Supporting Information

Eumelanin-inspired core derived from vanillin: A new building block for organic semiconductors

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General methods and materials

Anhydrous *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from solvent purification system under ultra-pure argon. All other commercial reagents were used as received. Unless otherwise specified, all reactions were run in oven-dried glassware. Reactions were monitored by thin layer chromatography on silica G TLC plates (Sorbent Technologies No. 1634126). Purifications were performed by column chromatography on silica gel (Sorbent Technologies, 40-63 μ m particle size) or neutral alumina (Sorbent Technologies, 32-63 μ m particle size). The saturated NaCl, NH₄Cl and NaHCO₃ used in work-up procedures were

aqueous solutions. ¹H- and ¹³C-NMR spectra were measured on a Bruker Avance 400 MHz instrument. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA 30071. Cyclic voltammetry was performed on a CH-instruments 6017E model with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in dry acetonitrile using a glassy carbon as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode with a scan rate of 100 mV/sec. The HOMO and LUMO energy values were calculated from the onset of the first oxidation and reduction potentials from the equations $E_{HOMO} (eV) = - [E_{ox}^{onset} - E_{1/2} (Fc/Fc^{+}) + 4.8] \text{ and } E_{LUMO} (eV) = - [E_{red}^{onset} - E_{1/2} (Fc/Fc^{+}) + 4.8],$ where $E_{1/2}$ (Fc/Fc⁺) was the cell correction. Gel permeation chromatography was performed using Waters pump with a Waters 2410 refractive index detector using THF as solvent at 30 °C with flow rate 1.0 mL/min. Polystyrene standards were used for calibration. UV-vis spectra were recorded on a Cary 5000 VIS-NIR spectrophotometer. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. Fluorescence and UV-vis measurements were taken in CHCl₃. Polymer film was prepared by drop-casting polymer dissolved in CHCl₃. Optical bandgap was calculated from wavelength corresponding to the energy absorption onset from the intersection of the leading edge tangent with the x-axis. The polymer thin film was prepared by spin-coating from a 20 mg/mL solution in chloroform onto a clean Si wafer at 1000 rpm. The AFM measurements are carried out in an NT-MDT NTEGRA Prima AFM under semicontact mode using a silicon tip (spring force constant = 1.2 - 6.4 N/m). Ouantum vield measurements were performed in dilute CHCl₃ solutions with absorbances ranging from 0.01 to 0.04. Quinine sulfate was used as the reference. The excitation wavelength of 313 nm was used to obtain the fluorescence spectra for each solution ranging from 320 to 600 nm. The fluorescence intensity (area of the fluorescence spectrum) was then calculated and recorded. (see table below) Quantum yields were calculated using following equation: $\Phi_s = \Phi_r (\frac{A_r F_s}{A_s F_r}) (\frac{n_s^2}{n_s^2})$. Φ_r is 0.51, $A_{s and} A_r$ are absorbances of the sample and reference solutions, respectively at the same excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities, n is the refractive index [CHCl₃ ($n_s = 1.445$) and 1 N H₂SO₄ ($n_r = 1.339$) were used]

Sampla	Abs.	Fluorescence	Emission	
Sample		Intensity	Maxima (nm)	
	0.01	14578	455	
Stor dowd	0.02	22858		
Standard	0.03	32544		
	0.04	46907		
	0.01	25335	436	
0	0.02	32126		
9a	0.03	40564		
	0.04	55604		
	0.01	27312	426	
015	0.02	35785		
90	0.03	47224		
	0.04	60870		
	0.01	19194		
Dolymon	0.02	23513	509	
roiymer	0.03	29978	508	
	0.04	37315		

 Table S1 Quantum yield experimental data.

Crystallography Experimental

Crystallographic data are collected in Table 1. A Bruker Ultra diffractometer equipped with a mini rotating-anode Mo source and microfocus optics was used for data collection with one-second, one-degree width images. Direct methods were used for structure solution and all non-hydrogen atoms were refined with anisotropic thermal parameters and without restraint. Hydrogen atoms were included as idealized contributions. All software was contained in the current packages of SHELX software as provided by the Bruker Corporation (Madison, WI).

Experimental section

3,4-Dimethoxybenzaldehyde (2): To a stirred solution of vanillin **1** (10.0 g, 65.7 mmol) in DMF (50 mL), was added potassium carbonate (13.68 g, 99.0 mmol), CH_3I (14.0 g, 99.0 mmol) and a crystal of 18-crown-6 and stirred it at room temperature for overnight. The crude reaction mixture was poured into ice-cold water to give off-white solid (10.4 g, 96%). This was taken as such to next step without any purification.

4,5-Dimethoxy-2-nitrobenzaldehyde (3): In a 500 mL Erlenmeyer flask with a magnetic stirrer, 50 mL nitric acid was taken. To this mixture compound **2** (10 g, 60.2 mmol) was crushed and added in small portions for about a period of 15 min. The internal temperature was checked and maintained in the range of 18-22 °C. After 15 min of stirring the reaction mixture was poured in aluminum foil covered beaker containing 500 mL of ice cold water. After stirring for 15 min in dark, the solid was filtered and dried to yield 11.34 g (89%). This was taken as such to next step without any purification.²



2,5-Dibromo-3,4-dimethoxy-6-nitrobenzaldehyde (**4**): In a 250 ml 3-neck round bottomed flask compound **3** (10.0g, 47.2 mmol) was taken along with concentrated sulfuric acid (40 mL). To this NBS (25.3g, 142.0 mmol) was added in portions over a period of 30 min. Then the reaction vessel was stoppered using septum and completely covered with aluminum foil to exclude light. After stirring the reaction mixture for 16 h at room temperature the reaction mixture was poured over 200 mL of ice cold water. The resulting precipitate was stirred for 15 min and filtered. The solid was washed again with water twice by transferring it to a beaker containing 150 mL of ice cold water, stirred for 10 min and filtered (Yield 84%). The crude product was taken as such to next step without purification.³



Methyl-3-(2,5-dibromo-3,4-dimethoxy-6-nitrophenyl)acrylate (5): In a Erlenmeyer flask, triphenylphosphine (3.3 mmol), methyl bromoacetate (3.4 mmol) and saturated aqueous solution of NaHCO₃ (15V) were taken and stirred for 1 h at room temperature, then compound **1** (5.0g, 13.5 mmol) was added to it and stirred at room temperature for 3 h. The reaction mixture was extracted with EtOAc (3×50 mL). The organic layer was washed with water, saturated NaCl, dried (Na₂SO₄), and concentrated under vacuum to give a thick brown liquid. The compound was purified using a silica gel column and eluted with Hexane/EtOAc (95:5). Evaporation of the solvent yielded product **2** (4.31 g, 78%) as a pale yellow solid.⁴ ¹H NMR (400 MHz, Chloroform-d) δ 7.57 (d, J = 16.3 Hz, 1H), 6.14 (d, J = 16.2 Hz, 1H), 3.96 (d, J = 8.6 Hz, 6H), 3.80 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.36, 152.56, 151.82, 147.06, 137.26, 125.83, 125.62, 119.80, 109.64, 61.40, 61.15, 52.18. *Anal.* Calcd for C₁₂H₁₁Br₂NO₆: C, 33.91; H, 2.61; N, 3.30. Found: C, 34.17; H, 2.55; N, 3.29.



Methyl-4,7-dibromo-5,6-dimethoxy-1H-indole-2-carboxylate (6): In a 100 mL 3-neck round bottomed flask compound **5** (2.0 g, 4.7 mmol) was taken along with triphenylphosphine (2.9 g,11.3 mmol) and MoO₂Cl₂(dmf)₂ (80.3 mg, 50 mol%) under nitrogen. The MoO₂Cl₂(dmf)₂ was prepared according to the reported procedure.¹ To this 40 mL of dry toluene was added and refluxed for 4 h, then 3 mL of DMSO was added and refluxed for 40 min. After the reaction was over, the solvent was evaporated and column purification was done using an alumina packed column. The product eluted with Hexane/EtOAc/Et₃N (83.5:15:1.5), to yield a while solid (1.34g, 72 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 3.99 – 3.89 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 161.47, 150.24, 146.97, 132.36, 128.16, 124.74, 110.07, 109.41, 98.84, 61.60, 61.41, 52.31. *Anal*. Calcd for C₁₂H₁₁Br₂NO₄: C, 36.67; H, 2.82; N, 3.56.



Methyl-4,7-dibromo-5,6-dimethoxy-1-methyl-1*H*-indole-2-carboxylate (7): To a stirred solution of compound 3 (4.6 g, 11.7 mmol) in DMF (40 mL), was added potassium carbonate (4.0 g, 29.4 mmol), CH₃I (4.1 g, 29.4 mmol) and a crystal of 18-crown-6 and stirred it at room temperature for 2 h. The crude reaction mixture was poured into ice-cold water to give off-white solid (3.93 g, 95 %). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.29 (s, 1H), 4.46 (s, 3H), 3.91 (d, J = 0.8 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 161.97, 150.55, 146.81, 133.22, 130.14, 125.33, 111.77, 109.59, 100.12, 61.51, 61.42, 52.14, 35.06. Elemental Anal. Calcd for C₁₃H₁₃Br₂NO₄: C, 38.36; H, 3.22; N, 3.44. Found: C, 38.48; H, 3.16; N, 3.43.



Methyl 5,6-dimethoxy-1-methyl-4,7bis(phenylethynyl)-1*H*-indole-2-carboxylate (9a): In a 8 mL reaction vial, compound 7 (50 mg, 0.123 mmol) was taken and under an argon atmosphere Pd(PPh₃)₄ (7.0 mg, 5 mol%), CuI (0.57 mg, 0.003 mmol), Et₃N (2 mL) and phenylacetylene (32.61 mg, 0.32 mmol) were added and sealed. The reaction vial was heated to 80 °C for a period of 16 h. After 16 h the solvent was evaporated. The resulting residue was purified using by column chromatography using alumina column using Hexane/EtOAc (98:2) to afford the yellow color solid in 98 % yield.⁵¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 4H), 7.44 – 7.37 (m, 7H), 4.56 (s, 3H), 4.06 (d, J = 2.0 Hz, 6H), 3.92 (s, 3H). ¹³C NMR (101 MHz, cdcl3) δ 162.23, 154.89, 150.24, 134.50, 131.88, 131.22, 129.08, 128.81, 128.72, 128.67, 128.53, 124.54, 123.40, 123.37, 111.07, 110.59, 104.92, 103.47, 99.91, 98.68, 83.55, 83.09, 61.95, 61.87, 51.88, 33.77. Elemental Anal. Calcd for C₂₉H₂₃NO₄0.2H₂O: C, 76.87; H, 5.21; N, 3.09. Found: C, 76.83; H, 5.47; N, 3.02.



Methyl 5,6-dimethoxy-4,7bis((4-methoxy-phenyl)ethynyl)-1-methyl-1*H*-indole-2carboxylate (9b): This compound was prepared using the procedure reported for 9a (Yield 76 %) ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.47 (m, 4H), 7.43 (s, 1H), 6.97 – 6.88 (m, 4H), 4.55 (s, 3H), 4.05 (d, *J* = 1.9 Hz, 6H), 3.92 (s, 3H), 3.86 (d, *J* = 0.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 162.15, 159.94, 159.88, 154.50, 149.86, 134.43, 133.23, 132.57, 128.74, 124.33, 115.47, 114.20, 114.05, 110.91, 110.56, 103.32, 99.79, 98.58, 82.24, 81.67, 61.74, 55.38, 51.70, 33.61, 29.71. Elemental Anal. Calcd for C₃₁H₂₇NO₆: C, 73.07; H, 5.34; N, 2.75. Found: C, 72.87; H, 6.41; N, 2.44.



1,4-dibromo-2,5-bis(dodedecyloxy)benzene (10a): To a mixture of 2,5-Dibromobenzene-1,4diol (2.0 g, 7.5 mmol) and K₂CO₃ (2.0 g, 15 mmol), 15 mL of dry DMF was added and stirred at room temperature for 1 h. Then 1-bromodecane (3.94 g, 15,8 mmol) was added dropwise into the reaction mixture and heated to 80 °C for 12 h. The reaction misture was cooled to room temperature and added to a beaker containing 80 mL of ice cold water, stirred for 20 min, and the resulting solid was filtered. The solid was purified using column chromatograph Hexane/EtOAc (99:1) to yield white color solid (68 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.86 – 1.74 (m, 4H), 1.56 – 1.41 (m, 4H), 1.41 – 1.23 (m, 32H), 0.92 – 0.84 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 150.08, 118.47, 111.14, 70.32, 31.93, 29.67, 29.65, 29.59, 29.56, 29.36, 29.31, 29.13, 25.94, 22.71, 14.13.



2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)bis(trimethylsilane) (**10b):** Dry THF (5 mL) was added to **10a** (1.0 g, 1.6 mmol) and to this a mixture of CuI, Pd(PPh₃)₄ and triethylamine taken inside a glove box was added and heated to 40 °C for 12 h. Solvent was evaporated and the resulting crude was purified using column chromatography using Hexane/EtOAc (96:4) to yield white color solid (98%).¹H NMR (400 MHz, Chloroform-*d*) δ 6.88 (s, 2H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.78 (dt, *J* = 14.7, 6.5 Hz, 4H), 1.48 (q, *J* = 7.2 Hz, 4H), 1.28 (d, *J* = 17.1 Hz, 32H), 0.92 – 0.84 (m, 6H), 0.25 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 154.05, 117.23, 113.97, 101.11, 100.11, 69.49, 31.97, 29.72, 29.68, 29.48, 29.40, 26.07, 22.74, 14.16.



1,4-bis(dodecyloxy)-2,5-diethynylbenzene (10): The compound **10b** (0.97 g, 1.5 mmol) was taken along with 20 mL methanol and 75 mL THF and stirred at room temperature for 16 h. To 200 mL of diethyl ether in separatory flask the reaction mixture was added followed by 100 mL of brine solution. Another 2 × 50 mL extraction was done, the organic layers were combined dried over anhy. Na2So4 and the solvent was evaporated to yield yellow solid (0.74 g, 99%).¹H NMR (400 MHz, Chloroform-*d*) δ 6.95 (s, 2H), 3.97 (t, *J* = 6.6 Hz, 4H), 3.32 (s, 2H), 1.85 – 1.73 (m, 4H), 1.50 – 1.40 (m, 4H), 1.34 – 1.24 (m, 32H), 0.92 – 0.83 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 153.98, 117.73, 113.24, 82.39, 79.79, 69.66, 31.93, 29.67, 29.65, 29.59, 29.57, 29.36, 29.33, 29.13, 25.90, 22.70, 14.13.

Polymer synthesis:

A 10 mL reaction vial compound **7** (50 mg, 0.122 mmol) and compound **10** was taken inside a glove box and added compound Pd(PPh₃)₄ (3.5 mg, 0.003 mmol), and CuI (0.6 mg, 0.003 mmol), followed by 1 mL of Et₃N and 1 mL of THF. The vial was sealed inside the glove box and brought outside and heated to 80 °C for 48 hours. Then the reaction mixture was cooled. The polymer was precipitated in beaker containing 40 mL of methanol, the resulting precipitate was filtered through a Soxhlet thimble, which was then subjected to methanol, hexane and chloroform extractions. The solvent was evaporated to yield the red polymer in 36 % yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.48-7.56 (broad, aryl and indole protons), δ 7.05-7.11 (broad, aryl and indole protons), δ 1.85-1.96 (broad, -CH₂), δ 1.54 (broad, -CH₂), δ 1.24-1.36 (broad, -CH₂), δ 0.85-0.88 (broad, CH₃).



¹³C NMR of **5**





¹³C NMR of **6**





¹³C NMR of **7**





¹³C NMR of **9a**



 1 H NMR of **9b**



¹³C NMR of **9b**





¹³C NMR of **10a**

¹³C NMR of **10**

¹H NMR polymer

Fig. S1 Emission spectra for compounds 9a and 9b

Fig. S2 Absorption spectra for polymer in solution and casted thin film

Fig. S3 Emission spectrum for polymer in solution

Fig. S6 Cyclic voltammogram of 9b

Fig. S5 Cyclic voltammogram of 9a

Fig. S7 Cyclic voltammogram of polymer

Fig. S7 X-ray crystal structure of compound 9a

Table 1. Crystal data and structure refinem	ent		
Identification code	nelson01		
Empirical formula	C29 H23 N O4		
Formula weight	449.48		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P -1		
Unit cell dimensions	a = 7.8653(6) Å	a= 105.750(2)°.	
	b = 12.7093(10) Å	$b = 100.500(2)^{\circ}$.	
	c = 12.7665(9) Å	$g = 105.510(2)^{\circ}$.	
Volume	1137.97(15) Å ³		
Z	2		
Density (calculated)	1.312 Mg/m ³		
Absorption coefficient	0.087 mm ⁻¹		
F(000)	472		
Crystal size	0.300 x 0.250 x 0.150 mm ³		
Theta range for data collection	2.762 to 31.137°.		
Index ranges	-11<=h<=10, -9<=k<=18, -18<=l<=17		

14731
6390 [R(int) = 0.0393]
99.6 %
Multi-scan
Full-matrix least-squares on F ²
6390 / 0 / 311
1.035
R1 = 0.0498, wR2 = 0.1161
R1 = 0.0819, wR2 = 0.1347
n/a
0.361 and -0.290 e.Å ⁻³

0.361 and -0.29

Fig. S8 800×800 nm AFM topography image of the polymer thin film on Si wafer

The morphology of the spin-coated polymer thin films was characterized by AFM, as shown in above. The polymer thin film appears to be composed of packed small grains varying in size and shape averaging 20 nm in diameter. Further quantitative analysis showed a surface RMS roughness of 1.8 nm for the polymer thin films.

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