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Synthesis and characterization of solution processable 6,11-dialkynyl substituted indeno[1,2-*b*]anthracenes

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ABSTRACT

Twelve indene-fused dialkynyl substituted anthracene derivatives (indenoanthracenes) were synthesized and their optical, electrochemical and thermal properties were described. These small molecules possess high quantum yields, thermal and photoxidative stabilities, and solubility in common organic solvents. Indenoanthracenes (57–92%) were prepared in two steps from four different indenoanthraquinones obtained via a highly selective and practical benzocyclobutendione based methodology. The photophysical properties of indenoanthracenes were investigated by UV–vis and fluorescence spectroscopies. From spectroscopic data of indenoanthracenes, quantum yields (Φ_f, 0.28–0.71) and optical HOMO–LUMO energy gaps were determined. Electrochemistry of indenoanthracenes was studied and electrochemical HOMO–LUMO energy gaps were also determined from the onset oxidation and reduction potentials. Density functional theory calculations were performed to obtain the geometry optimized structures and HOMO–LUMO energy levels. Fluorenylethynyl substituted indenoanthracene was employed as an emitting layer in a solution processed OLED device and the maximum current efficiency and luminance were found to be 1.02 cd/A and 1284 cd/m^2, respectively.

1. Introduction

Over the last two decades synthesis and characterization of π-conjugated organic polymers and small molecules have gained considerable importance both in academia and industry. These conjugated systems have been widely employed as an active semiconductor layer in organic based optoelectronic devices such as organic light-emitting diodes (OLEDs) [1–4], organic field effect transistors (OFETs) [5–8], and organic photovoltaics (OPV) [9–14] which are promising key elements of rapid-growing display and lighting technologies. For good quality devices, semiconducting π-conjugated systems must fulfill a number of basic requirements including thermal stability, amorphous morphology, enhanced hole/electron mobility and high fluorescence efficiency. Moreover, solubility of π-conjugated systems in organic solvents becomes another key property for their use in large-scale and low-cost device fabrication [15,16] via spin coating, drop casting or inkjet printing solution based techniques. In this manner, π-conjugated organic polymers generally possess the advantage of better solution processability compared to small molecules which are mostly insoluble and prone to crystallization or phase separation. However, the polydispersity in conjugation lengths of organic polymers needs to be controlled to achieve efficient device performances [17]. Semiconducting thin films from small conjugated organic molecules are mostly prepared by complicated and more expensive vacuum deposition techniques. On the other hand, small molecules can be easily obtained in high purity which plays a crucial role in governing the performance of devices. Furthermore, well-defined and uniform structures of conjugated small organic molecules allow reliable structure-property correlations to be established.

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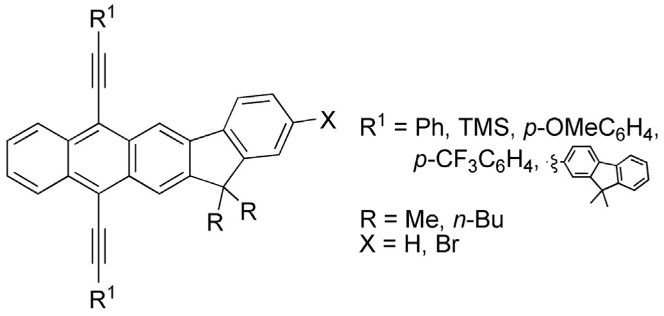
In recent years, significant effort has been devoted to designing solution processable small organic molecules which would provide advance device quality and new possibilities for the manufacturing of organic optoelectronics [18,19]. Among the small molecules, soluble anthracene derivatives have been extensively investigated since they usually possess high fluorescence quantum yield, wide-energy gap, good thermal and electronic stability [20–23]. In addition, various anthracene derivatives can be easily achieved via palladium-catalyzed cross-coupling reactions [24,25].

In this study, we described the synthesis and characterization of highly fluorescent and soluble indene-fused anthracene derivatives (indenoanthracenes) for use in OLEDs as emitting layers (Fig. 1). To date, indene-substituted [26] and particularly indene-fused (for example, indenofluorenes) [27–29] small conjugated organic molecules have been successfully employed in devices as active-layer materials since they exhibit intense fluorescence, thermal stability and improved solubility in common organic solvents. Herein, we obtained indenoanthracenes in two steps from indenoanthraquinones synthesized by a methodology based on the thermal rearrangement of reactive 2-fluorenyl-2-hydroxybenzocyclobutenones [30,31]. We envisaged that the indene fusion could increase the thermal stability and the solubility of dialkynyl substituted anthracene cores. Methyl and butyl groups were appended to the indene moiety because it is known that different alkyl groups allow control of solubility and molecular order in the solid state. Moreover, a bromo substituent was introduced to enable further derivatization of indenoanthracenes by cross-coupling reactions. Electronically different alkyne substituents were attached to the 9 and 10 positions of the anthracene core to tune the molecular energy levels of indenoanthracenes. We also reported here photophysical, electrochemical and thermal properties of indenoanthracene derivatives and finally tested their thin films deposited from solution as the emitting layer in OLED devices.

2. Experimental

2.1. General considerations

All reagents were used as purchased from commercial suppliers without further purification unless otherwise indicated. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl. Dichloromethane (CH_2Cl_2) was treated three times with H_2SO_4 and distilled over P_2O_5 and CaH_2 prior to use. Solvents for column chromatography, ethyl acetate and hexane were distilled in a rotary evaporator. Chromatographic separations were performed with Merck Silica 60 (200–400 or 70–230 mesh). TLC was performed with Merck TLC Silicagel60 F_{254} plates, detection was under UV light at 254 nm.



Indenoanthracene

Fig. 1. Structures of 6,11-dialkynyl substituted indenoanthracenes.

The following compounds were prepared according to known literature methods: 2-bromo-9,9-dimethyl-fluorene (**1a**) [32], 2-bromo-9,9-dibutyl-fluorene (**1b**) [33], 2,7-dibromo-9,9-dimethyl-fluorene (**1c**) [32], 2,7-dibromo-9,9-dibutyl-fluorene (**1d**) [34], 1-ethynyl-4-methoxybenzene [35], 1-ethynyl-4-(trifluoromethyl) benzene [36], (9,9-dimethylfluorene-2-yl)acetylene [37].

2.2. Instrumentation and measurement

NMR spectra were recorded with a Bruker Spectrospin Avance DPX400 Ultrashield (400 MHz for ^1H and 100.59 MHz for ^{13}C NMR) and Varian Inova 500 (500 MHz for ^1H and 125 MHz for ^{13}C NMR) instruments. Chemical shifts δ were given in ppm relative to residual peaks of deuterated solvents and coupling constants, J, were given in Hertz. The following abbreviations are used to describe spin multiplicities in ^1H NMR spectra: s = singlet; bs = broad singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; m = multiplets. Multiplicities in ^{13}C NMR spectra were determined by DEPT (Distortionless Enhancement by Polarization Transfer) or APT (Attached Proton Test) measurements. IR spectra were recorded on a NICOLET 6700 FT IR spectrometer. Low resolution mass spectra (API-ES, 70 eV, and APCI) were obtained on a Agilent 1100 LC-MS instrument equipped with a diode array UV–visible range detector and Thermo LCQ Deca Ion Trap Mass Spectrometer (Thermo Finnigan). High resolution mass spectra (HRMS) were obtained on a Waters Synapt Q-TOF-MS spectrometer.

UV–vis spectra were recorded with a Perkin–Elmer (Model Lambda 35) spectrophotometer at room temperature. Fluorescence spectra were taken with Shimadzu RF-5301 PC Spectrofluorometer. The absorption and fluorescence spectra of the dyes in liquid media were taken in a quartz cuvette which their dimension is 1.0 cm × 1.0 cm. Quantum yields of fluorescence (Φ_f) for indenoanthracenes were measured relative to perylene in cyclohexane [$\Phi_f = 0.73$ (1.0×10^{-5} M) at 404 nm excitation wavelength]. The relative fluorescence quantum yields of indenoanthracenes (Φ_f) were determined using the equation:

$$\phi_\mathrm{f} = \phi_\mathrm{f,\,ref}\left(\frac{A_\mathrm{ref}}{A}\right)\left(\frac{n_\mathrm{D}}{n_\mathrm{D,\,ref}}\right)^2\left(\frac{a_\mathrm{D}}{a_\mathrm{D,\,ref}}\right)$$

where ($\Phi_{f,\mathrm{ref}}$) is the fluorescence quantum yield of the reference compound, A is the absorbance of the solution at the excitation wavelength, n_D is the refraction index of the solvent and a is the area under the fluorescence peak.

Cyclic voltammetric measurements were performed on a Bioanalytical Systems BAS-100B electrochemical analyzer (Bioanalytical System Inc., Lafayette, IL, USA). A one-compartment electrochemical cell (BAS model C3-cell stand) was used with a three-electrode configuration. The working electrode was a platinum disc electrode (BAS Model MF-2013). Before experiments, the working electrode was successively polished with 1.0, 0.3, and 0.05 μm alumina slurries (Buehler) on microcloth pads (Buehler). After each polishing, the electrode was rinsed with distilled water and DMF. Platinum wire (BAS Model MW-1033) and Ag/AgCl/KCl(3.0 M) (BAS Model MF-2078) electrodes were used as counter and reference electrodes, respectively. All potentials were reported versus this reference electrode at room temperature. All voltammetric experiments were performed on 1.0 mM solutions in DMF using 0.1 M tetra-n-butylammonium perchlorate (n-Bu_4NClO_4) as supporting electrolyte at scan rate of 0.2 V s^{-1}. n-Bu_4NClO_4 was purchased from Fluka and used as received without further purification. During the electrochemical measurements, the solutions were degassed with nitrogen and kept in a nitrogen atmosphere.