Fine tuning of blue photoluminescence from indoles for device fabrication[†]

Jih Ru Hwu,*ab Yung Chang Hsu,a Thainashmuthu Josephrajana and Shwu-Chen Tsayc

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Functionalized indoles were synthesized as blue-light emitting materials through palladium-catalyzed heteroannulation. Fine tuning of their color from violet to blue photoluminescence in solution and thin film was accomplished by placement of electron-donating and -withdrawing substituents at the C2-, C3-, and C5-positions. A device of organic light-emitting diodes was made, which exhibited the desired blue light with the Commission International de L'Eclairage (CIE) coordinates x = 0.18 and y = 0.12.

Introduction

Manufacture of low-voltage multicolor displays with high efficiency requires organic light-emitting diodes (OLEDs).¹ The high need for blue-light emitting materials comes from their wide applicability.² In addition to being a component in blue-emitting devices, these materials can be used in light sources to generate low energy light from green to red with a color-conversion medium.³ Green and red emitters for organic electroluminescence devices have become readily available nowadays, while blue light emitting materials with excellent Commission International de L'Exclairage (CIE) coordinates are still rare. Moreover, light emitting materials are required for the preparation of electron-accepting and -transporting materials. These "n-type" materials are needed for use in n-type transistors, as the electronaccepting components in photovoltaic devices.⁴

Pope et al.⁵ first reported in 1963 that anthracene can give blue electroluminescence. Up to now, many blue-emitting materials have been developed, including anthracenes,² distyrylenes,² indole derivatives,⁶ 1,3,4-oxadiazoles,⁷ spirobifluorenes,⁸ as well as metal chelates such as aluminium, beryllium, boron, and lithium complexes.⁹ Among various light-emitting materials, we selected the indole nucleus as the basic chromophore for development of new OLED materials because it may emit photoluminescence (PL) in the blue–UV region with high quantum efficiency.¹⁰ Attachment of appropriate auxochromes at the C2-, C3-, and C5-positions of indoles 1 may allow us to tune its emitting light with bathochromic and hypsochromic shifts through conjugation. A C5-auxochrome with electron-donating or -withdrawing capability could influence the resonance contribution between the canonical form 2 and the parent structure 1 (Scheme 1). Furthermore, we planned to attach

a methoxycarbonyl group at the C3-position for the possible resonance structure **3**, in which the electrons delocalize between the veratrole and the methoxycarbonyl groups.

An intriguing part of our design also came from the possibility that the plane of the C2-veratrole group may not lie in the same plane as the indole nucleus. Steric congestion between the COOMe group at the C3 position and hydrogen atoms on the C2-veratrole group may generate a dihedral angle between these two planes. As a result, the resonance effect would be discounted. This possible non-planarity, however, may offer an advantage for molecules 1 to become ideal OLED materials. This is because amorphous materials are highly desirable for multilayer devices.¹¹ Their use can suppress formation of grain boundaries during operation and strain-driven failure in a thermally stressed OLED.

Compounds with a single veratrole group often do not exhibit photo- or electro-luminescence. In the presence of oxidants (such as chloranil, quinones, and perchlorate) under acidic conditions, their trimers (*i.e.*, triphenylene derivatives) can be generated through the para positions of the methoxy groups.¹² On the other hand, veratrole is not appreciably oxidized under typical Scholl conditions involving nitrobenzene and aluminium chloride.¹³ Our choice of a C2 veratrole group was based on its capability of contributing to the resonance shown in **3**. This moiety may not be easily oxidized in compounds **1** because one of the para positions of the methoxy group is blocked by an indole nucleus. Steric hindrance resulting from this nucleus can also retard the oxidation from occurring at the other para position.



Scheme 1 The canonical forms of indoles 1.

^aDepartment of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, 30013, R.O.C. E-mail: jrhwu@mx.nthu.edu.tw; Fax: +886-35-721594; Tel: +886-35-725813

^bDepartment of Chemistry, National Central University, Jhongli, Taiwan, 32001, R.O.C.

^cWell-being Biochemical Corporation, Neihu Technology Park, Taipei, 114, Taiwan, R.O.C.

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In continuation of our ongoing research on this topic,¹⁴ we report herein our successful development and syntheses of indole–veratrole conjugates as new OLED materials with blue CIE coordinates. More important is the establishment of a way to tune the blue color of indoles to the desired chromaticity.

Results and discussion

Synthesis of new indoles

We applied the Larock heteroannulation method¹⁵ as the key step for the convergent-type synthesis¹⁶ of our desired multisubstituted indoles **1** (see Scheme 2). Heteroannulation of **5** with various 4-substituted-2-iodo-1-anilines **4** (1.0 equiv) was performed in the presence of $(PPh_3)_2PdCl_2$ (0.050 equiv), *n*-Bu₄NBr (1.0 equiv), and NaOAc in DMF at 100 °C. The target molecules **1a–g** were obtained in 30–65% yields with an H, Me, F, Cl, CN, COOMe, or NO₂ group at the C5 position.

Anthracene possesses electron-donating and electroluminescent properties.^{2,5} We applied the same synthetic strategy shown in Scheme 3 for incorporating an anthracene moiety into an indole nucleus. Consequently, 2-anthracenylindoles **8a,b** were obtained from (dibromovinyl)anthracene **6**¹⁷ through consecutive debromohydrogenation, carbomethoxylation, and Larock heteroannulation.



Scheme 2 Synthesis of indoles 1a-g.



Scheme 3 Synthesis of indoles 8a,b.



Fig. 1 Molecular framework of **1f**: (a) ORTEP diagram obtained by X-ray diffraction analysis; and (b) molecular modeling obtained by CVFF calculations.

Structures of these potentially new OLED materials **1a–g** and **8a,b** were fully characterized by ¹H NMR, ¹³C NMR, IR, UV, PL and mass spectroscopic methods. For example, indole **1f** exhibited two characteristic singlets at 8.86 and 7.21 ppm in its ¹H NMR spectrum, for the C4- and C'2-aromatic protons, respectively. In its ¹³C NMR spectrum, resonance occurred at 145.86 and 104.88 ppm for the C2- and C3-carbons, respectively. In its IR spectrum, two strong (*i.e.*, 1708 and 1695 cm⁻¹) and one medium (*i.e.*, 1548 cm⁻¹) absorption bands appeared for the two C=O and C=C stretching vibrations, respectively. These data clearly indicate the formation of an α,β -unsaturated ester moiety.

Moreover, we unequivocally confirmed the molecular framework of 1f by single crystal X-ray diffraction analysis (see Fig. 1(a)). Its monoclinic crystals possessed the space group $P2_1/c$ with a = 12.396(2), b = 14.120(2), c = 13.920(2) Å, $\beta =$ 114.759(4)°. The dihedral angle was 50.3° between the indole nucleus and the dimethoxybenzene moiety. The structure observed from the solid state is consistent with that obtained from our CVFF calculations of the molecular geometry of 1f (*i.e.*, 54.4° in Fig. 1(b)). Compounds with an asymmetric or nonplanar structure generally have a lower tendency to pack into a crystal lattice and hence favor amorphous morphology.¹¹ These data indicate that the aryl moiety attached at the C2-position is not co-planar with the indole nucleus and, thus, may increase its amorphous application during device fabrication. Our molecular modeling also provides a convenient and reliable protocol for design and prediction of indole OLED materials to be developed in the future.

Thermal stability

For regular high performance OLEDs, materials are often required to possess good thermal stability and the ability to form amorphous thin films.¹¹ While our single crystal X-ray structure shown in Fig. 1 discloses valuable information on the possibility of amorphousness related to indoles 1, it was crucial for us to obtain amorphous molecular materials with a high glass transition temperature (T_g). Accordingly, we performed a differential scanning calorimetry analysis and found that the T_g was 136 °C for indole 1e. Given our best knowledge through literature search, it is higher than those of any other indole derivatives reported (55–126 °C)⁶ and general organic materials used for OLEDs ($\geq 60 °C$).¹⁸ Furthermore, our synthesized indoles were found with $T_m \geq 192 °C$ and $T_d \geq 274 °C$, except 1a, by thermal gravimetric analysis. For example, the melting point was measured as 260 °C for compound 8a, which decomposed at 274 °C.

Photo-physical properties

The absorption and photoluminescence (PL) spectral data are given in Table 1 for indole derivatives **1a–f** and **8a**. In the solution of dichloromethane, compounds **1a–f** emitted violet light (397–404 nm) for a variety of substituents (*i.e.*, H, Me, F, Cl, CN and COOMe) attached to the C5 position. We successfully tuned the light from violet to blue (444 nm) by incorporating an anthracene unit at the C2 position (*i.e.*, **8a**).

As prepared in solid film where the molecules are fixed, we found that the emitting light shifted bathochromically by 12-41 nm in comparison with the same samples prepared in solution. Moreover, by placing a CN or a COOMe substituent at the C5 position, we found that the solid films of 1e and 1f emitted blue light with wavelengths of 439 and 431 nm, respectively. In addition, placement of an anthracene substituent at the C2 position allowed 8a to emit blue light at 456 nm. The bathochromic shift caused by CN-, COOMe-, and anthracenecontaining indoles was due to the interactions between these auxochromes with the chromophore in the excited state.¹⁹ The photoluminescence, however, was not observed at all from indole 1g with a C5 nitro group; thus it has no applicability as an OLED material. Given the results in Table 1 and the photoluminescence spectra in Fig. 2(a), we conclude that the wavelengths of emitting light resulting from indoles can be tuned by following the orders listed in Fig. 2(b).

Moreover, all of these new indole derivatives exhibited appealing quantum yields Φ_{PL} (in dichloromethane) between 0.411 and 0.592. These values are greater than those of reported indole derivatives.⁶

Table 1 Absorption and photoluminescent data of 1a-f and 8a

Indole ^{<i>a</i>}	C5 group	$\begin{array}{c} UV \; \lambda_{max}{}^{abs} \\ (nm) \end{array}$	$\frac{PL \lambda_{max}}{(nm)}$	$\frac{PL \lambda_{max}{}^{film}}{(nm)}$	$\Phi_{\mathrm{PL}}{}^{\mathrm{soln}}$
1a	Н	306	402	418	0.545
1b	Me	306	404	416	0.567
1c	F	302	398	405	0.534
1d	Cl	308	399	414	0.478
1e	CN	284, 322	398	439	0.592
1f	COOMe	278, 320	397	431	0.556
1g	NO_2	290, 305			
8a	H^{b}	282, 366, 386	444	456	0.411

^{*a*} Concentration for UV, PL λ_{max} , and Φ_{PL} : [M] = 1.0 × 10⁻⁵ in CH₂Cl₂ at 298 K. ^{*b*} C2 with an anthracene moiety.



Fig. 2 A trend for various substituents for tuning the violet-blue light emitted by indoles: (a) photoluminescence spectra of indole derivatives **1a–f** and **8a**; (b) the orders of substituents causing hypsochromic shifts in dichloromethane solutions and thin film.

Electrochemistry

Khan, Bredas, Marder, and co-workers²⁰ reported a reliable method for direct measurements and comparison with experimental and theoretical estimates of electron affinities. The most direct experimental probes of ionization potentials and electron affinities are photoelectron spectroscopy and inverse-photoelectron spectroscopy, respectively. On the other hand, cyclic voltammetry has been applied widely for determination of the HOMO²¹ and LUMO levels of organic compounds, particularly in the area of developing electroluminescent materials and OLEDs. Thus we recorded the cyclic voltammetry scans against an Ag/AgCl reference electrode at a scan rate of 0.20 V/sec by using 0.10 M [NBu₄]PF₆ as a supporting electrolyte in dry,

Table 2 Energy alignment in indole derivatives

Indole	$E_{\rm ox}$ (V)	HOMO (eV)	LUMO (eV)	Energy gap (eV)
1a	1.34	-5.6	-2.1	3.5
1b	1.37	-5.6	-2.1	3.5
1d	1.40	-5.7	-2.1	3.6
1e	1.53	-5.7	-2.2	3.5
1f	1.46	-5.7	-2.2	3.5
8a	1.57	-5.7	-2.6	3.1

degassed CH_2Cl_2 solution. Ferrocene (4.8 eV) was applied as an internal reference for calibration of redox potentials.²²

We calculated the LUMO energy from the HOMO and the lowest energy absorption edge of the UV/Vis absorption spectra. Their first oxidation potential (E_{ox}), HOMO energy, LUMO energy, and energy gaps are listed in Table 2. These estimated HOMO and LUMO values fall into the ranges of -5.6 to -5.7 eV and -2.1 to -2.6 eV, respectively. 4.4'-Bis[2-(1.1'-diphenyl)vinyl]biphenyl (DPVBI)^{2,23} is proven as a good blue light OLED material. Both the HOMO and the LUMO energy levels of our synthesized compound **8a** are very close to those of DPVBI.

Fabrication of OLED devices and measurement

For device fabrication, we chose **1e** as the candidate because of its higher PL quantum yield (Φ_{PL} 0.592) and better thermal stability (*e.g.*, T_d 289 °C) than other synthesized indoles. Accordingly, the OLED device was fabricated by use of vacuumdeposition of NPB, indole **1e**, TPBI, Alq₃, and an Mg–Ag electrode on top of an ITO glass substrate. The device structure was ITO/NPB (30 nm)/**1e** (25 nm)/TPBI (10 nm)/Alq₃ (40 nm)/Mg–Ag (55 nm), where ITO, NPB, TPBI, Alq₃, Mg–Ag represent indium tin oxide, 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl, 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene, tris(8-hydroxyquinoline)aluminium, and magnesium–silver alloy (~10:1), respectively. NPB and Alq₃ were used as the hole and electron transporting materials, respectively. TPBI functioned as the hole blocking material.

The substrate was an indium-tin-oxide (ITO) coated glass possessing a resistance of < 30 Ω /square. The ITO glass was etched for the anode electrode pattern and organic materials were deposited under vacuum. The thermal evaporation of organic materials was carried out at a chamber pressure of 10^{-6} torr. The deposition rates for organic materials, Mg and Ag were about 0.10, 0.50, and 0.050 nm/s, respectively. The cathode Mg_{1.0}Ag_{0.1} alloy was deposited (55 nm) by co-evaporation and followed by a thick silver capping layer. Current–voltage–luminescence (I–V–L) characteristics and CIE color coordinates were then determined simultaneously.

As a result, our fabricated device including **1e** had a turn-on voltage of 6.0 V. Its brightness reached 184 cd/m² at 20 mA and 8.3 V as well as 783 cd/m² at 100 mA and 10.2 V. The observed maximum brightness in this device was at 2417 cd/m² at 551 mA and 15.0 V. The external maximum quantum and power efficiency for the device were 0.87% and 0.45 lm/W, which were achieved at 7.6 V (4.1 mA/cm², 46 cd/m). The electroluminescence spectrum of a **1e**-based device showed the emission maximum at 443 nm (see Fig. 3). The color of our device was blue



Fig. 3 The electroluminescence spectrum of cyano-containing indole 1e and its CIE chromaticity coordinates represented by \blacksquare . They were obtained by use of a Keithley 2400 Source meter and a Newport 1835C optical meter equipped with a Newport 818-ST silicon photodiode, respectively.

(x = 0.18, y = 0.12) in the Commission International de L'Exclairage (CIE) chromaticity coordinates. These results indicate our success in the development of an OLED device for emitting pure blue light. For electroluminescence performance as an undoped device, we compared **1e** with two known blue-emitters: 9,10-bis(4-(2,2-diphenylvinyl)phenylanthracene (DPVPA) and 2-methyl-9,10-di(2-naphthyl)anthracene (MADN).² Both DPVPA and MADN possess greater external quantum efficiencies (3% and 1.5%, respectively) than that of **1e** (0.87%). However, DPVPA exhibits a "greener" color with CIE x = 0.14, y = 0.17, while the "blue" emitter **1e** has CIE x = 0.18, y = 0.12. Moreover, the T_g values are higher for indole **1e** (136 °C) than polyarene MADN (120 °C). Thus the former compound developed by us possesses better thermal stability.

Conclusions

Use of the Larock heteroannulation method led to a series of substituted indole derivatives. These new compounds may possess a 3,4-dimethoxybenzyl or an anthracenyl group at the C2 position, meanwhile, an H, Me, F, Cl, CN, COOMe, or NO₂ group at the C5 position. Their emitting photoluminescence from the thin film can be tuned by attachment of various groups at the C2 and the C5 positions of indoles following the order from violet to blue: 5-F < 5-Cl < 5-Me < 5-H < 5-COOMe < 5-CN < 2-anthracene. The device with a configuration ITO/NPB/1e/TPBI/Alq₃/Mg–Ag was prepared, which successfully emitted blue electroluminescence with good color purity.

Experimental

General details

All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen unless as indicated otherwise. Acetone from Mallinckrodt was dried with 4Å molecular sieves and distilled. Tetrahydrofuran (reagent grade) from Mallinckrodt was dried by distillation from sodium and benzophenone under an atmosphere of nitrogen. N,N-Dimethylformamide

from Mallinckrodt was dried and distilled from MgSO₄ under reduced pressure and then stored in serum-capped bottles over 4Å molecular sieves under nitrogen. Chloroform, dichloromethane, ethyl acetate, and hexanes from Mallinckrodt Chemical Co. were dried and distilled from CaH₂. The following compounds and reagents were purchased from Aldrich Chemical Co.: 2-iodoaniline (4a), 4-cyano-2-iodoaniline (4e), methyl 4-amino-3-iodobenzoate (4f), 2-iodo-4-nitroaniline (4g), methyl chloroformate, and (PPh₃)₂PdCl₂. The following compounds were synthesized by following the literature methods: 2-iodo-4-methylaniline²⁴ (4b), 4-fluoro-2-iodoaniline²⁵ (4c), 4-chloro-2-iodoaniline²⁴ (4d), methyl (3,4-dimethoxyphenyl)propiolate²⁶ (5), and 9-(2,2-dibromovinyl)anthracene¹⁷ (6).

Melting points were obtained with a Büchi 535 melting point apparatus. Analytical thin layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254), purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a 25 m cross-linked methyl silicone gum capillary column (0.32-mm i.d.). Nitrogen gas was used as a carrier gas and the flow rate was kept constant at 14.0 mL/min. The retention time $t_{\rm R}$ was measured under the following conditions: injector temperature 260 °C, the initial temperature for column 70 °C, duration 2.00 min, increment rate 15 °C/min, and the final temperature for column 280 °C. Gas chromatography and low resolution mass spectral analyses were performed on an Agilent Technologies 6890N Network GC System equipped with an Agilent 5973 Network Mass Selective Detector and a capillary HP-1 column. Purification by gravity column chromatography was carried out by use of Merck Reagents Silica Gel 60 (particle size 0.063-0.200 mm, 70-230 mesh ASTM).

Photoluminescence spectra were measured on a Hitach F-4500 fluorescence spectrophotometer. Ultraviolet (UV) spectra were measured on a Hitach U3300 UV-vis spectrophotometer. Cyclic voltammograms were measured on a CH Instruments, Inc. 600A Electrochemical Analyzer. Infrared (IR) spectra were measured on a Jasco FT/IR-5300 Fourier transform infrared spectrometer. The wavenumbers reported are referenced to the polystyrene 1601 cm⁻¹ absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. Proton NMR spectra were obtained on a Varian Unity-400 (400 MHz) spectrometer by use of chloroform-d as solvent and tetramethylsilane as internal standard. Carbon-13 NMR spectra were obtained on a Varian Unity-400 (100 MHz) spectrometer by use of chloroform-d as solvent. Carbon-13 chemical shifts are referenced to the center of the CDCl₃ triplet (77.0 ppm) or DMSO- d_6 pentet (39.54 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; J, coupling constant (hertz). High-resolution mass spectra were obtained by means of a JEOL JMS-HX110 mass spectrometer. Electrospray ionization mass spectrometry (ESI-MS) analyses were performed on a quadrupole ion trap mass analyzer fitted with an electrospray ionization source (Finnigan LCQ, Finnigan MAT, San Jose, CA).

Computation was performed on a Silicon Graphics O2+ workstation. The program Builder was used for the construction of 3,5-dimethyl 2-(3,4-dimethoxyphenyl)indole-3,5-dicarboxylate (**3f**). The program Discover was used for energy minimization. The energies for all conformations were minimized with the consistent valence forcefield (CVFF) until the maximum derivative was less than 0.001 kcal mol⁻¹ \mathring{A}^{-1} .

Standard procedure for the syntheses of indoles 1a–g and 8a,b. A solution containing *o*-iodoaniline (1.0 equiv), an alkyne (1.6– 3.0 equiv), (PPh₃)₂PdCl₂ (0.050 equiv), *n*-Bu₄NBr (1.0 equiv), and NaOAc (5.0 equiv) in DMF was stirred at 100–120 °C for 30 min (1a–g) or 10 h (8a,b). After the reaction mixture was cooled to room temperature, it was quenched with water (50 mL), neutralized with saturated aqueous NH₄Cl, and extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL), dried over MgSO₄ (s), filtered, and concentrated under reduced pressure. The residue was purified by use of gravity column chromatography on silica gel with 25% EtOAc (except 8a,b with 10% EtOAc) in hexanes as eluant to provide the desired indoles with purity >99.0%, as checked by GC.

Methyl 2-(3,4-dimethoxyphenyl)indole-3-carboxylate (1a). The standard procedure was followed by use of 2-iodoaniline (4a, 165.0 mg, 0.7533 mmol, 1.0 equiv), methyl (3,4-dimethoxyphenyl)propiolate (5, 497.2 mg, 2.258 mmol, 3.0 equiv), (PPh₃)₂PdCl₂ (26.3 mg, 0.0375 mmol, 0.050 equiv), n-Bu₄NBr (242.6 mg, 0.7526 mmol, 1.0 equiv), NaOAc (310.0 mg, 3.779 mmol, 5.0 equiv), and DMF (30 mL) to give 1a (152.2 mg, 0.489 mmol, 65%) as white solids; mp 154.2-154.8 °C (from CH₂Cl₂); $(R_{\rm f} = 0.35, 20\% \text{ EtOAc in hexanes}); \nu_{\rm max}/\rm{cm}^{-1} 3317 (m, N-H),$ 2950 (m), 2840 (w), 1682 (s, C=O), 1605 (w), 1584 (w), 1548 (m), 1502 (s), 1456 (s), 1331 (m), 1257 (s) and 1121 (s); $\delta_{\rm H}$ (500 MHz; CDCl₃) 3.83 (s, 3 H, C(=O)OCH₃), 3.86 (s, 3 H, ArOCH₃), 3.88 $(s, 3 H, ArOCH_3), 6.88 (d, J = 8.5 Hz, 1 H, ArH), 7.18-7.25 (m, 4)$ H, $4 \times \text{ArH}$), 7.35 (d, J = 6.5 Hz, 1 H, ArH), 8.17 (d, J = 6.0 Hz, 1 H, ArH) and 8.65 (s, 1 H, NH); $\delta_{\rm C}(125 \text{ MHz}; \text{CDCl}_3)$ 50.86, 55.89, 55.96, 103.99, 110.69, 110.87, 113.00, 122.03, 122.07, 122.15, 123.10, 124.39, 127.65, 134.96, 144.51, 148.40, 149.87 and 165.84 (C=O); m/z (EI) 311 (M+, 100), 296 (8), 280 (43), 236 (15), 207 (19), 140 (7); HRMS calcd for C₁₈H₁₇NO₄: 311.1157, found 311.1156.

Methyl 2-(3,4-dimethoxyphenyl)-5-methylindole-3-carboxylate (1b). The standard procedure was followed by use of 2-iodo-4methylaniline (4b, 175.4 mg, 0.7526 mmol, 1.0 equiv), methyl (3,4-dimethoxyphenyl)propiolate (5, 500.1 mg, 2.271 mmol, 3.0 equiv), (PPh₃)₂PdCl₂ (26.9 mg, 0.0383 mmol, 0.050 equiv), n-Bu₄NBr (242.0 mg, 0.7507 mmol, 1.0 equiv), NaOAc (308.8 mg, 3.764 mmol, 5.0 equiv), and DMF (30 mL) to give 1b (101.2 mg, 0.301 mmol, 40%) as white solids; mp 211.3-211.5 °C (from CH₂Cl₂); ($R_f = 0.35$, 20% EtOAc in hexanes); ν_{max}/cm^{-1} 3291 (m, N-H), 2941 (w), 2838 (w), 1698 (s, C=O), 1607 (m), 1585 (m), 1546 (m), 1502 (s), 1442 (s), 1301 (m), 1260 (s), 1247 (s) and 1118 (s); $\delta_{\rm H}(400 \text{ MHz}; \text{ CDCl}_3)$ 2.47 (s, 3 H, CH₃), 3.82 (s, 3 H, C(=O)OCH₃), 3.86 (s, 3 H, ArOCH₃), 3.88 (s, 3 H, ArOCH₃), 6.87 (d, J = 8.0 Hz, 1 H, ArH), 7.06 (d, J = 8.0 Hz, 1 H, ArH),7.16–7.24 (m, 3 H, 3 × ArH), 7.96 (s, 1 H, C4-ArH) and 8.54 (s, 1 H, NH); δ_C(100 MHz; CDCl₃) 21.61, 50.72, 55.85, 55.92, 103.58, 110.48, 110.74, 113.11, 121.66, 122.09, 124.59, 124.63, 127.92, 131.45, 133.29, 144.44, 148.39, 149.81 and 165.91 (C=O); m/z (EI) 325 (M+, 100), 294 (32), 278 (6), 250 (12), 223 (4), 207 Downloaded by UNIVERSITY OF SOUTH AUSTRALIA on 25 July 2012 Published on 23 March 2009 on http://pubs.rsc.org | doi:10.1039/B821246E (10), 162 (6); HRMS calcd for $C_{19}H_{19}NO_4$: 325.1314, found 325.1311.

Methyl 2-(3,4-dimethoxyphenyl)-5-fluoroindole-3-carboxylate (1c). The standard procedure was followed by use of 4-fluoro-2-iodoaniline (4c, 183.9 mg, 0.7759 mmol, 1.0 equiv), methyl (3,4-dimethoxyphenyl)propiolate (5, 505.5 mg, 2.295 mmol, 3.0 equiv), (PPh₃)₂PdCl₂ (27.2 mg, 0.0387 mmol, 0.050 equiv), n-Bu₄NBr (249.0 mg, 0.7724 mmol, 1.0 equiv), NaOAc (320.0 mg, 3.901 mmol, 5.0 equiv), and DMF (30 mL) to give 1c (102.4 mg, 0.301 mmol, 40%) as white solids; mp 188.5-189.0 °C (from CH₂Cl₂); ($R_f = 0.35$, 20% EtOAc in hexanes); ν_{max}/cm^{-1} 3316 (s, N-H), 2949 (m), 2838 (w), 1683 (s, C=O), 1586 (m), 1503 (s), 1452 (s), 1300 (m), 1261 (s), 1204 (m), 1122 (s) and 1025 (m); $\delta_{\rm H}(400 \text{ MHz}; \text{CDCl}_3) 3.81 \text{ (s, 3 H, C}(=0)\text{OCH}_3), 3.82 \text{ (s, 3 H,}$ ArOCH₃), 3.84 (s, 3 H, ArOCH₃), 6.82 (d, J = 8.0 Hz, 1 H, ArH), 6.95 (t, J = 10 Hz, 1 H, ArH), 7.14–7.24 (m, 3 H, 3 × ArH), 7.81 (d, J = 10 Hz, 1 H, ArH) and 8.85 (s, 1 H, NH); $\delta_{C}(100$ MHz; CDCl₃) 50.83, 55.85, 55.94, 104.19, 107.38 (d), 110.81, 111.35 (d), 111.63 (d), 113.14, 122.12, 124.12, 128.47 (d), 131.46, 145.99, 148.46, 150.08, 159.22 (d), and 165.54 (C=O); m/z (EI) 329 (M+, 100), 314 (9), 298 (42), 282 (8), 254 (16), 149 (7); HRMS calcd for C₁₈H₁₆FNO₄: 329.1063, found 329.1062.

Methyl 5-chloro-2-(3,4-dimethoxyphenyl)indole-3-carboxylate (1d). The standard procedure was followed by use of 4-chloro-2-iodoaniline (4d, 191.2 mg, 0.7545 mmol, 1.0 equiv), methyl (3,4-dimethoxyphenyl)propiolate (5, 499.1 mg, 2.266 mmol, 3.0 equiv), (PPh₃)₂PdCl₂ (26.5 mg, 0.0378 mmol, 0.050 equiv), n-Bu₄NBr (245.2 mg, 0.7606 mmol, 1.0 equiv), NaOAc (311.9 mg, 3.802 mmol, 5.0 equiv), and DMF (30 mL) to give 1d (121.3 mg, 0.351 mmol, 47%) as white solids; mp 196.8–197.2 °C (from CH₂Cl₂); ($R_{\rm f} = 0.40, 20\%$ EtOAc in hexanes); $\nu_{\rm max}/{\rm cm}^{-1}$ 3310 (s, N-H), 2949 (m), 2837 (w), 1681 (s, C=O), 1503 (s), 1465 (s), 1441 (s), 1295 (m), 1263 (s), 1206 (s), 1121 (s) and 1025 (m); $\delta_{\rm H}(400 \text{ MHz}; \text{CDCl}_3) 3.84 \text{ (s, 3 H, C}(=0)\text{OCH}_3), 3.87 \text{ (s, 3 H)}$ H, ArOCH₃), 3.89 (s, 3 H, ArOCH₃), 6.88 (d, J = 8.0 Hz, 1 H, ArH), 7.17–7.27 (m, 4 H, $4 \times$ ArH), 8.14 (s, 1 H, C4-ArH) and 8.65 (s, 1 H, NH); δ_C(100 MHz; CDCl₃) 50.97, 55.93, 56.04, 103.89, 110.84, 111.83, 113.11, 121.72, 122.14, 123.48, 123.92, 127.89, 128.81, 133.30, 145.62, 148.57, 150.22 and 165.32 (C=O); m/z (EI) 345 (M+, 100), 314 (22), 270 (16), 207 (9), 172 (4), 157 (6); HRMS calcd for C₁₈H₁₆ClNO₄: 345.0768, found 345.0770.

Methyl 5-cyano-2-(3,4-dimethoxyphenyl)indole-3-carboxylate (1e). The standard procedure was followed by use of 4-cyano-2-iodoaniline (4e, 175.2 mg, 0.7179 mmol, 1.0 equiv), methyl (3,4-dimethoxyphenyl)propiolate (5, 480.2 mg, 2.181 mmol, 3.0 equiv), (PPh₃)₂PdCl₂ (25.1 mg, 0.0358 mmol, 0.050 equiv), *n*-Bu₄NBr (238.6 mg, 0.7401 mmol, 1.0 equiv), NaOAc (305.2 mg, 3.720 mmol, 5.0 equiv), and DMF (30 mL) to give 1e (95.8 mg, 0.285 mmol, 38%) as white solids; mp 220.0–220.5 °C (from CH₂Cl₂); ($R_f = 0.30$, 20% EtOAc in hexanes); ν_{max}/cm^{-1} 3296 (s, N–H), 2954 (w), 2840 (w), 2221 (s), 1694 (s, C=O), 1614 (w), 1505 (s), 1470 (s), 1443 (s), 1375 (m), 1265 (s), 1215 (s) and 1120 (s); δ_H (400 MHz; CDCl₃) 3.88 (s, 3 H, C(=O)OCH₃), 3.90 (s, 3 H, ArOCH₃), 3.91 (s, 3 H, ArOCH₃), 6.94 (d, *J* = 8.4 Hz, 1 H, ArH), 7.23 (d, *J* = 8.6 Hz, 1 H, ArH), 7.25 (s, 1 H, C2'-ArH), 7.43

(d, J = 8.4 Hz, 1 H, ArH), 7.48 (d, J = 8.4 Hz, 1 H, ArH), 8.54 (s, 1 H, C4-ArH) and 8.78 (s, 1 H, NH); $\delta_{\rm C}(100$ MHz; DMSO- d_6) 50.87, 55.75, 55.72, 102.71, 103.55, 111.23, 113.08, 113.83, 120.35, 122.82, 122.90, 125.37, 126.23, 127.25, 137.31, 146.89, 148.05, 150.08 and 164.38 (C=O); m/z (EI) 336 (M+, 100), 321 (9), 305 (35), 261 (9), 203 (5); HRMS m/z calcd for C₁₉H₁₆N₂O₄: 336.1110, found 336.1107.

3,5-Dimethyl 2-(3,4-dimethoxyphenyl)indole-3,5-dicarboxylate (1f). The standard procedure was followed by use of methyl 4-amino-3-iodobenzoate (4f, 208.4 mg, 0.7522 mmol, 1.0 equiv), methyl (3,4-dimethoxyphenyl)propiolate (5, 496.2 mg, 2.253 mmol, 3.0 equiv), (PPh₃)₂PdCl₂ (26.6 mg, 0.0379 mmol, 0.050 equiv), n-Bu₄NBr (240.8 mg, 0.7470 mmol, 1.0 equiv), NaOAc (306.9 mg, 3.741 mmol, 5.0 equiv), and DMF (30 mL) to give 1f (92.2 mg, 0.250 mmol, 33%) as white solids; mp 192.4-192.8 °C (from CH₂Cl₂); ($R_{\rm f} = 0.30$, 20% EtOAc in hexanes); $\nu_{\rm max}/{\rm cm}^{-1}$ 3305 (m, N-H), 2951 (m), 2839 (w), 1709 (s, C=O), 1695 (s, C=O), 1619 (m), 1587 (w), 1505 (s), 1441 (s), 1378 (w), 1285 (s), 1257 (s) and 1122 (s); $\delta_{\rm H}(400 \text{ MHz}; \text{ CDCl}_3)$ 3.82 (s, 3 H, C(=O)OCH₃), 3.85 (s, 6 H, 2 × ArOCH₃), 3.92 (s, 3 H, $C(=O)OCH_3$, 6.84 (d, J = 8.0 Hz, 1 H, ArH), 7.18–7.21 (m, 2 H, $2 \times \text{ArH}$, 7.34 (d, J = 8.4 Hz, 1 H, ArH), 7.91 (d, J = 8.4 Hz, 1 H, ArH), 8.86 (s, 1 H, C4-ArH) and 9.16 (s, 1 H, NH); $\delta_{\rm C}(100$ MHz; CDCl₃) 51.06, 51.96, 55.87, 55.94, 104.88, 110.75, 110.77, 113.05, 122.23, 123.77, 123.91, 124.49, 124.79, 127.24, 137.63, 145.86, 148.48, 150.14, 165.42 (C=O) and 168.07 (C=O); m/z (EI) 369 (M+, 100), 338 (42), 294 (9), 281 (9), 207 (18), 169 (11), 131 (12); HRMS calcd for C₂₀H₁₉NO₆: 369.1212, found 369.1213.

Methyl 2-(3,4-dimethoxyphenyl)-5-nitroindole-3-carboxylate (1g). The standard procedure was followed by use of 2-iodo-4-nitroaniline (4g, 199.5 mg, 0.7555 mmol, 1.0 equiv), methyl (3,4-dimethoxyphenyl)propiolate (5, 499.2 mg, 2.267 mmol, 3.0 equiv), (PPh₃)₂PdCl₂ (26.8 mg, 0.0382 mmol, 0.050 equiv), *n*-Bu₄NBr (241.9 mg, 0.7504 mmol, 1.0 equiv), NaOAc (309.5 mg, 3.773 mmol, 5.0 equiv), and DMF (30 mL) to give 1g (79.7 mg, 0.224 mmol, 30%) as yellow solids; mp 241.2-241.6 °C (from CH₂Cl₂); ($R_f = 0.35, 20\%$ EtOAc in hexanes); ν_{max}/cm^{-1} 3306 (s, N-H), 2950 (w), 2840 (w), 1694 (s, C=O), 1555 (m), 1503 (s), 1471 (s), 1338 (s), 1264 (s), 1209 (m), 1086 (m) and 1021 (m); $\delta_{\rm H}(400 \text{ MHz}; \text{CDCl}_3)$ 3.91 (s, 6 H, 2 × ArOCH₃), 3.93 (s, 3 H, $C(=O)OCH_3$, 6.95 (d, J = 8.4 Hz, 1 H, ArH), 7.25 (d, J = 8.0Hz, 1 H, ArH), 7.27 (s, 1 H, C2'-ArH), 7.42 (d, J = 8.8 Hz, 1 H, ArH), 8.15 (d, J = 8.8 Hz, 1 H, ArH), 8.84 (s, 1 H, C4-ArH) and 9.08 (s, 1H, NH); $\delta_{\rm C}(100 \text{ MHz}; \text{DMSO-}d_6)$ 51.41, 56.03, 56.04, 104.18, 111.58, 112.71, 113.95, 117.90, 118.34, 123.14, 123.25, 127.25, 139.06, 142.70, 148.29, 148.41, 150.49, and 164.78 (C=O); m/z (EI) 356 (M+, 100), 341 (9), 325 (32), 278 (19), 235 (5), 139 (9), 31 (17); HRMS calcd for C₁₈H₁₆N₆O₆: 356.1008, found 356.1009.

Methyl (9-anthracenyl)propiolate (7). To a solution of 9-(2,2dibromovinyl)anthracene (6, 9.05 g, 25.0 mmol, 1.0 equiv) in dry THF (150 mL) was added *n*-butyl lithium (1.78 M, 35.4 mL, 62.5 mmol, 2.5 equiv) at -78 °C. After the solution was stirred at -10 °C for 60 min, methyl chloroformate (4.73 g, 50.0 mmol, 2.0 equiv) was then added at -78 °C and the reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with saturated aqueous NH₄Cl (125 mL) and extracted with ether $(3 \times 100 \text{ mL})$. The combined organic layers were dried over MgSO₄ (s), filtered, and concentrated under reduced pressure. The residue was purified by use of gravity column chromatography on silica gel (1.0% EtOAc in hexanes as eluent) to give 7 (5.460 g, 21.0 mmol, 84%) as yellow solids: mp 113.8-114.2 °C (from CH₂Cl₂); ($R_f = 0.25$, 1% EtOAc in hexanes); ν_{max} / cm⁻¹ 3057 (w), 2957 (w), 2203 (s), 1716 (s, C=O), 1434 (m), 1358 (m), 1237 (s), 1158 (m), 1085 (m), 738 (m) and 732 (m); $\delta_{\rm H}(400$ MHz; CDCl₃) 3.94 (s, 3 H, C(=O)OCH₃), 7.52 (t, J = 7.4 Hz, 2 H, 2 × ArH), 7.63 (t, J = 7.2 Hz, 2 H, 2 × ArH), 8.02 (d, J = 8.4Hz, 2 H, 2 × ArH), 8.53 (d, J = 8.8 Hz, 2 H, 2 × ArH) and 8.54 (s, 1 H, ArH); $\delta_{C}(100 \text{ MHz}; \text{CDCl}_{3})$ 52.80 (CH₃), 83.73, 91.17, 112.70, 125.92, 126.03, 127.77, 128.81, 130.78, 130.82, 134.11 and 154.77 (C=O); m/z (EI) 260 (M+, 100), 229 (35), 215 (11), 202 (85), 114 (15), 100 (31); HRMS calcd for $C_{18}H_{12}O_2$: 260.0837, found 260.0837.

Methyl 2-(9-anthracenyl)indole-3-carboxylate (8a). The standard procedure was followed by use of 2-iodoaniline (4a, 166.6 mg, 0.7607 mmol, 1.0 equiv), methyl (9-anthracenyl)propiolate (7, 313.0 mg, 1.203 mmol, 1.6 equiv), (PPh₃)₂PdCl₂ (26.7 mg, 0.0380 mmol, 0.050 equiv), n-Bu₄NBr (247.6 mg, 0.7681 mmol, 1.0 equiv), NaOAc (309.0 mg, 3.767 mmol, 5.0 equiv), and DMF (30 mL) to give 8a (89.9 mg, 0.256 mmol, 34%) as yellow solids; mp 259.5–260.0 °C (from CH₂Cl₂); ($R_f = 0.30$, 10% EtOAc in hexanes); ν_{max}/cm^{-1} 3249 (m, N–H), 3051 (w), 2948 (w), 1674 (s, C=O), 1543 (w), 1457 (s), 1441 (s), 1424 (m), 1335 (m), 1193 (s) and 1087 (s); $\delta_{\rm H}(400 \text{ MHz}; \text{CDCl}_3)$ 3.47 (s, 3 H, C(=O)OCH₃), 7.33–7.47 (m, 7 H, 7 × ArH), 7.58 (d, J = 8.8 Hz, 2 H, 2 × ArH), 8.04 (d, J = 8.0 Hz, 2 H, 2 × ArH), 8.36 (d, J = 8.0 Hz, 1 H, ArH), 8.56 (s, 1 H, ArH) and 8.60 (s, 1 H, NH); $\delta_{C}(100 \text{ MHz};$ DMSO-d₆) 50.34 (CH₃), 106.96, 111.94, 121.10, 121.57, 122.75, 125.43, 125.44, 125.59, 126.44, 127.31, 127.88, 128.43, 130.44, 130.69, 136.06, 141.47 and 164.40 (C=O); m/z (EI) 351 (M+, 100), 320 (62), 291 (40), 207 (9), 145 (34); HRMS calcd for C₂₄H₁₇NO₂: 351.1259, found 351.1259.

Methyl 2-(9-anthracenyl)-5-methylindole-3-carboxylate (8b). The standard procedure was followed by use of 2-iodo-4-methvlaniline (4b, 175.4 mg, 0.7527 mmol, 1.0 equiv), methyl (9anthracenyl)propiolate (7, 311.9 mg, 1.198 mmol, 1.6 equiv), (PPh₃)₂PdCl₂ (26.2 mg, 0.0373 mmol, 0.050 equiv), n-Bu₄NBr (241.8 mg, 0.7500 mmol, 1.0 equiv), NaOAc (312.3 mg, 3.807 mmol, 5.0 equiv), and DMF (30 mL) to give 8b (82.5 mg, 0.226 mmol, 30%) as yellow solids; mp 215.7-216.1 °C (from CH₂Cl₂); $(R_{\rm f} = 0.30, 10\% \text{ EtOAc in hexanes}); \nu_{\rm max}/\text{cm}^{-1} 3320 \text{ (m, N-H)},$ 2954 (w), 1689 (s, C=O), 1450 (s), 1265 (m), 1218 (m), 1149 (s) and 1079 (s); $\delta_{\rm H}(400~{\rm MHz};{\rm CDCl_3})$ 2.57 (s, 3 H, CH₃), 3.45 (s, 3 H, C(=O)OCH₃), 7.17 (d, J = 8.0 Hz, 1 H, ArH), 7.31–7.36 (m, 3 H, $3 \times \text{ArH}$), 7.44 (t, J = 8.0 Hz, 2 H, $2 \times \text{ArH}$), 7.58 (d, J = 8.8Hz, 2 H, 2 × ArH), 8.04 (d, J = 8.8 Hz, 2 H, 2 × ArH), 8.16 (s, 1 H, ArH), 8.47 (s, 1 H, NH) and 8.55 (s, 1 H, ArH); $\delta_{\rm C}(100 \text{ MHz};$ CDCl₃) 21.66, 50.63, 108.47, 110.76, 121.52, 124.88, 125.29, 125.83, 126.27, 126.74, 127.17, 128.45, 128.47, 130.97, 131.03, 131.80, 133.90, 141.00 and 165.24 (C=O); m/z (EI) 365 (M+, 100), 334 (47), 319 (16), 306 (25), 253 (14), 191 (10). HRMS calcd for C₂₅H₁₉NO₂: 365.1416, found 365.1421.

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