was also used as a hole transport material. The substrates were then transferred into a deposition chamber to deposit the remaining layers with a base pressure of 10⁻⁵ torr. In case of device III, Bathocuproine (BCP, Sigma Aldrich) as the hole blocking material and tris-(8-hydroxyquinoline)aluminum (Alq₃, Sigma Aldrich) as the electron transport material were deposited in sequences and thicknesses appropriate for the device structure by thermal evaporation. Finally, to improve electron injection, a bilayer cathode consisting of lithium fluoride (LiF, Sigma Aldrich) and aluminium (Al, Alfa Aesar) layers were sequentially deposited on the electron transporting material as a cathode. Here, LiF works as electron injecting material. All organic materials and cathode layers were deposited by thermal evaporation at a chamber pressure of 5 x 10⁻⁶ Torr. The deposition rates of LiF and Al layers were maintained at 0.5 Å s⁻¹, 0.1 Å s⁻¹ and 6 Å s⁻¹, respectively. The cathode was deposited on the top of the structure through a shadow mask. The light-emitting area was 1.6 mm² as defined by the overlap of the cathode and anode. Electroluminescence spectra was acquired using a Horiba Jobin Yvon iHR320 spectrophotometer with an attached charge-coupled device (CCD) camera. The opt-electrical characteristics were recorded in a customized setup using a computer-controlled programmable Keithley 2400 SMU for recording the current-voltage

characteristics while the luminance was measured by a Keithley 6485 picoammeter using a calibrated Si photodiode (SM1PD2A). CIE coordinates were calculated from the EL spectra. Devices were driven under DC conditions. All the measurements were carried out at room temperature under dark and ambient conditions without any encapsulation.

2. Synthesis scheme



Scheme 1. Reagents and conditions: Na₂S₂O₄, KOH, Bu₄NBr, C₁₂H₂₅Br, 1:1 H₂O and THF, RT, 48 hrs, 75%; (b) CH₃COCl, AlCl₃, DCM, -5 to 25 °C, 1h, 80 %; (c) K₂CO₃, KI, *n*-RBr, DMF, 75 °C, 12hrs, 69-85 %; (d) LAH, anhydrous THF, -5 °C– 25 °C, 18 hrs, 83-92 %; \in PCC, dry DCM, 3 hrs, 80-63 %; (f) ethyl cyanoacetate, ammonium acetate, EtOH, 16 hrs, 25-36 %

3. Experimental Section

Synthesis of 9,10-bis(dodecyloxy)phenanthrene (2)

A mixture of 9,10-phenanthrenequinone (5 g, 24.0 mmol), Na₂S₂O₄ (22.78 g, 144 mmol) and Bu₄NBr (4.64 g, 14.4 mmol) in 200 mL THF: H₂O (1:1, v/v) was stirred for 15 mins. To this mixture, dodecyl bromide (17.95 g, 72 mmol) followed by aqueous KOH (20 g, 360 mmol, in 100 mL of H₂O) was added slowly and the stirring was continued for further 48 hrs. The reaction mixture was diluted with 150 mL of water and then extracted with ethyl acetate (200 mL × 2). The combined organic layers was washed with water, brine, then dried over anhydrous Na₂SO₄ and evaporated the solvent to dryness. Finally recrystallized using methanol to yield product **2** as pure white solid (yield, 75 %). ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 8.66 (m, 2H), 8.26 (m, 2H), 7.65 (m, 4H), 4.23 (t, 4H, *J* = 7 Hz,), 1.94 (m, 4H), 1.59 (m, 2H), 1.42 (m, 34H), 0.91 (t, *J* = 7 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 143.24, 129.64, 128.62, 126.70, 125.63, 122.58, 122.30, 73.66, 31.96, 30.56, 29.71, 29.62, 29.41, 26.31, 22.73, 14.15; FTIR (ATR, v_{max} in cm⁻¹): v- 3071 (Ar C-H), 2915 (Ar C-H), 2847 (Aliph C-H), 1620 (Ar C=C); Elemental Anal. Calcd (%) for C₃₈H₅₈O₂: C 83.46, H 10.69; Found: C 83.39, H 11.09.

Synthesis of 1-(9,10-bis(dodecyloxy)XXXhenanthrene-3-yl)ethanone (3)

The compound **3** (5 g, 9.15 mmol) was taken in 75 mL of dry DCM, to which acetyl chloride (0.71 g, 9.15 mmol) was added and stirred at -5 °C under an argon atmosphere. At the same conditions, anhydrous AlCl₃ (1.46 g, 10.98 mmol) was then added in portion wise. The mixture was stirred at same temperature for about 30 mins, then gradually warmed to room temperature. After confirming the completion of the reaction by TLC, the mixture was poured into icecooled water, extracted with DCM (50 mL ×2) and dried over Na₂SO₄ and passed through Celite. The solvent was removed under reduced pressure and crude product was purified by silica gel column chromatography (100-200 mesh size) using pet-ether and ethyl acetate (2:8) as eluents to give product **3** as pale white solid (yield, 80%). ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 9.02 (s, 1H), 8.66 (dd, 1H, *J* = 6.0 3.5 Hz), 8.21 (dd, 1H, *J* = 8.5, 4.0 Hz), 8.08 (m, 2H), 7.69 (m, 2H), 4.18 (t, 2H, *J* = 6.5 Hz), 4.12 (t, 2H, *J* = 6.5 Hz), 2.72 (s, 3H), 1.87-1.81 (m, 4H), 1.52-1.46 (m, 8H), 1.35-1.19 (m, 28H), 0.81 (t, 6.5 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 198.07, 145.68, 142.71, 133.93, 132.88, 129.90, 129.08, 127.95, 127.30, 126.36, 125.63, 123.76, 122.68, 122.62, 122.61, 73.77, 31.96, 30.53, 30.48, 29.60, 26.86, 26.25, 22.72, 14.14; FTIR (ATR, v_{max} in cm⁻¹): v- 2912 (Ar C-H), 2847

(Aliph C-H), 1666 (ketone C=O), 1612 (Ar C=C); Elemental Anal. Calcd (%) for C₄₀H₆₀O₃: C 81.58, H 10.27; Found: C 81.61, H 10.33.

For **7a**, ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ- 9.83 (s, 1H), 7.09 (s, 2H), 4.04 (m, 6H), 1.85-1.72 (m, 6H), 1.5-1.3 (m, 30H), 0.9 (m, 9H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ- 191.19, 153.52, 143.88, 131.47, 107.87, 73.61, 69.23, 31.84, 30.34, 29.48, 29.30, 26.03, 22.66, 14.06; FTIR (ATR, ν_{max} in cm⁻¹): ν- 2922 (Ar C-H), 2854 (Aliph C-H), 2728 (aldehyde C-H), 1694 (aldehyde C=O), 1583 (Ar C=C); Elemental Anal. Calcd (%) C₃₁H₅₄O₄: C 75.87, H 11.09; Found: C 75.85, H 11.12.

For **7b**, ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 9.84 (s, 1H), 7.10 (s, 2H), 4.06 (m, 6H), 1.86-1.75 (m, 6H), 1.64-1.28 (m, 54H), 0.9 (t, 9H, J = 5.5 Hz); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 191.24, 153.53, 143.91, 131.46, 107.89, 73.63, 69.26, 31.93, 30.35, 29.58, 29.27, 26.03, 22.69, 14.09; FTIR (ATR, v_{max} in cm⁻¹): v- 2915 (Ar C-H), 2847 (Aliph C-H), 2730 (aldehyde C-H), 1692 (aldehyde C=O), 1580 (Ar C=C); Elemental Anal. Calcd (%) for C₄₃H₇₈O₄: C 78.36, H 11.93; Found: C 78.26, H 12.01.

For **7c**, ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 9.84 (s, 1H), 7.10 (s, 2H), 4.06 (m, 6H), 1.86-1.75 (m, 6H), 1.64-1.28 (m, 78H), 0.9 (t, 9H, J = 6.0 Hz); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 191.24, 153.53, 143.91, 131.46, 107.90, 73.63, 69.26, 31.93, 30.35, 29.71, 29.67, 29.63, 29.55, 29.37, 29.27, 26.03, 22.69, 14.10; FTIR (ATR, ν_{max} in cm⁻¹): ν - 2913 (Ar C-H), 2847 (Aliph C-H), 2730 (aldehyde C-H), 1691 (aldehyde C=O), 1585 (Ar C=C); Elemental Anal. Calcd (%) for C₅₅H₁₀₂O₄: C 79.80, H 12.55; Found: C 79.89, H 12.05.

General procedure for synthesis of phenanthrene-cyanopyridone hybrids Py-1 to Py-3

A mixture of compound **3** (1 g, 1.6 mmol), **7a** (0.83 g, 1.6 mmol), ethyl cyanoacetate (0.23 g, 2.03 mmol) and ammonium acetate (1.30 g, 16.99 mmol) in 30 mL of absolute ethanol was heated to 70 °C for 16 hrs. The mixture was then allowed cool to RT, the obtained precipitate was filtered and washed with ethanol. The final compound was isolated from the mixture by columnar chromatographic method using 2 % of the ethyl acetate in the pet-ether solvent and finally recrystallized with DCM and methanol mixture to get greenish yellow gummy solid (yield, 36%). ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 12.35 (s, 1H), 9.1 (s, 1H), 8.81 (d, 1H, *J* = 8.0 Hz), 8.32 (d, 1H, *J* = 8.5 Hz), 8.21 (d, 1H, *J* = 8.5 Hz), 7.91 (d, 1H, *J* = 8.5 Hz), 7.68 (t, 1H, *J* = 7.0 Hz,) 7.60 (t, 1H, *J* = 7.5 Hz), 6.83 (s, 2H), 6.82 (s, 1H), 4.18 (t, 2H, *J*

= 6.5 Hz), 4.12 (t, 2H, *J* = 6.5 Hz), 3.98 (m, 6H), 1.85 (m, 4H), 1.79-1.68 (m, 6H), 1.52-1.20 (m, 66H), 0.83 (m, 15H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ- 163.65, 161.20, 153.39, 150.42, 145.57, 142.47, 140.47, 131.86, 130.81, 130.05, 128.90, 128.65, 128.55, 127.61, 126.92, 124.36, 123.83, 122.54, 121.86, 106.94, 99.39, 73.79, 69.48, 31.88, 30.46, 29.50, 26.21, 22.69, 14.11; FTIR (ATR, v_{max} in cm⁻¹): v- 2920 (Ar C-H), 2851 (Aliph C-H), 2216 (C=N), 1627 (amide C=O), 1594 (Ar C=C); Elemental Anal. Calcd (%) for C₇₄H₁₁₂N₂O₆: C 78.96, H 10.03, N 2.49; Found: C 78.76, H 10.23, N 2.42; HRMS (ESI+) exact mass calculated for C₇₄H₁₁₂N₂O₆ (M+1): 1125.8812, Found: 1125.8801.

Compounds **Py-2** and **Py-3** were prepared by adopting the similar procedure as described for **Py-1**.

For **Py-2**, greenish yellow (yield, 28%), ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 12.65 (s, 1H), 9.22 (s, 1H), 8.93 (d, 1H, J = 8.0 Hz), 8.41 (d, 1H, J = 8.5 Hz), 8.30 (d, 1H, J = 8.0 Hz), 8.0 (d, 1H, J = 8.5 Hz), 7.78 (t, 1H, J = 7.0 Hz) 7.69 (t, 1H, J = 7.5 Hz), 6.92 (s, 3H), 4.28 (t, 2H, J = 6.5 Hz), 4.22 (t, 2H, J = 6.5 Hz), 4.07 (m, 6H), 1.92 (m, 4H), 1.87-1.78 (m, 6H), 1.63-1.27 (m, 90 H), 0.90 (m, 15H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 163.82, 161.18, 153.39, 150.51, 145.57, 142.47, 140.45, 131.84, 130.82, 130.02, 128.91, 128.65, 128.47, 127.57, 126.94, 124.43, 123.36, 122.51, 121.95, 106.93, 99.32, 73.79, 69.49, 31.94, 30.50, 29.62, 26.22, 22.70, 14.12; FTIR (ATR, v_{max} in cm⁻¹): v- 2918 (Ar C-H), 2849 (Aliph C-H), 2218 (C=N), 1643 (amide C=O), 1595 (Ar C=C), Elemental Anal. Calcd (%) for C₈₆H₁₃₆N₂O₆: C 79.82, H 10.59, N 2.16; Found: C 80.01, H 10.60, N 2.18.

For **Py-3**, greenish yellow (yield, 25%), ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 12.70 (s, 1H), 9.22 (s, 1H), 8.91 (d, 1H, J = 8.0 Hz), 8.41 (d, 1H, J = 8.5 Hz), 8.30 (d, 1H, J= 8.0 Hz), 8.0 (d, 1H, J = 8.5 Hz), 7.78 (t, 1H, J = 7.5 Hz) 7.69 (t, 1H, J = 7.5 Hz), 6.92 (s, 3H), 4.28 (t, 2H, J = 6.5 Hz), 4.22 (t, 2H, J = 6.5 Hz), 4.07 (m, 6H), 1.94 (m, 4H), 1.88-1.79 (m, 6H), 1.63-1.27 (m, 114 H), 0.89 (m, 15H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ in ppm): δ - 163.82, 161.17, 153.39, 150.51, 145.57, 142.47, 140.45, 131.84, 130.82, 130.02, 128.91, 128.65, 128.46, 127.57, 126.95, 124.43, 123.78, 122.51, 121.95, 106.95, 99.32, 73.79, 69.49, 31.95, 30.49, 29.63, 26.23, 22.70, 14.12; FTIR (ATR, v_{max} in cm⁻¹): v- 2919 (Ar C-H), 2849 (Aliph C-H), 2217 (C=N), 1656 (amide C=O), 1630 (Ar C=C), Elemental Anal. Calcd (%) for C₉₈H₁₆₀N₂O₆: C 80.49, H 11.03, N 1.92; Found: C 80.13, H 11.59, N 1.89; HRMS (ESI+) exact mass calculated for C₉₈H₁₆₀N₂O₆ (M+1): 1463.2399, Found: 1463.2533.

4. FTIR Characterization





5. NMR Characterization



Figure S4: ¹H NMR (500 MHz) spectrum of intermediate 2 recorded in CDCl₃



Figure S6: ¹H NMR (500 MHz) spectrum of intermediate 3 recorded in CDCl₃



Figure S7: ¹³C NMR (125 MHz) spectrum of intermediate 3 recorded in CDCl₃



Figure S8: ¹H NMR (500 MHz) spectrum of intermediate 7a recorded in CDCl₃



Figure S9: ¹³C NMR (125 MHz) spectrum of intermediate 7a recorded in CDCl₃



Figure S10: ¹H NMR (500 MHz) spectrum of intermediate 7b recorded in CDCl₃



Figure S12: ¹H NMR (500 MHz) spectrum of intermediate 7c recorded in CDCl₃

2.00

6.00

3.95 2.10 5.14 5.14 9.06

1.02



Figure S13: ¹³C NMR (125 MHz) spectrum of intermediate 7c recorded in CDCl₃



Figure S14: ¹H NMR (500 MHz) spectrum of Py-1 recorded in CDCl₃



Figure S16: ¹H NMR (500 MHz) spectrum of Py-2 recorded in CDCl₃



Figure S18: ¹H NMR (500 MHz) spectrum of Py-3 recorded in CDCl₃



6. HRMS characterization









7. XRD Characterization



Figure S22. XRD pattern of Py-2 obtained: (a) for Col_h phase and (b) for Col_r phase



Figure S23. XRD pattern of Py-3 obtained: (a) for Col_h phase and (b) for Col_r phase

8. Optical characterization



Figure S24. Absorption and emission spectra of Py-1 to Py-3 in DCM at $c = 2 \times 10^{-5}$ M



Figure S25. (a) Absorption and (b) emission spectra of Py-1 recorded in solvents of varied polarity

Solvent	$\lambda_{abs}(nm)$	$\lambda_{em}(nm)$	Stokes shift (cm ⁻¹)
Hexane	394	481	4591
DCM	394	501	5420
Ethyl acetate	385	472	4788
Toluene	391	475	4522
THF	382	473	5037
DMF	398	499	5085

Table S1. Solvatochromic data of Py-1

9. Electrochemical cauterization







Figure S27. Calibration of electrochemical cell using ferrocene



Figure S28. Cyclic voltammograms of Py-1: (a) full spectra (b) zoomed reduction wave and (c) zoomed oxidation wave



Figure S29. Cyclic voltammograms of Py-2: (a) full spectra (b) zoomed reduction wave and (c) zoomed oxidation wave



Figure S30. Cyclic voltammograms of Py-3: (a) full spectra (b) zoomed reduction wave and (c) zoomed oxidation wave

References

[1] H. Ulla, M.R. Kiran, B. Garudachari, T.N. Ahipa, K. Tarafder, A.V. Adhikari, G. Umesh, M.N. Satyanarayan, *Journal of Molecular Structure* **2017**, *1143*, 344.