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The Production and Characterisation of Novel Conducting Redox-Active Oligomeric Thin Films From Electrooxidised Indolo[3,2,1-*jk*]carbazole

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Abstract: Indolo[3,2,1-ik]carbazole (IC) has been synthesised on a gram scale by flash vacuum pyrolysis. In contrast to a previous suggestion, IC is planar and it is also highly fluorescent, with a solution quantum yield of 0.41. Electro-oxidation of IC at a rotating disc electrode resulted in the passage of steady-state currents and the reproducible formation of conducting, redox-active films with constituent species that are also highly fluorescent. Unusually for coupled electroactive Nheterocyclic systems, electrochemical

Introduction

Redox-active and photoactive oligomers and polymers, produced from *N*-heteroaromatic monomers such as pyrroles,^[1] indoles^[2] and carbazoles,^[3] have received a great deal of attention in recent years. Typically they display efficient luminescence and form extended π -conjugated thin-film materials that show semiconducting-to-conducting electronic properties and redox activity with relatively low cost, good processability, attractive mechanical properties and the ready tuning of properties through chemical functionalisation. This makes them attractive for a variety of applications, including the active film in organic electronic devices, sensors, supercapacitors and in electroluminescent materials.^[4] In particular, there has recently been much interest in the chemical synthesis and characterisation of films formed from selected

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and spectroscopic characterisation revealed the film to consist exclusively of three redox-active (2,2', 5,5' and 2,5' coupled) IC dimers with no polymeric products. Calculations showed this coupling pattern to be consistent with IC radical-cation coupling through the accessible sites of highest unpaired electron density. The unusual combination

Keywords: conducting materials • electrochemistry • luminescence • synthesis design • thin films of a high dimer second oxidation potential and a negligible dimer-dimer coupling rate explains the lack of further coupling. The identities of the dimeric species were confirmed by independent syntheses involving the Suzuki-Miyaura coupling of IC boronic acids as the key step. Electro-oxidation of the IC system therefore offers a ready route to novel conducting. redox-active molecular films and their redox-active, luminescent dimer constituents.

carbazoles, isoindoles and indolocarbazoles. Carbazole^[5] and indolocarbazole^[6] derivatives have been reported as efficient hole transport materials with potential applications in organic thin-film transistors. Isoindoles are highly fluorescent and have been investigated for light-emitting devices.^[7] Poly(Narylcarbazol-2,7-ylene) shows blue photoemission with an enhanced quantum yield over N-alkyl-substituted polymers for light-emitting diode applications.^[8] Indolo[2,3-a]carbazole has also been investigated as a potential anion-sensing material.^[9] There is real interest in producing such systems as molecular films as small molecules (both monomers and oligomers) can form crystalline or homogeneous multilayers due to their efficient packing, which should result in enhanced materials properties.^[10] However, in reality, smallmolecule thin-film production is often problematic as oligomer formation often requires specific chemical synthesis (both monomer formation and site-specific coupling), which can increase the complexity and cost and decrease the yield, and there is difficulty in establishing optimum molecular ordering when depositing thin films from solution.^[11] Although conducting polymeric thin films such as polypyrrole can be readily synthesised and deposited by monomer oxidation and coupling at electrodes, the distribution of the conducting polymer chain lengths and the resulting film inhomogeneity and structural irreproducibility often affects the con-



trol and reproducibility of the performance of thin-film materials.

In this paper we report an alternative synthetic route to the N-heteroaromatic indolo[3,2,1-jk]carbazole (IC) monomer and characterise its properties and the new thin-film materials readily formed by its electro-oxidation. The resulting film formation is reproducible under controlled hydrodynamic conditions and results in conducting redox-active films that, unusually, consist entirely of three specific dimer species, which, like IC, are fluorescent in solution. Such specific electrochemical IC film formation through monomer oxidation and selective coupling demonstrates a route to controlled thin-film formation through monomer design, electrochemical oligomer synthesis and film deposition. A combination of electrochemical, spectroscopic, luminescence, synthetic and theoretical data are presented to identify and characterise the IC dimers formed in these films and to give an insight into the molecular properties that underpin this unusual behaviour.

Results and Discussion

Synthesis of indolo[3,2,1-*jk*]carbazole: Indolo[3,2,1-*jk*]carbazole has previously been synthesised by Dunlop and Tucker^[12] by decomposition of the diazonium salt derived from *N*-(2-aminophenyl)carbazole. However, we have recently shown that flash vacuum pyrolysis (FVP) of 1-(2-nitrophenyl)indole (1) at 875 °C leads to the formation of pyrrolo[3,2,1-*jk*]carbazole (2) via an aryl radical intermediate.^[13] Application of this strategy to *N*-(2-nitrophenyl)carbazole^[14] (3) readily gave IC (4) in a yield of 71% on a gram scale, which is more than adequate for electrochemical film production (Scheme 1). This procedure is one step shorter than the method of Dunlop and Tucker and complements the range of substituted IC derivatives that can be synthesised.

For reference, a complete ¹H and ¹³C NMR analysis of IC was carried out (see the Supporting Information). When IC was prepared by Dunlop and Tucker^[12] it was thought that it



Scheme 1. The FVP synthetic route to pyrrolo[3,2,1-jk]carbazole 2 and indolo[3,2,1-jk]carbazole 4.

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would be bowl-shaped due to the strain in the central threering system and the preference for nitrogen to adopt a more trigonal pyramidal form. In this work we have obtained an X-ray crystal structure of the picrate of IC (Figure 1), which



Figure 1. X-ray crystal structure of **4** from the IC picrate crystal showing the crystallographic numbering scheme.

clearly shows that the molecule is in fact planar. (CCDC 610408 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data_request/cif.)

IC forms co-crystals with picric acid in alternating planes, which suggests that the central nitrogen atom is not basic enough to form a picrate salt. The considerable strain imposed by the central three-ring pyrrolo[3,2,1-hi]indole substructure is accommodated almost entirely by bond length and angular distortion of the central benzene ring and around the central nitrogen atom. The driving force for this system to be planar therefore outweighs the need to relieve this serious distortion in the bond lengths and angles. This planar configuration, as with other heteroaromatics, should enable effective intermolecular π -stacking.

IC in DMF exhibits peak excitation and emission fluorescence wavelengths at 361 and 378 nm, respectively (Figure 2). Its quantum yield, estimated by making a comparative measurement using indole as a standard,^[15] is 0.41, which is comparable to systems such as the highly fluorescent indolizino[3,4,5-*ab*]isoindoles.^[7] This makes **4** of interest



Figure 2. Steady-state excitation and emission spectra for a) IC monomer **4** at fixed emission and excitation wavelengths of 410 and 340 nm, respectively and b) the dissolved film formed from IC electro-oxidation in DMF at fixed emission and excitation wavelengths of 400 and 360 nm, respectively.

for fluorescence and UV light emission applications. The fluorescence lifetime of IC was measured to be 12.7 ns.

Electro-oxidation of IC (4): Typical CVs for 1 mm IC oxidation^[16] (low concentration) are shown in Figure 3. The monomer oxidation peak can clearly be seen at +1.1 V; the



Figure 3. Cyclic voltammograms (CVs) of 1 mm IC 4 in background electrolyte (MeCN/0.1 m LiClO₄) at a sweep rate, $v = 50 \text{ mV s}^{-1}$. The initial direction of sweep is to positive potential, *E*, from the negative potential limit. The cycle numbers are shown.

variation of peak height with the square root of sweep rate (see the Supporting Information) is consistent with a solution reaction under diffusion control. The associated reduction peak near ± 1.0 V is clearly attenuated, increasingly with decreasing sweep rate (see the Supporting Information), consistent with the loss of monomer radical cation through coupling and film formation. On repeated cycling, peaks centred at ± 0.7 V (oxidation) and ± 0.6 V (reduction) can be seen to grow in size; these are the redox peaks of the conducting film.

Electro-oxidation at higher concentrations (2.5, 5, 10, 15 and 20 mM) was also carried out at a rotating disc electrode (RDE) with $E = \pm 1.19 V^{[17]}$ at different rotation speeds, W. In all cases, after initial surface film formation and the onset of steady-state mass transport,^[18] a reproducible steady-state current was observed at each W (Figure 4). Large, essentially steady-state currents,^[19] *i*, were observed over several hundred seconds, which corresponds to thick IC films of the order of several microns;^[20] this indicates the formation of highly reproducible electronically conducting films under hydrodynamic control. Analysis of these currents (Figure 5^[21]) showed that all the data obey the Koutecky– Levich^[22] equation [Eq. (1)],

$$\frac{1}{i} = \left(\frac{0.6435v^{1/6}}{nFAc_{\rm IC}D_{\rm IC}^{2/3}W^{1/2}}\right) + \frac{1}{i_{\infty}} \tag{1}$$

in which *n* is the number of electrons for IC oxidation, *F* is the Faraday constant, *A* is the electrode area, D_{IC} is the dif-



Figure 4. Current-time response observed at an RDE when E = +1.19 V was applied at t=1 s. The onset of steady-state currents at each value of W (shown in Hz) can clearly be seen.^[21]



Figure 5. Koutecky–Levich plot of i^{-1} versus $W^{-1/2}$ for IC oxidation. The lines through the data are those calculated theoretically from Equation (1) with $D_{\rm IC}=3.0\times10^{-5}$ cm²s^{-1[23]} and n=1.5.^[24]

fusion coefficient of IC, $c_{\rm IC}$ is the bulk concentration of IC, ν is the kinematic viscosity of the electrolyte and i_{∞} is the mass-transport-independent current observed as W tends to infinity. Equation (1) applies when first-order mass-transport-dependent and -independent reactions occur in series. Such behaviour has been seen for indoles^[2b] and has been interpreted as film growth through the mass transport of the monomer to the electrode followed by mass-transport-independent adsorption, oxidation and radical-cation coupling.^[25] These IC data are therefore consistent with the general coupling reaction established for indoles and pyrroles [Eq. (2)]:^[1a,2b]

$$n\mathbf{M} \xrightarrow{-ne^{-}} n\mathbf{M}^{+} \xrightarrow{-n\mathbf{H}^{+}} (\mathbf{M})_{n} \xrightarrow{-e^{-}} (\mathbf{M})_{n}^{+}$$

$$\tag{2}$$

Electro-oxidation of the monomer, M, produces radical cations which then couple and are deposited on the electrode, thereby producing the redox-active surface film, $(M)_n$, which is then oxidised to the redox species, $(M)_n^+$, at the electro-oxidation potential. Least-squares fitting of these

data to Equation (1) gives $D_{\rm IC} = (3.0 \pm 0.1) \times 10^{-5} \, {\rm cm}^2 {\rm s}^{-1[23]}$ with $n = 1.5^{[24]}$ and $i_{\infty}/A = 10.9 \pm 0.5 \, {\rm mA \, cm}^{-2}$ for the highest concentrations (10, 15 and 20 mM). This corresponds to the maximum coupling current density for film formation with the rate-determining step being the surface IC coupling rate.

CVs of the films in background electrolyte show the characteristic film redox peaks previously seen in Figure 3 centred at +0.7 V (see the Supporting Information) due to the reversible redox reaction of the film [Eq. (3)], and the linear variation of peak current with sweep rate (see the Supporting Information) is consistent with a film of high electronic conduction and fast redox kinetics.

$$(\mathbf{M})_{n} \stackrel{-\mathbf{e}^{-}}{\underset{\mathbf{+}\mathbf{e}^{-}}{\overset{\mathbf{-}}}} (\mathbf{M})_{n}^{+}$$
(3)

The charge calculated from each redox peak area corresponds to $33\pm3\%$ of the total polymerisation charge, which indicates that n=2, that is, the film consists of electroactive dimers formed by the covalent attachment of two monomers with the loss of two hydrogen atoms.^[26] This was confirmed by FAB mass spectrometry as the parent ion peak was that of this protonated dimer (m/z=481). The steady-state fluorescence of the dissolved film (Figure 2b) shows a significant redshift in emission compared with **4**, consistent with dimer formation. The emission intensity was comparable to IC, as was the measured fluorescence lifetime of 9.5 ns, which suggests dissolved dimers have comparable redox properties, makes these dimers of potential interest in electroluminescent applications.

Chemical oxidation of IC was also carried out with exactly 1 molequiv of $FeCl_3$ in anhydrous MeCN. The precipitate that formed was shown by ¹H NMR spectroscopy and high-resolution mass spectrometry to be the same mixture of dimers 5–7, produced in a yield of 30% and in a similar ratio to that formed during electro-oxidation, which suggests that this ratio of products is fundamental and not due to the effects of surface adsorption on the electrode.

IC dimer film characterisation: By analogy with indoles and pyrroles^[1a,2b] as coupling [Eq. (2)] involves monomer radical cations, we argue that the most likely coupling sites are those with the largest electron spin density, where there will be the highest propensity for radical-coupling and bond formation. DFT calculations on the IC monomer and the IC radical cation produce a theoretical oxidation potential peak of +1.10 V, identical to and certainly within the expected experimental error of a few tens of millivolts^[15] of the observed value of +1.10 V. The calculated spin density distribution in the radical cation (Figure 6) shows the highest unpaired electron density at the 2-position, the equivalent 5and 11-positions as well as the equivalent 7- and 9-positions (cf. Scheme 1). The 7- and 9-positions are sterically hindered due to the close proximity of their hydrogen atoms; this therefore predicts a propensity for 5.5' (5), 2.2' (6) and 2.5'(7) covalently coupled dimers in the film (Figure 7b). An HPLC analysis of the reaction mixture (Figure 8) confirmed

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Figure 6. Electron spin density for the IC radical cation mapped onto the electron density; blue and red regions indicate areas of the highest and lowest electron spin density.^[28]

the presence of three major components in an approximate ratio of 1:2:1. The NMR analysis described in the Supporting Information (the ¹H NMR spectrum is shown in Figure 7a and the assignments are summarised in Figure 7c) clearly identified substructures associated with two 2-substituted ICs (as in 6 and 7) and with two 1,2,4-trisubstituted benzenoid systems (present in both 5 and 7), consistent with the assignments suggested by the DFT calculations. However, some ambiguity remained regarding the exact location of the trisubstituted aromatic substructures in the dimers, so 5– 7 were unambiguously characterised by the total syntheses described below.

Synthesis of IC dimers: The key step in the synthesis of dimers **5–7** was the formation of the biaryl unit by Suzuki–Miyaura^[30] coupling, which requires regioselective synthesis of the bromo compounds **8** and **11** and their transformation into boronic acids **10** and **13** via the esters **9** and **12**, respectively.



The bromo compound **11** was readily obtained (60%) by FVP of 9-(4-bromo-2-nitrophenyl)carbazole (**14**), but this method could not be used to prepare **8** regioselectively. However, bromination of IC (**4**) with NBS in dichloromethane gave a 75:25 mixture of **8** and **11** from which pure **8** was obtained in 55% yield by recrystallisation from acetic acid.^[31]

The standard method for the formation of the arylboronic $acids^{[32]}$ involves halogen-metal exchange of an aromatic bromo compound with butyllithium at -78 °C followed by reaction with triisopropyl borate at room temperature. The aryllithium species derived from both 8 and 11 proved to be

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Figure 7. a) Typical 600 MHz ¹H NMR spectrum of IC film dissolved in $[D_6]$ acetone/ $[D_6]$ DMSO. b) The dimer species present, as deduced from this spectrum, with their labelled monomer substructures. c) Summary of the ¹H and ¹³C NMR assignments for these dimers.^[29]

very unreactive under these conditions, although the boronic acids **10** (ca. 80%) and **13** (also ca. 80%) were both obtained when 10 equiv of triisopropyl borate were used and the reaction was carried out at 60°C followed by hydrolysis.^[32] The presence of the boronic acids **10** and **13** was confirmed by ESI mass spectrometry and by the cross-coupling



Figure 8. HPLC trace of the dimer mixture 5+6+7 (Spherisorb S5-ODS1 column, eluent $A = H_2O/MeCN$ (9:1)+1% NH₄OAc; eluent B =MeCN; solvent gradient: time 0 min = 5% B, gradient increase in B over 30 min to 95% B, eluent mixture then maintained at this level until 55 min; detection wavelength = 254 nm).

reactions described below, but full characterisation was complicated by the probable presence of boroxine trimers, which give a second signal in the ¹¹B NMR spectra of the boronic acids.

Compounds 5, 6 and 7 were then produced in yields of 65, 80 and 55%, respectively, by Suzuki-Miyaura coupling of the appropriate heteroaryl bromide (8 or 11) and aryl boron species (10 or 13) with [Pd(PPh₃)₄] and K₂CO₃ in dioxane/ water (3:1).^[33] These were characterised by a range of NMR techniques (see the Supporting Information) and by highresolution EI mass spectrometry. HPLC analysis of these synthetic dimers was carried out under equivalent conditions to those used for the dissolved films (Figure 8) and showed similar elution peaks in the order 6, 7 and 5; when a dissolved film sample was individually spiked with each dimer the appropriate peak increased in intensity whilst retaining its shape, confirming the identity of 5, 6 and 7 in the film. NMR spiking experiments also led to an enhancement of the appropriate ¹H NMR peaks. CVs of the drop-coated synthetic samples (see the Supporting Information) each showed redox peaks centred near +0.7 V and the solution fluorescence of 5, 6 and 7 (see the Supporting Information) were each similar to one another and to the fluorescence of the dissolved film. These data confirm that 5, 6 and 7 are indeed the constituents of the dissolved film obtained by the electro-oxidation of IC 4.

Rationale for dimer film formation: It is highly unusual for electro-oxidation of an aromatic heterocycle to result exclusively in dimer rather than polymer film formation, as found with **4**. For pyrrole^[1b] the accepted mechanism is that monomer electro-oxidation and radical-cation coupling produces a series of oligomers, M_n , whose oxidation potential for radical-cation formation decreases with increasing *n*. At the electrode potential required for monomer oxidation, oligomer radical-cation formation and coupling then readily occur, which leads to progressively larger oligomers and re-

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sults in a film with a distribution of polymer chain lengths. For indoles,^[34] electro-oxidation initially produces an asymmetric, redox-active cyclic trimer [n=3 in Eq. (2)] that can be further oxidised at potentials below the monomer oxidation potential; these species then couple to form a polymer of linked trimers. Figure 9 shows typical CVs of the dimer film formed from **4** cycled to more positive potentials in background electrolyte to induce further oxidation.



Figure 9. CVs of a dimer film formed from electro-oxidised **4** in background electrolyte scanned over an extended potential range at 50 mV s^{-1} . The potential used to form these films from a solution of **4** (+1.19 V) is shown.

As expected, the film's redox peaks can be clearly seen centred near +0.7 V. However, in contrast to pyrrole and indole, further oxidation only starts to occur near the applied electrode potential of +1.19 V for monomer oxidation and film formation, which indicates unusually high further oxidation potentials for these dimers. There is also no evidence that this further oxidation leads to significant dimer coupling as the charges passed during this oxidation and its associated reduction near +1.0 V are comparable^[35] and remain stable with repeated cycling; this suggests that these further oxidised dimers are kinetically stabilised towards coupling. These effects combine to ensure that dimers are exclusively formed on monomer electro-oxidation and film formation.

Conclusions

Indolo[3,2,1-*jk*]carbazole (IC, **4**) has been prepared by FVP and fully characterised in terms of its structural, luminescence and electrochemical properties. X-ray studies revealed a planar structure capable of π -stacking and electro-oxidation resulted in the reproducible, hydrodynamically controlled formation of conducting films on the electrode surface, which characterisation and synthesis have shown to consist exclusively of three redox-active species, the 2,2', 2,5' and 5,5' dimers, which show solution luminescence comparable to IC. We have shown through computation that these dimers are most likely formed through specific radicalcation coupling. This opens up the prospect of exploiting the attractive properties of **4** in thin-film materials applications. In particular, judicious substitution at the 2- and/or 5-positions of the parent IC molecule should enable both selective dimer production and the tuning of film characteristics (including film composition, conductivity, homogeneity, redox potentials and luminescence properties) for specific enhancement of thin-film properties. The FVP synthetic route is readily able to produce these substituted ICs; a systematic study of these systems will be the subject of a future publication.

Experimental Section

General methods: ¹H NMR spectra were recorded on Bruker AVA600 (600 MHz), Bruker DPX360 (360 MHz) or Bruker ARX250 (250 MHz) spectrometers. ¹³C NMR spectra were recorded on Bruker DPX360 (91 MHz) or Bruker ARX250 (63 MHz) spectrometers. Chemical shifts ($\delta_{\rm H}$ and $\delta_{\rm C}$) are quoted in ppm relative to tetramethylsilane. ¹¹B NMR spectra were recorded on a Bruker DPX360 spectrometer at 115 MHz. Chemical shifts ($\delta_{\rm B}$) are quoted in in ppm relative to boron trifluoride etherate. Mass spectra were recorded on a Kratos MS50 TC instrument under electron impact conditions unless otherwise stated. Chemicals were purchased from Aldrich and were used without purification. X-ray data were collected with Mo_{Kα} radiation using a Bruker Smart Apex diffractometer equipped with an Oxford Cryosystems low temperature device operating at 150K. The structure was solved using DIRDIF and refined by least squares analysis (Saint).

9-(2-Nitrophenyl)carbazole (3): Carbazole (3.0 g, 18 mmol) and 2-fluoronitrobenzene (2.5 g, 18 mmol) were dissolved in DMSO (50 cm³). Caesium carbonate (6.4 g, 20 mmol) was added to the solution with stirring. The suspension was stirred for 15 h before being diluted with water (50 cm³), when a yellow precipitate formed. The mixture was extracted with CHCl₃ ($3 \times 100 \text{ cm}^3$) and the extract washed with water ($3 \times 100 \text{ cm}^3$) before being dried over MgSO4. The solvent was removed by distillation under reduced pressure to yield 9-(2-nitrophenyl)carbazole (3; 4.9 g, 95%). M.p. 155–156°C (lit.:^[12] 156°C); ¹H NMR (250 MHz, CDCl₃): $\delta =$ 8.15–8.08 (m, 3H), 7.79 (dt, ${}^{3}J=7.5$, ${}^{4}J=1.5$ Hz, 1H), 7.68–7.58 (m, 2H), 7.36 (td, ${}^{3}J=7.7$, ${}^{4}J=1.4$ Hz, 2H), 7.27 (td, ${}^{3}J=7.5$ ${}^{4}J=1.2$ Hz, 2H), 7.09 ppm (dd, ${}^{3}J = 7.8$, ${}^{4}J = 1.0$ Hz, 2H); ${}^{13}C$ NMR (63 MHz, CDCl₃): $\delta =$ 140.62, (2 C_q), 134.14 (CH), 131.28 (CH), 131.11 (C_q), 129.03 (CH), 126.20 (2 CH), 125.83 (CH), 123.71 (2 C_q), 120.55 (2 CH), 120.48 (2 CH), 120.42 (C_q), 108.93 ppm (2 CH); MS (EI): m/z (%): 288 (100) [M]⁺, 241 (73), 178 (75), 121 (27), 89 (14).

9-(4-Bromo-2-nitrophenyl)carbazole (14): Carbazole (1.48 g, 8.9 mmol) and 5-bromo-2-fluoronitrobenzene (1.67 g, 8.9 mmol) were dissolved in DMSO (30 cm³). Caesium carbonate (3.45 g, 10.7 mmol) was added to the solution with stirring. The suspension was stirred for 15 h before being diluted with water (50 cm³) when an orange precipitate formed. The mixture was extracted with $CHCl_3$ (3×100 cm³) and the extract washed with water (3×100 cm³) before being dried over MgSO₄. The CHCl₃ layer was concentrated under reduced pressure and the residue was pre-adsorbed onto silica for purification by dry flash chromatography (hexane/ethyl acetate) to yield 9-(4-bromo-2-nitrophenyl)carbazole (14; 2.35 g, 72%). M.p. 151–153°C (lit.:^[36] 152–154°C); ¹H NMR (250 MHz, CDCl₃): $\delta = 8.22$ (d, ${}^{4}J = 2.2$ Hz, 1 H), 8.03 (d, ${}^{3}J = 7.5$ Hz, 2 H), 7.84 (dd, ${}^{3}J = 8.5, {}^{4}J = 2.3$ Hz, 1 H), 7.44 (d, ${}^{3}J = 8.5$ Hz, 1 H), 7.34–7.16 (m, 4 H), 7.00 ppm (d, ${}^{3}J = 8.0$ Hz, 2H); ${}^{13}C$ NMR (63 MHz, CDCl₃): $\delta = 147.38$, (C_q), 140.35 (2 C_q), 137.25 (CH), 132.56 (CH), 130.24 (C_q), 128.91 (CH), 126.33 (2 CH), 123.85 (2 Cq), 121.93 (Cq), 120.83 (2 CH), 120.54 (2 CH), 108.80 ppm (2 CH); MS (EI): m/z (%): 368 (8) [M]+, 366 (8) [M]+, 241 (10), 219 (63), 167 (100), 140 (6), 113 (21), 94 (79).

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Flash Vacuum Pyrolysis (FVP): The substrate was volatilised at low pressure into a silica tube $(30 \times 2.5 \text{ cm})$ heated by a laboratory tube furnace. Organic products were collected in a dry-ice/acetone cold-finger (situated at the exit point of the furnace) and gaseous materials (consisting of NO_x byproducts from cleavage of the nitro group) were collected in a subsequent liquid nitrogen cooled U-tube trap (cf. ref.^[13]). FVP parameters are reported as follows: mass of substrate m_a , furnace temperature T_{fs} inlet temperature T_{is} pressure p and sublimation/distillation time t_m .

Indolo[3,2,1-*jk***]carbazole (4):** FVP of **3** (m_a =3.2 g (13 mmol), T_f =875 °C, T_i =120–160 °C, p=2.0×10⁻² Torr, t_m =190 min) produced indolo[3,2,1-*jk*]carbazole **4** (1.9 g, 71 %) after purification by dry flash chromatography using hexane with an increasing gradient of ethyl acetate as eluent. M.p. 155–156 °C (lit.:^[12] 156 °C); ¹H NMR (360 MHz, CDCl₃): δ =8.14 (d, ³*J*=7.8 Hz, 2 H), 8.04 (d, ³*J*=7.4 Hz, 2 H), 7.89 (d, ³*J*=8.1 Hz, 2 H), 7.59 (t, ³*J*=7.3 Hz, 1 H), 7.55 (td, ³*J*=7.6, ⁴*J*=1.5 Hz, 2 H), 7.36 ppm (td, ³*J*=7.5, ⁴*J*=1.2 Hz, 2 H); ¹³C NMR (63 MHz, CDCl₃): δ =143.59 (C_q), 138.54 (2 C_q), 129.88 (2 C_q), 126.54 (2 CH), 123.01 (2 CH), 122.68 (CH), 121.53 (2 CH), 119.26 (2 CH), 118.31 (2 C_q), 112.02 ppm (2 CH); MS (EI): *m/z* (%): 241 (100) [*M*]⁺, 178 (38), 121 (21), 89 (6), 57 (3).

5-Bromoindolo[3,2,1-*jk*]carbazole (11): FVP of 9-(4-bromo-2-nitrophenyl)carbazole ($m_a = 0.594$ g (1.9 mmol), $T_f = 875$ °C, $T_i = 160-220$ °C, $p = 3.8 \times 10^{-2}$ Torr, $t_m = 40$ min) gave 5-bromoindolo[3,2,1-*jk*]carbazole (11; 0.312 g, 60%) after purification by dry flash chromatography using hexane with an increasing gradient of ethyl acetate as eluent. M.p. 141–143 °C (lit.;^{136]} 144–145 °C); ¹H NMR (360 MHz, CDCl₃): $\delta = 8.25$ (d, ⁴J = 1.8 Hz, 1H), 8.14 (d, ³J = 7.9 Hz, 1H), 8.06 (d, ³J = 7.6 Hz, 1H), 8.00 (d, ³J = 7.6 Hz, 1H), 7.86 (d, ³J = 8.3 Hz, 1H), 7.76 (d, ³J = 8.6 Hz, 1H), 7.79 (d, ³J = 8.6 Hz, 1H), 7.79 (d, ³J = 7.9, $^{4}J = 1.4$ Hz, 1H), 7.38 ppm (td, ³J = 7.6 Hz, 1H), 7.55 (td, ³J = 7.9, ⁴J = 1.4 Hz, 1H), 7.38 ppm (td, ³J = 7.6 (Cq), 136.90 (Cq), 131.34 (Cq), 129.75 (Cq), 128.98 (CH), 126.67 (CH), 125.76 (CH), 117.06 (Cq), 114.33 (Cq), 112.88 (Cq), 111.96 ppm (CH); MS (EI): m/z (%): 321 (49) [M]⁺, 319 (49) [M]⁺, 239 (19), 167 (100), 139 (11), 120 (21), 84 (9).

2-Bromoindolo[3,2,1-*jk*]carbazole (8): Indolo[3,2,1-*jk*]carbazole (4; 1.17 g, 4.8 mmol) and N-bromosuccinimide (0.86 g, 4.8 mmol) were dissolved in dichloromethane (50 cm³) in the absence of light. Silica gel (10 g) was added and the mixture was left to stir for 15 h. The mixture was filtered and the silica was washed with dichloromethane $(5 \times 50 \text{ cm}^3)$. The combined dichloromethane fractions were washed with water $(3 \times$ 50 cm³) and dried over MgSO₄ before being concentrated under reduced pressure to yield a pale-brown solid. The solid was dissolved in the minimum quantity of refluxing glacial acetic acid. A small amount of solvent was distilled under reduced pressure before cooling was allowed to occur. A white solid precipitated and was filtered and washed with glacial acetic acid before being dried under vacuum to yield 2-bromoindolo[3,2,1*jk*]carbazole (8; 0.86 g, 55%). M.p. 208–210°C (lit.:^[12] 205–210°C); ¹H NMR (360 MHz, CDCl₃): $\delta = 8.06$ (s, 2H), 7.99 (d, ³J=7.8 Hz, 2H), 7.79 (d, ${}^{3}J=8.1$ Hz, 2H), 7.54 (td, ${}^{3}J=7.9$, ${}^{4}J=1.1$ Hz, 2H), 7.33 ppm (td, ${}^{3}J=7.8, {}^{4}J=1.0 \text{ Hz}, 2 \text{ H}$; ${}^{13}\text{C} \text{ NMR}$ (63 MHz, CDCl₃): δ =141.65 (C_q), 138.68 (2 C_a), 128.94 (2 C_a), 127.20 (2 CH), 123.13 (2 CH), 122.07 (2 CH), 121.82 (2 CH), 119.33 (Cq), 115.54 (2 Cq), 112.07 ppm (2 CH); MS (EI): m/z (%): 321 (99) $[M]^+$, 319 (100) $[M]^+$, 240 (82), 213 (14), 167 (32), 120 (7), 80 (7), 56 (23).

Indolo[3,2,1-*jk*]carbazoleboronic acids (10) and (13): Anhydrous THF (10 cm³) was added to a dry round-bottomed flask under an atmosphere of argon. The flask and solvent were cooled to -78 °C in a dry-ice/ace-tone bath and a solution of *n*BuLi in hexanes (1.6 M, 1 cm³, 1.94 mmol) was added. A solution of the appropriate bromoarene (8 or 11, 1.56 mmol) in anhydrous THF (15 cm³) was added dropwise over 30 min at -78 °C through a syringe pump to form a bright-yellow solution, which was stirred at -78 °C for 45 min. A solution of triisopropyl borate (19.4 mmol) in anhydrous THF (10 cm³) was added over 30 min, stirred for 30 min and then warmed to room temperature. The solution became cloudy, was stirred for a further 30 min, warmed to 60 °C and stirred first for 12 h and then for a further 15 h after acidification with HCl (2 M). The resulting mixture was diluted with water (5 cm³), extracted with dichloromethane (3 × 50 cm³) and the extract washed with water (2 ×

50 cm³) and dried over MgSO₄. Concentration of this extract under reduced pressure yielded creamy white solids, the ¹H NMR spectra of which showed the correct substitution pattern for **10** and **13**. However, the ¹H integrals were not consistent and the ¹¹B NMR spectra showed that there were two different boron species in the mixtures, which suggested the presence of boroxine trimers. The boronic acids **10** and **13** were both made by following this method.

Indolo[3,2,1-*jk*]**carbazole-2-boronic acid (10**): Yield: 0.399 g, 80 % by mass, mixture **10**; ¹H NMR (360 MHz, $[D_6]$ DMSO): $\delta = 8.67$ (s, 2H), 8.32 (d, ³*J* = 7.2 Hz, 2H), 8.30 (dd, ³*J* = 7.3, ⁴*J* = 1.1 Hz, 2H), 8.22 (d, ³*J* = 7.2 Hz, 2H), 7.68–7.62 (m, 4H), 7.46–7.42 (m, 3H), 7.34 ppm (brs, 2H); ¹¹B NMR (115 MHz, DMSO): $\delta = 35.63$ (brs), 25.41 ppm (brs, minor); MS (ESI): m/z (%): 283 (¹⁰B, 30) [M-H]⁻, 284 (¹¹B, 100) [M-H]⁻; IR (film): $\tilde{v} = 3397$ (OH), 1340 cm⁻¹ (B-O).

Indolo[3,2,1-*jk*]**carbazole-5-boronic acid (13)**: Yield: 0.400 g, 80 % by mass, mixture **13**; ¹H NMR (360 MHz, $[D_6]DMSO$): δ =8.71 (s, 1H), 8.34–8.26 (m, 5H), 8.24–8.18 (m, 3 H), 8.10 (dd, ${}^{3}J$ =8.2, ${}^{4}J$ =1.2 Hz, 1H), 7.68–7.62 (m, 2H), 7.47–7.40 ppm (m, 2H); ¹¹B NMR (115 MHz, DMSO): δ =34.58 (brs), 22.67 ppm (brs, minor); MS (ESI): *m/z* (%):283 (¹⁰B, 30) [*M*–H]⁻, 284 (¹¹B, 100) [*M*–H]⁻; IR (film): $\tilde{\nu}$ =3419 (OH), 1340 cm⁻¹ (B–O).

Suzuki–Miyaura coupling—general method:^[31] The appropriate heteroaryl bromide (8 or 11; 50.0 mg, 0.156 mmol) and arylboron species (10 or 13; 44.5 mg, 0.156 mmol), potassium carbonate (43 mg, 0.312 mmol) and $[Pd(PPh_3)_4]$ (7.2 mg, 4 mol%) were heated at reflux with stirring in 3:1 dioxane/water (10 cm³) for 4 h. The precipitate formed was filtered and washed with water and dioxane before being dried under vacuum. The specific purification procedure for each dimer is shown below. The dimers prepared were insoluble in most solvents, but sparingly soluble in DMSO/acetone mixtures and THF. All the NMR spectroscopic data were recorded in either $[D_6]DMSO$ or $[D_8]THF$. Each dimer was characterised by ¹H, COSY, NOESY and HSQC NMR techniques. For 5 and 6, full ¹³C NMR spectroscopic data were obtained by using HSQC and HMBC techniques. The following products were obtained by this method:

5,5'-Biindolo[3,2,1-*jk***]carbazole (5)**: The product (0.061 g, 65%) was collected by filtration and washed with water and dioxane. M.p. >360°C; ¹H NMR (360 MHz, [D₈]THF): δ = 8.66 (d, ⁴*J* = 1.9 Hz, 2 H), 8.22 (d, ³*J* = 8.3 Hz, 2 H), 8.21 (dm, ³*J* = 7.2, ⁴*J* = 1.1, ⁵*J* = 0.7 Hz, 2 H), 8.19 (d, ³*J* = 7.5 Hz, 2 H), 8.16 (dd, ³*J* = 7.7, ⁴*J* = 1.0 Hz, 2 H), 8.12 (d, ³*J* = 7.2 Hz, 2 H), 8.04 (d, ³*J* = 7.4 Hz, 2 H), 7.62 (t, ³*J* = 7.6 Hz, 2 H), 7.58 (dt, ³*J* = 8.3, ⁴*J* = 1.4 Hz, 2 H), 7.38 ppm (t, ³*J* = 7.9 Hz, 2 H); ¹³C NMR (91 MHz, [D₈]THF, CH resonances only): δ = 127.96 (2 CH), 127.28 (2 CH), 124.12 (2 CH), 124.08 (2 CH), 122.87 (2 CH), 122.85 (2 CH), 122.81 (2 CH), 122.79 (2 CH), 113.49 (2 CH), 113.47 ppm (2 CH); MS (EI): *m*/*z* (%): 480 (2) [*M*]⁺, 190 (38), 156 (100), 128 (21) and 78 (14). HRMS (EI): *m*/*z*: calcd for C₃₆H₂₀N₂: 480.1627 [*M*]⁺; found: 480.1621.

2,2'-Biindolo[3,2,1-*jk***]carbazole (6)**: The product (0.075 g, 80%) was collected by filtration and washed with water and dioxane. M.p. >360°C; ¹H NMR (360 MHz, [D₈]THF): δ =8.47 (4H, s), 8.21 (dm, ³*J*=8.1, ⁴*J*=1.2, ⁵*J*=0.7 Hz, 4H), 8.04 (dm, ³*J*=8.3, ⁴*J*=1.1, ⁵*J*=0.7 Hz, 4H), 7.54 (ddd, ³*J*=8.3, ³*J*=7.6, ⁴*J*=1.1 Hz, 4H), 7.34 ppm (ddd, ³*J*=8.0, ³*J*=7.2, ⁴*J*=1.1 Hz, 4H); ¹³C NMR (91 MHz, [D₈]THF): δ =144.29 (2 C_q), 140.97 (2 C_q), 140.27 (4 C_q), 131.22 (4 C_q), 127.65 (4 CH), 123.90 (4 CH), 122.62 (4 CH), 121.12 (4 CH), 119.62 (4 C_q), 113.24 ppm (4 CH); MS (EI): *m/z* (%): 480 (100) [*M*]⁺, 240 (61), 167 (13). HRMS (EI): *m/z*: calcd for C₃₆H₂₀N₂: 480.1627 [*M*]⁺; found: 480.1622.

2,5'-Biindolo[**3,2,1**-*jk*]**carbazole** (**7**): The product (0.051 g, 55%) was purified by dry flash chromatography (hexane/ethyl acetate). M.p. 297–300°C; ¹H NMR (360 MHz, [D₆]acetone/[D₆]DMSO): δ =8.77 (d, ⁴*J*=1.5 Hz, 1 H), 8.64 (s, 2 H), 8.43–8.40 (m, 3 H), 8.34–8.32 (m, 3 H), 8.29 (d, ³*J*=8.1 Hz, 2 H), 8.24 (d, ³*J*=7.4 Hz, 1 H), 8.12 (dd, ³*J*=8.3, ⁴*J*=1.8 Hz, 1 H), 7.72–7.66 (m, 4 H), 7.48–7.44 ppm (m, 3 H); ¹³C NMR (150 MHz, [D₆]acetone/[D₆]DMSO): δ =145.35 (C_q), 144.58 (C_q), 140.47 (2 C_q), 139.94 (C_q), 139.29 (C_q), 138.92 (C_q), 138.79 (C_q), 131.94 (C_q), 131.00 (2 C_q), 131.17 (C_q), 128.85 (2 CH), 128.83 (CH), 128.70 (CH), 125.05 (2 CH), 124.81 (CH), 124.76 (CH), 124.34 (CH), 123.67 (2 CH), 123.58 (CH), 121.54 (CH), 121.43 (CH), 121.21 (2 CH), 120.12 (2 C_q), 120.06

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 (C_q) , 119.90 (C_q) , 114.41 (CH), 114.37 (2 CH), 114.27 ppm (CH); MS (EI): m/z (%): 480 (8) $[M]^+$, 240 (5), 190 (78), 156 (100), 128 (26), 78 (14). HRMS (EI): m/z: calcd for $C_{36}H_{20}N_2$: 480.1627 $[M]^+$; found: 480.1622.

Electrochemistry: All electrochemical experiments were carried out by using a modular potentiostat with combined waveform generator and voltage sources (Oxford Electrodes Ltd). The platinum rotating-disc working electrode (RDE), area 0.387 cm², was controlled by using a rotator and motor controller (Oxford Electrodes Ltd) with data collection using in-house software written in Visual Designer (Intelligent Instruments). The counter electrode was a 2 cm² platinum gauze and the reference electrode (Bioanalytical Systems Inc.) consisted of a silver wire dipped in a solution of AgClO₄ (0.01 M) in a background electrolyte of LiClO₄/MeCN (0.1 M). This reference electrode has a potential of +0.298 V with respect to the saturated calomel electrode and +0.542 V with respect to the standard hydrogen electrode.^[37] The electrolyte solution was thoroughly purged with nitrogen gas.

Indolo[3,2,1-jk]carbazole (4) dimer film—bulk electrosynthesis for NMR and mass spectrometry: A 20 mM solution of indolo[3,2,1-jk]carbazole (4) in 0.1 M LiClO₄/MeCN was electro-oxidised at +1.19 V using the platinum disc electrode rotating at 4 Hz for periods of 10 min. The film was then reduced to its neutral redox form by stepping the potential down to 0 V and was carefully scraped off the electrode surface. This process was repeated until about 10 mg of film was produced. The product was analysed by ¹H NMR spectroscopy and was found to be a mixture of 5,5'biindolo[3,2,1-jk]carbazole (5), 2,2'-biindolo[3,2,1-jk]carbazole (6) and 2,5'-biindolo[3,2,1-ik]carbazole (7) in a ratio of 1:1:2. The ¹H NMR (600 MHz, [D₆]acetone/[D₆]DMSO) spectra exhibited signals and empirical integrals as follows: $\delta = 8.80$ (d, ${}^{4}J = 1.5$ Hz, 2H), 8.79 (d, ${}^{4}J = 1.5$ Hz, 1H), 8.57 (s, 2H), 8.56 (s, 4H), 8.45-8.39 (m, 6H), 8.37-8.28 (8H, m), 8.26–8.22 (10 H, m), 8.14 (dd, ${}^{3}J = 8.3$, ${}^{4}J = 1.6$ Hz, 2 H), 8.13 (dd, ${}^{3}J = 8.3$, ⁴J=1.6 Hz, 1 H), 7.73-7.66 (m, 14 H), 7.51-7.43 ppm (m, 10 H); some variability in the chemical shifts with solvent and concentration was noted; MS (FAB): m/z: 481 [MH]+; HRMS (FAB): m/z: calcd for C₃₆H₂₁N₂: 481.1660 [MH]+; found: 481.1628.

Chemical oxidation of indolo[3,2,1-*jk*]**carbazole (4)**: Indolo[3,2,1-*jk*]**car**bazole (4; 0.064 g, 0.266 mmol) was dissolved in acetonitrile (7 cm³) under nitrogen. Anhydrous iron(III) chloride (0.043 g, 0.266 mmol) was dissolved in acetonitrile (2 cm³) under nitrogen and added to this solution. A deep-purple colour appeared immediately and the solution was stirred at room temperature under nitrogen until this colour faded. A fine green/black suspension was formed, which was filtered and dried under vacuum to yield a mixture of 5,5'-biindolo[3,2,1-*jk*]carbazole (5), 2,2'-biindolo[3,2,1-*jk*]carbazole (6) and 2,5'-biindolo[3,2,1-*jk*]carbazole (7) in a similar ratio to that formed electrochemically (0.019 g, 30%). ¹H NMR (600 MHz, [D₆]acetone/[D₆]DMSO): δ = 8.81 (d, ⁴*J* 1.7 Hz, 2 H), 8.80 (d, ⁴*J* 1.7 Hz, 11H), 8.61 (s, 2H), 8.60 (s, 4H), 8.47-8.41 (m, 6H), 8.38-8.27 (m, 8H), 8.27-8.23 (m, 10H), 8.15-8.13 (m, 3H), 7.73-7.68 (m, 14H), 7.50-7.42 ppm (m, 10H); MS (FAB): *m/z*: 481 [MH]⁺.

Fluorescence spectroscopy: Steady-state fluorescence spectra were measured by using a Jobin Yvon Spex Fluoromax spectrofluorometer (Instruments S.A. group) with fused silica cuvettes. The excitation source was a 150 W continuous ozone-free xenon lamp with modified Czerny–Turner spectrometers in both the emission and excitation positions. Datamax data acquisition and data manipulation software were used throughout (DataMax for Microsoft Windows, DataMax Version 2.20, **1997**, Developer Instruments SA, Inc.). Time-correlated single-photon-counting (TCSPC) experiments were performed at the Collaborative Optical Spectroscopy Micromanipulation and Imaging Centre (COSMIC) at The University of Edinburgh. All decays were measured by using an Edinburgh Instruments TCSPC spectrometer coupled with a Hammamatsu R3809U-50 series micro-channel plate detector. Samples were excited by using a mode-locked Ti-sapphire laser.

Calculations: Structures were calculated by using the Gaussian $03^{[38]}$ program at the uB3LYP/6-311+G(d,p) level of theory with acetonitrile solvation modelled by the SCRF method. It has previously been shown that the accurate calculation of absolute values of experimental indole oxidation potentials is possible to within a few tens of millivolts, which makes

this suitable as a reference redox reaction.^[39] Calculation of the free energy of the reaction $4^+ + In \rightarrow 4 + In^+$ gives the standard reduction potential of $4^+/4$ relative to the indole (In) redox couple In⁺/In. This can then be converted into a calculated peak oxidation potential on any reference scale by using the experimentally measured value of the indole peak oxidation potential if the reactants and products have similar diffusion coefficients in solution.^[15]

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- [16] All electrochemical experiments were carried out at a platinum disc electrode (area 0.387 cm²) using MeCN/0.1 M LiClO₄ as the background electrolyte and Ag/Ag⁺ (0.01 M) in the background electrolyte as the reference electrode unless otherwise stated.
- [17] Chosen to ensure a sufficiently reactive electrode to ensure the oxidation reaction is not under electrochemical control.
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- [19] In fact there was a gradual increase in current over long times. This is consistent with two-dimensional film growth (growth laterally as well as perpendicular to the disc electrode).
- [20] The thickness can be readily estimated from the volume occupied by each IC in the crystal structure, the charge passed during film formation, the area of the electrode and by assuming 1.5 electrons are passed during the electro-oxidation for each monomer for IC film formation and deposition.
- [21] Taking the earliest time steady-state currents, when the films were relatively thin and the effective area for further film growth could be made equal to the electrode area.
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- [23] This is consistent with values found for other similar sized heteroaromatics.^[2b]
- [24] Calculated by assuming dimer products and deposition of the dimer in the one-electron oxidised form, removing three electrons per two monomers in the dimer [Eq. (2)].
- [25] The coupling of two radical cations in solution would give a secondorder dependency on concentration.
- [26] The total number of electrons passed per $(M)_n$ unit in film formation is n+1 and in the film redox reaction is 1. This gives a ratio of redox to polymerisation charge of $(n+1)^{-1}$.
- [27] The quantum yield, ϕ , is related to the radiative (fluorescent) and non-radiative decay rates, $k_{\rm R}$ and $k_{\rm NR}$, and lifetimes, $\tau_{\rm R}$ and $\tau_{\rm NR}$, by $\phi = \frac{k_{\rm R}}{k_{\rm R}+k_{\rm NR}} = \frac{\tau_{\rm r}^{-1}}{\tau_{\rm R}^{-1}+\tau_{\rm NR}^{-1}}$. The observed fluorescence lifetime is given by $\frac{1}{\tau_{\rm R}^{-1}+\tau_{\rm NR}^{-1}}$ and therefore for similar classes of molecules a similar fluorescence lifetime indicates a similar quantum yield.
- [28] The output was viewed using Jmol, an open-source Java viewer for chemical structures in 3D (http://www.jmol.org/). Rendered by using the Persistence of Vision Raytracer (POV-Ray) freeware (http://www.povray.org).

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