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COMMUNICATION

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

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An eumelanin-inspired core derived from the natural product, vanillin (vanilla bean extract) was utilized for the synthesis of eumelanin-inspired small molecules and polymer via Sonogashira cross coupling. The materials demonstrate that the methyl 4,7-dibromo-5,6-dimethoxy-*N*-methyl-1*H*-indole-2-carboxylate core can serve as a new building block for organic semiconductors.

Organic semiconductors have attracted considerable attention due to the promise of low cost, lightweight, and flexible large area electronic devices.¹ Most of these materials are derived from petroleum-based starting materials. Due to the increasing demand on oil, it would be advantageous to seek alternative sources for building blocks to develop new organic semiconductors.

In terms of chemical and functional diversity, nature is a great source of new building blocks for bioinspired organic semiconductors. One such inspiration is the biopolymer, melanin which is a class of naturally occurring pigments found in the hair, eyes, skin, and the brain of mammals and acts as a natural photoprotector against the harmful effects of UV radiation.² Eumelanin is the black-brown variety of melanin and exist as a heterogeneous network, formed by the oxidative polymerization of two monomers 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA) (Fig. 1).³

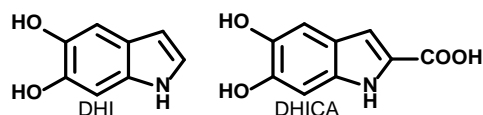
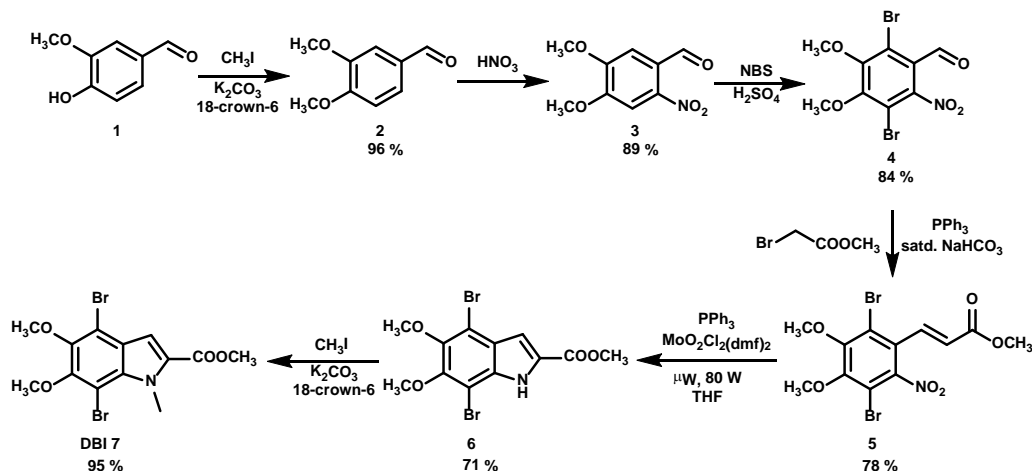


Fig. 1 Structures of DHI and DHICA.

Extensive research has been done on the optical, electronic, physical, metal chelating, and structural properties of natural and synthetic eumelanins.³⁻⁴ McGinness and Proctor's groundbreaking work on electrical switching established eumelanins as amorphous organic semiconductors.⁵ These eumelanins have excellent light absorption ranging from 200 nm to 700 nm in the electromagnetic spectrum, electrical conductivity reaching 10^{-5} Scm^{-1} and exhibit good charge mobility as high as $2.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶ Hence, it seems appropriate and fitting to utilize the eumelanin indole moiety as a platform for the development of new organic semiconductors.^{2a}

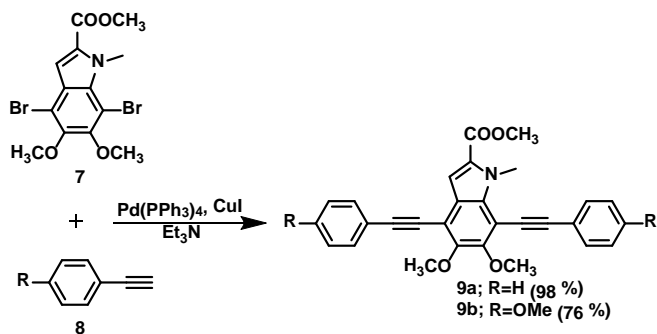
Here, we present the synthesis of a eumelanin-inspired core molecule from the natural product, vanillin. The eumelanin-inspired building block was designed so that functionalization on the 4,7-positions on the central indolic benzene ring can be feasible via transition metal-catalyzed cross-coupling reactions. Two new eumelanin-inspired compounds with interesting optoelectronic properties were synthesized by Sonogashira cross-coupling.

The synthesis of the methyl 4,7-dibromo-5,6-dimethoxy-*N*-methyl-1*H*-indole-2-carboxylate (DBI) eumelanin-inspired core **7** is shown in Scheme 1. Vanillin (**1**) was methylated to give dimethoxybenzaldehyde (**2**), which was nitrated to yield **3**.⁷ Bromination of **3** using *N*-bromosuccinimide resulted in compound **4**.⁸ A modified procedure was used to synthesize the olefin **5** using methyl bromoacetate in aqueous sodium bicarbonate, followed by microwave-assisted Cadogan synthesis to afford **6**.⁹ Finally, the indole was *N*-methylated to avoid unwanted by-products during the cross coupling reactions. Compound **7** was synthesized with bromo groups at the 4 and 7 positions of the indole moiety so it could serve as a universal partner for metal-catalyzed coupling reactions. This approach allowed for the functionalization at the 4 and 7 positions with alkynyl substituents using Sonogashira cross-coupling (scheme 2). The ethynyl group was chosen because of its ability to alter optoelectronic properties by extended effective π -conjugation length.¹⁰



Scheme 1 Synthesis of eumelanin-inspired core (DBI) 7 from vanillin.

The coupling reaction was carried out using $\text{Pd}(\text{PPh}_3)_4$, CuI and triethylamine (Et_3N) as solvent and base to afford the products **9a** and **9b** in high yields.¹¹ X-ray quality crystals of **9a** were grown from a vapour diffusion of ether and dichloromethane solutions (see Supporting Information for the crystallographic data).



Scheme 2 Synthesis of compounds **9a** and **9b**.

The UV-vis absorption (Figure 2) and photoluminescence (PL) of the eumelanin-inspired small molecules were investigated and summarized in the Table 1. The 4,7-substituted eumelanin-inspired small molecules **9a** and **9b** featured red-shifted absorbance maxima due to extended conjugation of the system compared to the unsubstituted core **7** (abs λ_{max} 308 nm). While the absorption band at lower wavelength (~300 nm) corresponds to the indole core, the ethynyl substitution extends the conjugation through the eumelanin inspired core which resulted in the absorption band ca. 400 nm. Moreover, the incorporation of the methoxy group at the *para* position of the phenyl ring (**9b**) resulted in a slight red shift in absorption spectrum compared to **9a**. The DBI core displayed very weak fluorescence whereas **9a** and **9b** had PL maxima of 436 nm and 449 nm, respectively. The PL quantum yields of the **9a** and **9b** in dilute chloroform solutions were 0.82 and 0.91, respectively (details in supporting information). Optical bandgaps were estimated from the onset of the absorption are shown in Table 1. The compound **7** had a bandgap of 3.25 eV and as expected the 4,7-substituted molecules **9a** and **9b** with extended conjugation showed reduced optical bandgaps of 2.94 and 2.87 eV, respectively.

Cyclic voltammetry measurements were carried out in dry degassed acetonitrile under inert atmosphere using 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. A Ag/Ag^+

reference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc^+) redox couple. The HOMO and LUMO energy values were calculated from the onset of the first oxidation and reduction potentials from the equations E_{HOMO} (eV) =

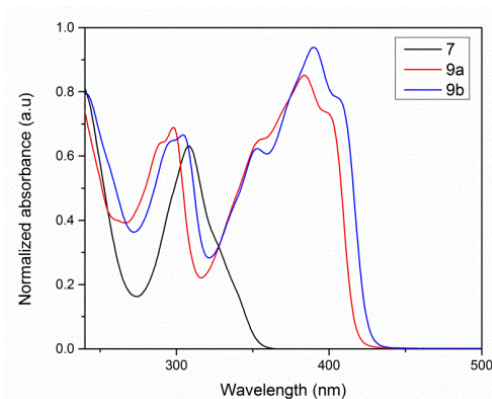


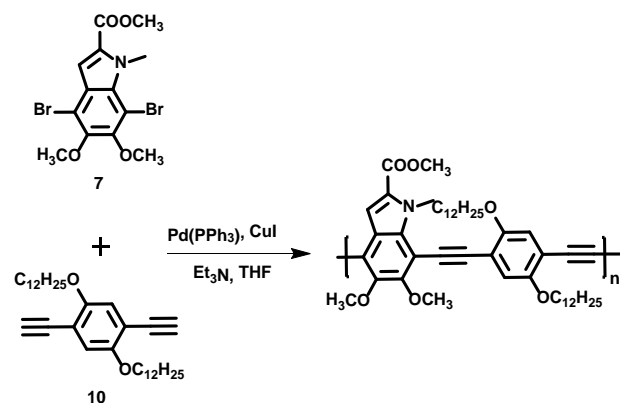
Fig. 2 The UV-Vis absorption spectra of **7**, **9a** and **9b**.

$- [E_{\text{ox}}^{\text{onset}} - E_{1/2}(\text{Fc}/\text{Fc}^+) + 4.8]$ and E_{LUMO} (eV) = $- [E_{\text{red}}^{\text{onset}} - E_{1/2}(\text{Fc}/\text{Fc}^+) + 4.8]$, where $E_{1/2}(\text{Fc}/\text{Fc}^+)$ was the cell correction. The oxidation potential for DBI was -5.76 eV whereas **9a** and **9b** values correspond to -5.55 eV and -5.45 eV, respectively. Both **9a** and **9b** had higher LUMO energy levels than the DBI core (see Table 1). The calculated bandgap values were 2.89 eV, 2.85 eV and 2.80 eV for the **7**, **9a** and **9b**, respectively, which indicated that the electron donating methoxy group resulted in the lower bandgap. This trend was also observed for the estimated optical bandgaps. From the voltammograms (**S18**), it was evident that the compounds had irreversible reduction and oxidation potentials.

Table 1 Optical and electrochemical properties of **7**, **9a** and **9b**.

	λ_{abs}^a (nm)	λ_{em}^a (nm)	Φ_{re}^b	E_{opt}^c (eV)	E_{ox}^d (eV)	E_{red}^d (eV)	$E_{\text{ox-red}}$ (eV)
7	308 [*]	-	-	-3.25	-5.76	-2.87	2.89
9a	384 [*] , 298, 239	436	0.82	-2.94	-5.55	-2.70	2.85
9b	390 [*] , 353, 304, 241	449	0.91	-2.87	-5.45	-2.65	2.80

^{*} λ_{max} , ^aMeasured in dilute chloroform, ^bquantum yields measured in dilute chloroform solutions relative to quinine sulfate, ^cmeasured from onset of absorption, ^dcalculated from onset of oxidation and reduction potential.



Scheme 3 Synthesis of the eumelanin-inspired polymer.

To further demonstrate the utility of the eumelanin inspired core **7** as a building block for organic semiconductors, we attempted the synthesis of a model conjugated polymer via Sonogashira cross-coupling conditions. The polymerization of **7** and 1,4-bis(dodecyloxy)-2,5-diethynylbenzene (**10**), was selected because of the similarity of **10** to methoxy monomer **9b**. This resulted in a red polymer with 36 % yield (Scheme 3). The polymer was soluble in various solvents including THF, chloroform, toluene and chlorobenzene, and the structure was confirmed by ^1H NMR spectroscopy. Gel permeation chromatography showed a number average molecular weight (M_n) of 13.6 kDa, PDI = 1.88. The photophysical characteristics of the polymer, both in dilute solutions and thin films, were examined using UV-vis absorption and fluorescence spectroscopy. The polymer exhibited an absorption maximum at 485 nm in solution and a red-shifted absorption maximum of 526 nm for polymer thin films. Green fluorescence was observed for the polymer with an emission maximum at 508 nm and the quantum yield in dilute chloroform was 0.60 (details in supporting information). The electrochemical properties of the polymer were investigated. The HOMO level for the polymer was similar to **9b** (-5.47 eV); however, LUMO level was deepened to -3.44 eV. The morphology of the polymer thin film was characterized by AFM, as shown in the Supporting Information. The polymer thin film appears to be composed of packed small grains varying in size and shape averaging 20 nm in diameter. Currently, work is continuing to optimize the polymerization conditions in order to improve yield and obtain higher molecular weight polymers.

Conclusions

In summary, we demonstrate that an eumelanin-inspired core molecule derived from the vanillin can serve as a building block for the development of eumelanin-inspired organic semiconductors. Two new eumelanin-inspired small molecules were synthesized in good yields. These materials exhibited red-shifted absorption and emission compared to the eumelanin-inspired core **DBI**. This is attributed to the extended conjugation due to the phenyleneethynylene linkage. Moreover, an eumelanin-inspired polymer was synthesized which showed promise for optoelectronic devices. Current efforts focus on the synthesis and evaluation of optical and electronic properties of oligomers and polymers based on the eumelanin-inspired core moieties.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Details of the synthesis and characterization of all the compounds are available. Crystallographic data for **9a** is also available]. See DOI: 10.1039/c000000x/

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