Organic & Biomolecular Chemistry

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 8073

Received 20th August 2013,
Accepted 10th October 2013

DOI: 10.1039/c3ob41701h

www.rsc.org/obc

A novel neutral organic electron donor with record half-wave potential†

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Tricyclic donor **26** has been prepared and is the most reducing neutral ground-state organic molecule known, with an oxidation potential 260 mV more negative than the previous record. Cyclic voltammetry shows that a 2-electron reversible redox process occurs in DMF as solvent at −1.46 V *vs.* Ag/AgCl.

Introduction

The most challenging electron transfer reductions, such as Birch reductions,[1] acyloin couplings[2,3] and reduction of dinitrogen in nitrogenase enzymes,[4] are achieved by reactive metals and their complexes.[5] Recently, a number of organic electron donors have been synthesized that are very strong reducing agents (**1–8**). All of these compounds critically contain nitrogen atoms that are capable of stabilizing both positive charge and radical character, as the donors undergo oxidation. The aromaticity of their oxidation products (radical cations and dications) following loss of one and two electrons respectively, also plays an important role in determining the strength of these electron donors. Table 1 compares the oxidation potentials of these compounds with the widely used sulfur-containing electron donor, tetrathiafulvalene (TTF).[6]

Among the nitrogen-containing electron-donors, TDAE (**1**) is the parent compound in the series and the standard by which the others can be judged.[7] Neither **1** nor its oxidized products is aromatic. Compound **2** could be considered anti-aromatic[8] if planar and so its oxidation through loss of two electrons might expect to be strongly driven; however it is quite deformed from planarity and it contains two aromatic pyrrole rings – as a result it is not a strong reducing agent. Compound **3**[9] is already aromatic and hence its oxidation does not benefit from aromatization as a driving force, and so it also is not a strong donor of electrons. In contrast, donors **4–8** are all converted into aromatic products upon oxidation[10–19] and this adds to their strength as reducing agents. To illustrate the aromaticity that arises, the oxidation products of compound **8** are also shown in Fig. 1. Loss of one electron leads to radical cation **13** featuring one pyridinium ring, while loss of a second electron affords the aromatic disalt **14**. In terms of the applications of these stronger electron donors, benzimidazole-derived **6** converts iodoarenes into aryl radicals,[15] while the stronger donors **7** and **8** reduce the same substrates to aryl anions.[12,14] Donors **7** and **8** are also able to reduce arenesulfonamides,[16] Weinreb amides[17] and acyloin derivatives.[18]

Table 1 Oxidation potentials of neutral organic electron donors

Compound	$E^1_{1/2}$	$E^2_{1/2}$	Solvent	$E^1_{1/2}$ *vs.* SCE (converted)	$E^2_{1/2}$ *vs.* SCE (converted)
TTF[6]	+0.37 V (SCE)	+0.67 V (SCE)	DCM	+0.37 V	+0.67 V
1[7]	−0.78 V (SCE)	−0.61 V (SCE)	MeCN	−0.78 V	−0.61 V
2[8]	−0.59 V (Fc/Fc^+)	−0.26 V (Fc/Fc^+)	THF	−0.14 V	+0.19 V
3[9]	−0.32 V (SCE)	—	MeCN	−0.32 V	—
4[13]	−1.33 V (Fc/Fc^+)	−1.14 V (Fc/Fc^+)	DMF	−0.88 V	−0.69 V
5[11]	−1.48 V (Fc/Fc^+)	−1.48 V (Fc/Fc^+)	THF	−1.03 V	−1.03 V
6[10]	−0.82 V (SCE)	−0.76 V (SCE)	DMF	−0.82 V	−0.76 V
7[10]	−1.20 V (SCE)	−1.20 V (SCE)	DMF	−1.20 V	−1.20 V
8[14,19]	−1.69 V (Fc/Fc^+)	−1.69 V (Fc/Fc^+)	DMF	−1.24 V	−1.24 V

Although these are highly reactive organic compounds, their reducing power is significantly less than that of the strongest metals (*e.g.* the oxidation potential of Li, $E^0 = -3.02$ V)[20] and questions arise about whether a limit is being approached in the design of organic neutral donors.

Molecule **5a** features a number of rings, all of which could become aromatic (**5b**) on loss of two electrons.[11] However, if such a donor has a sufficient number of linked rings, the aromatic stabilization energy might ensure that the ground-state of **5a** will instead be diradical **5c** and then the oxidation to **5b** by loss of two electrons would only convert the two terminal

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†Electronic supplementary information (ESI) available: Computational coordinates and NMR spectra are provided. See DOI: 10.1039/c3ob41701h

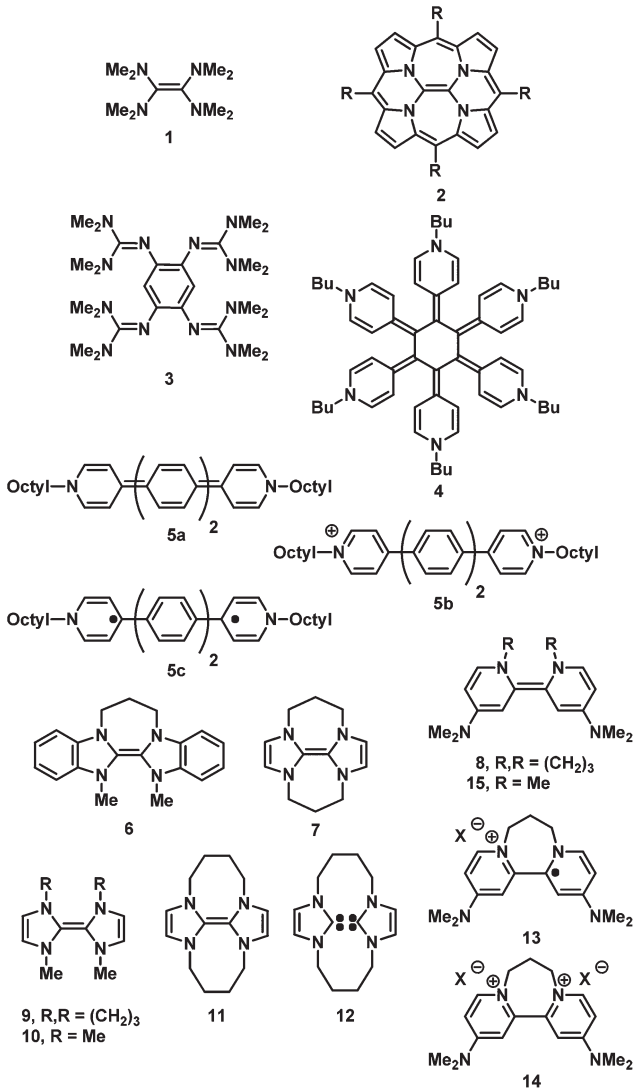


Fig. 1 Known neutral organic electron donors **1–8** and related compounds.

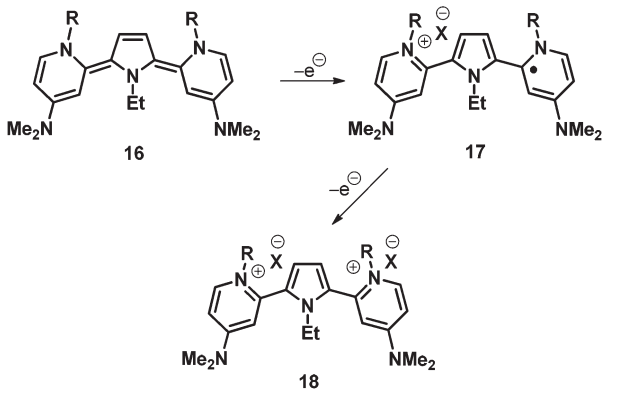
rings to aromatic rings. Whether **5** exists as **5a** or **5c** is not entirely settled. The compound did not afford a well-defined NMR spectrum that would characterize a closed-shell structure,[11] indicating that it might be a diradical, although no EPR evidence for radical character was seen. The second indication of a reactivity limit related to the imidazole-derived compounds **7**, **9–12**. Although the doubly trimethylene-tethered compound **7** has been fully characterized, efforts to make simpler analogues of this compound, for example **9–11**, had proved impossible.[21,22] Attempted preparations of compound **11** had instead led to dicarbene **12**, possibly through spontaneous rupture of the central alkene to the dicarbene, but more likely through activation by a proton source or by a metal cation[23] – the dicarbene **12** is not an electron donor. The instability of the tetraazafulvalene central double-bond was evident also from calculations that showed bond strength for molecule **10** of only 4 kJ mole^{-1}.[21] In fact, compound **9** and **10** have recently been prepared in our laboratories,[24] but have been shown to be very short-lived.

Results and discussion

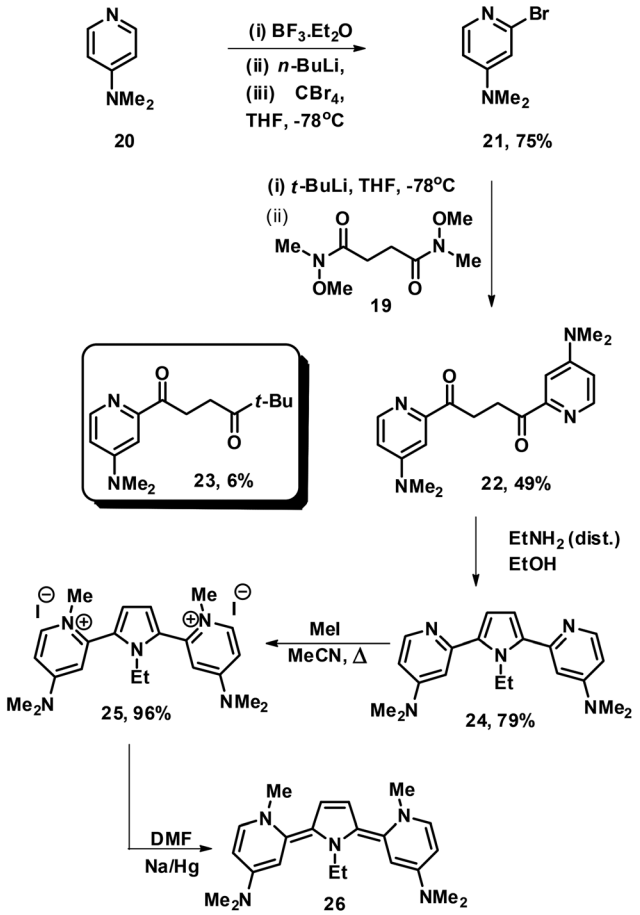
To probe whether more powerful donors could be prepared, it was therefore important to avoid compounds like **7** and **9–12**. Compound **8** offered the best design lead. This compound was a purple solid and was stable in the absence of air and moisture. Unlike imidazole-derived **7**, which required both trimethylene bridges, it had been possible to synthesise some analogues of the pyridine-derived **8**, including the compound **15** that features no trimethylene bridges. These compounds were, together with **7**, the strongest neutral organic ground-state donors known. To enhance the donor strength, two possibilities were considered: (i) introduction of appropriately placed electron-releasing substituents on the pyridine-derived rings or (ii) extension of the polycyclic system by inclusion of more rings. We recently reported that our initial efforts to prepare analogues derived from 2-(dialkylamino)pyridines had led in an unexpected direction[25,26] but we now address both points in extending the polycyclic system.

The strategy for development of extended donors and more powerful donors involved using pyrrole-derived units.[27–30] Interpolation of a pyrroldiylidene between the two pyridine-derived rings of donor **15** would result in **16**. Here, five nitrogen atoms would stabilize the transition states and products of oxidation, and three rings would develop aromaticity in the two-electron conversion to pyrrole-dipyridinium salt **18** (Scheme 1).

The synthesis of **16** was achieved as shown in Scheme 2.[31] Initially, the synthesis of diketone **22** directly from Weinreb amide **19** and 4-DMAP **20** was attempted using Fort's direct deprotonation protocol,[32] however this was unsuccessful. Kessar[33] used *N*-trifluoroboration of pyridine to acidify the 2-position of the ring, and the resulting pyridinium ylide was used for C–C bond-formation. The same BF_3 adduct has also been utilized by Sammakia[34] and Vedejs.[35] The trifluoroborate salt was easily prepared (76% yield) from reaction of **20** with $BF_3{\cdot}Et_2O$ followed by filtration of the hygroscopic white solid. Formation of diketone **22** from lithiation of the BF_3 adduct was unsuccessful using LDA, *n*-BuLi or *t*-BuLi and so a lithium–halogen exchange using 2-bromo-4-DMAP **21** followed by addition of Weinreb amide **19** was attempted. The synthesis



Scheme 1 Proposed new electron donors **16**.



Scheme 2 Synthesis of new electron donor **26**.

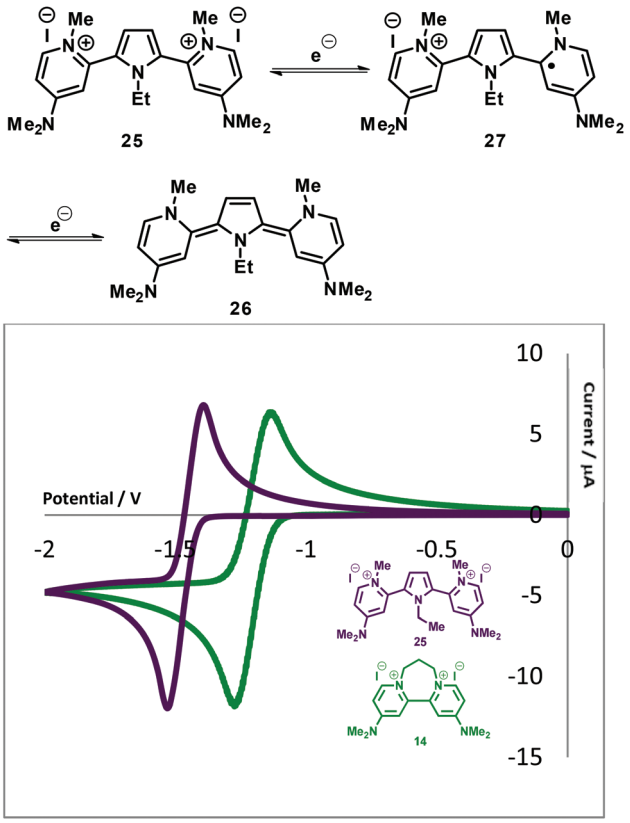


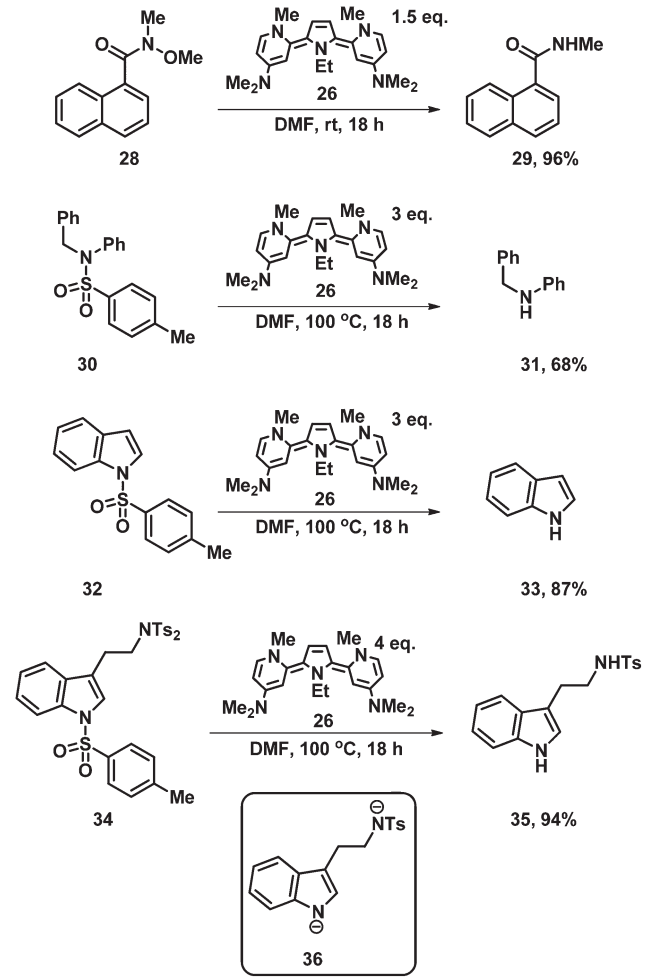
Fig. 2 Comparison of cyclic voltammograms of **25** (**purple**) and **14** (**green**) *vs.* Ag/AgCl in DMF at 50 mV s^{-1} scan rate.

of **21** was successful and optimized by forming the trifluoroborate adduct *in situ* and using tetrabromomethane as the halogenation source, as opposed to bromine. A minor side-product **23** arose from nucleophilic attack by *t*-BuLi. From **22**, formation of the central pyrrole ring to give compound **24** was efficient, as was the methylation of the pyridine rings to give dication **25** (79% and 96% yields respectively, Scheme 2).

Cyclic voltammetry of compound **25** (Fig. 2 shows the voltammogram together with that of **14**) revealed a reversible two-electron wave at $E_{1/2}$ = −1.46 V *vs.* Ag/AgCl in DMF (equating to −1.50 V *vs.* SCE). This is 260 mV more negative than the half-wave potential for **8**, and so compound **26** is now by far the most powerful neutral ground-state organic electron donor yet synthesized. Donor **26** was prepared by reduction of disalt **25** with sodium amalgam in DMF. The compound was then removed from the amalgam for analysis and to explore its reactivity.

Characterisation of **26** proved interesting. As previously seen for compound **5**, this compound did not give a well resolved ^{1}H NMR spectrum in DMF-d_7. Attempts to achieve a sharper spectrum by cooling, or by heating to 90 °C, were not successful, and so we sought further information at room temperature. To do this, ESR spectra were recorded and a weak signal detected that was consistent with an organic radical, but not with a triplet diradical. This species may be the radical cation **27** or may be another radical derived from **26**. Quantitative ESR measurements undertaken using diphenylpicrylhydrazyl (DPPH) as a calibrant indicated that the radical concentration accounted for only 0.012% of the concentration of **26**, and so this cannot be the cause of the broadness in the NMR spectrum. The alternative possibility of rotation about the inter-ring C=C bonds through a suitable low-energy triplet was also explored. A low energy triplet (M05-2X/cc-pVTZ: $\Delta U_{T,calc}$ = 11.0 (12.9) kcal mol^{-1}, gas phase (DMF)) exists (see ESI† file); however since this is not observed in ESR, it could only be a conduit between configurational isomers about the inter-ring C=C bonds. However, the energies of the configurational isomers are very high relative to **26**, (density functional calculations using the B3LYP 6-31G* options in a DMF continuum (Spartan'10 V1.1.0, Wavefunction Inc.) show that changing one of the inter-ring alkenes from *E* to *Z* affords the next most favourable isomer, but that is 23 kcal mol^{-1} higher in energy than **26**) and accordingly, populations of minor isomers arising in this way are unlikely as the cause of the broad signals in the NMR spectrum.

The product of the oxidation of **26** by molecular iodine was characterized as the diiodide salt **25**. Further characterization of donor **26** was achieved through performing the experiment quantitatively by using titration. The compound **26** was treated with excess iodine to afford **25**; following this reaction, the unreacted residual iodine was then back-titrated with sodium



Scheme 3 Reduction of organic substrates using donor **26**.

thiosulfate. This titration showed that the donor had reacted with exactly one equivalent of iodine, in line with expectation for two-electron donor **26**.

The reactivity of **26** towards organic substrates was now tested. Donor **26** reduced Weinreb amide **28** (96% yield) using just 1.5 eq. of donor at room temperature (Scheme 3). Reduction of tosylamides **30**, **32** and **34** was then carried out. Substrate **30** was of interest as 4-DMAP-based donor **8** had reduced substrate **30** with difficulty in 22% yield at 100 °C, and six equivalents of imidazole-based donor **7** had been required to reduce **32** in 96% yield at 110 °C. However, donor **26** now reduced **30** and **32** in 68% and 87% yield respectively, both times requiring only 3 equivalents of donor at 100 °C indicating that it is more efficient at performing difficult reductions. It has been previously established that the deprotection of these sulfonamides affords nitrogen anions and sulfinate anions. In this way, reaction of substrate **34** affords dianion **36**, leading to isolated sulfonamide **35**, on workup. Overall, pyrroldiylidene donor **26** represents a new generation of highly electron-rich and purely organic reducing agents with a half-wave potential of −1.5 V *vs*. SCE and the ability to carry out ever more challenging reductions.

Conclusions

A new powerful neutral organic electron donor **26** has been synthesized and is able to reduce appropriate tosylamides with greater efficiency than any previously synthesized neutral organic donor. With a half-wave potential of −1.46 V *vs*. Ag/AgCl in DMF (equating to of −1.5 V *vs*. SCE), it is the most reducing neutral organic species known.

Experimental section

General

Proton NMR (^{1}H) spectra were recorded at 500 MHz (on a Bruker® AV500™ spectromer) or at 400.13 MHz (on a Bruker® DPX 400™ or Bruker® AV400™ spectrometer). Carbon NMR (^{13}C) spectra were recorded at 125 MHz or 100 MHz using a J-mod pulse program to determine carbon assignments. Experiments were carried out using deuterated chloroform ($CDCl_3$) unless otherwise stated and chemical shifts are reported in parts per million (ppm), calibrated on the solvent residual peak and referenced to tetramethylsilane. Coupling constants *J* are reported in hertz (Hz). The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad singlet.

High resolution mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre, Swansea on a JLZX 102™, VGZAB-E™ or a VG™ micromass instrument. Low resolution mass spectra were recorded at the University of Strathclyde Mass Spectrometry Service on a ThermoFinnigan™ PolarisQ Ion Trap Spectrometer and trace GC instrument using a ZB-5 column (30 metres).

Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR™ spectrometer as films applied on sodium chloride plates or mixed and pressed into potassium bromide disks. Melting points were recorded using either a Griffin or a Gallenkamp melting point apparatus.

Column chromatographies on silica gel were performed using Prolabo 35–75 μm particle sized silica gel 60 (200–400 mesh). Crude mixtures were studied using thin layer chromatography (TLC) carried out on Merck silica gel 60 F_{254} precoated aluminium plates. Visualization was achieved under UVP mineralight UVG-11 lamp or by developing plates with methanolic vanillin or potassium permanganate.

Concentration of solutions under reduced pressure (1–10 mbar) was achieved using a diaphragm pump vacuum. Drying of solids under reduced pressure was performed at room temperature firstly under 1–10 mbar using a diaphragm pump vacuum then under 0.001–0.01 mbar using a rotary oil pump.

All reagents were obtained from commercial suppliers and used without further purification unless stated otherwise. Tetrahydrofuran, dichloromethane, hexane, diethyl ether and toluene were dried and deoxygenated with a Pure-Solv 400 solvent purification system (by Innovative Technology Inc., USA). *n*-BuLi was obtained as a 2.5 M solution in hexane and

t-BuLi as a 1.7 M solution in hexane. Titration of both reagents, prior to use, was achieved by dropwise addition of either reagent solution *via* syringe to a solution of diphenylacetic acid (1 mmol) in THF (10 mL) under argon. Addition was stopped with the first appearance of a yellow colour (diphenylacetate dianion) and the volume of lithiating reagent was measured. The procedure was carried out *in triplicate* so that an average concentration could be calculated for each reagent. *N*,*N*-Dimethylformamide was obtained from commercial suppliers as anhydrous (99.98%) and used directly. Sodium hydride was supplied as a 60% suspension in mineral oil and was washed with hexane to remove oil prior to use. Dry acetonitrile was dried by distillation over phosphorus pentoxide. All reactions were carried out under argon unless otherwise stated.

Calculations

All calculations in the ESI file were performed using the Gaussian09 suite of programs.[36] The M05-2X hybrid functional[37] was employed in combination with a cc-pVTZ basis set.[38] All stationary points were fully optimised and characterised *via* a vibrational analysis. The influence of solvation was taken into account *via* a polarisable continuum model (scrf=pcm).[39]

Cyclic voltammetry conditions

Cyclic voltamograms were carried out using a glassy carbon working electrode, Ag/AgCl reference electrode and platinum counter electrode. The electrolyte solution used was 0.1 M tetrabutylammonium hexafluorophosphate in degassed anhydrous DMF and the concentrations of the ferrocene external standard and analyte were also 0.1 M. All solutions were prepared in the glovebox under an inert atmosphere. A three-electrode set up was used to obtain the cyclic voltammograms. Electrochemical measurements were carried out using the Autolab®/PGSTAT302N potentiostat.

General procedure for reductions using pyrrole-based tricyclic electron donor 26

Sodium amalgam was prepared by addition of freshly cut sodium (50 mg) to a flame-dried 25 mL round bottom flask containing mercury (5 g) under a strong flow of argon. To this was added anhydrous DMF (15 mL) followed by pyrrole-based diiodide salt **25**. The formation of a deep purple colour indicated donor formation and at this stage the reaction was left stirring for 3 h to ensure reaction had gone to completion. The purple solution was transferred by cannula to a flask containing the desired substrate and left to stir overnight at the stated temperature. There was no transfer of sodium amalgam to the flask containing the substrate. This was further verified by inspecting the flask for traces of mercury at the work-up stage. The reaction solution was partitioned between EtOAc (100 mL) and water (50 mL). The organic phase was washed with water (2 × 50 mL) to remove traces of DMF and brine (50 mL). After drying over Na_2SO_4 and concentrating under reduced pressure, the residue was purified using column chromatography with the stated eluent mixture.

Preparation of *N*,*N*′-dimethoxy-*N*,*N*′-dimethylsuccinamide 19

Potassium hydroxide (50.95 g, 908 mmol, 6 eq.) was added to a solution of *N*,*O*-dimethylhydroxylamine hydrochloride (59.05 g, 605 mmol, 4 eq.) in water (150 mL) slowly at 0 °C with vigorous stirring. The free amine was distilled from the solution at 42 °C and added *via* dropping funnel to a solution of succinyl chloride (16.6 mL, 151 mmol, 1 eq.) in dry DCM (300 mL) under argon at −10 °C with vigorous stirring. The reaction mixture was brought to room temperature and left stirring under argon atmosphere for 16 h. The reaction mixture was concentrated under reduced pressure to 100 mL, washed with 0.5 M hydrochloric acid (5 × 50 mL), $NaHCO_{3(aq)}$ (3 × 50 mL), brine (50 mL) and dried over Na_2SO_4. The crude solution was concentrated under reduced pressure and purified by column chromatography (firstly with neat EtOAc to remove less polar impurities then 20% MeOH–EtOAc) to afford *N*,*N*′-dimethoxy-*N*,*N*′-dimethylsuccinamide **19** (20.1 g, 65%) as a clear oil, which crystallised on standing to give white crystals; m.p. 73–75 °C (lit.:[40] 73–75 °C); [Found: (ESI$^+$) $(M + H)^+$ 205.1185, $C_8H_{17}N_2O_4$ (MH) requires 205.1183]; ν_{max}(film)/cm^{-1} 3493, 2963, 2942, 2830, 1731, 1660, 1460, 1422, 1390, 1194, 1097, 994, 934, 795, 745; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.78 (4H, s, CH_2), 3.12 (6H, s, NCH_3), 3.74 (6H, s, OCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 25.9 (CH_2), 31.1 (NCH_3), 60.7 (OCH_3), 172.9 (C); *m*/*z* (ESI$^+$) 205 ($[M + H]^+$, 100%), 239 (21), 351 (7), 515 (2).

Preparation of 2-bromo-4-dimethylaminopyridine 21

(a) Preparation of 4-dimethylaminopyridinium trifluoroborate. To a solution of 4-dimethylaminopyridine (4.89 g, 40 mmol, 1 eq.) in a 1 : 1 mixture of dry THF (50 mL) and Et_2O (50 mL) was added boron trifluoride diethyl etherate (6.01 mL, 48.9 mmol, 1.22 eq.) dropwise. The white suspension was stirred at room temperature for 3 h and the precipitate was filtered *via* argon pressure onto a sinter funnel. The white solid was dissolved in DCM (100 mL), washed with water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford 4-dimethylaminopyridinium trifluoroborate (5.80 g, 76%) as a white solid; mp: 128–130 °C (lit.:[41] 129.8–130.9 °C); [Found: (ESI$^+$) $(M + NH_4)^+$ 208.1226; $C_7H_{14}(^{11}B)F_3N_3$, $(M + NH_4)$ requires 208.1227]; ν_{max}(KBr)/cm^{-1} 2939, 1646, 1568, 1404, 1113, 914; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.18 (6H, s, NCH_3), 6.64 (2H, s, J = 7.3 Hz, ArH), 8.12 (2H, d, J = 7.3 Hz, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 40.0 (CH_3), 106.3 (CH), 142.2 (CH), 156.9 (C); ^{19}F-NMR (125 MHz, $CDCl_3$) δ 152.07–152.18 (BF_3); *m*/*z* (ESI$^+$) 207 ($[M + NH_4]^+$, ^{10}B, 22%), 208 ($[M + NH_4]^+$ ^{11}B, 100%), 213 $[(M + Na)^+$, 68], 231 (13).

(b) Preparation of 2-bromo-4-dimethylaminopyridine 21. To a solution of 4-dimethylaminopyridine (25.45 g, 208 mmol, 1 eq.) in dry THF (300 mL) at room temperature was added freshly purchased boron trifluoride diethyl etherate (30.9 mL, 250 mmol, 1.2 eq.) and solution was stirred for 30 min before cooling to −78 °C under vigorous flow of argon. *n*-BuLi in hexane (100 mL, 250 mmol, 1.2 eq.) was added dropwise under argon to the cream-coloured suspension, keeping

the temperature below −70 °C. After 30 min, a solution of carbon tetrabromide (82.91 g, 250 mmol, 1.2 eq.) in dry THF (100 mL) was added dropwise *via* cannula under argon (again keeping temperature below −70 °C) and the dark brown reaction mixture was left to warm to room temperature overnight. THF was removed under reduced pressure and the residue was partitioned between DCM (250 mL) and sat. $NaHCO_{3(aq)}$ (100 mL). The organic layer was washed with sat. $NaHCO_{3(aq)}$ (2 × 100 mL), brine (100 mL) and dried over Na_2SO_4. The crude solution was concentrated under reduced pressure and purified by column chromatography (10–30% EtOAc–hexane) to afford 2-bromo-4-dimethylaminopyridine **21** (30.59 g, 75%) as an orange semi-solid; [Found: (ESI^+) $(M + H)^+$ 202.0022; $C_7H_9(^{79}Br)N_2$ requires MH, 202.0022]; ν_{max}(film)/cm^{-1} 2932, 2820, 1594, 1520, 1441, 1222, 1131, 1073, 978; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.99 (6H, s, NCH_3); 6.43 (1H, dd, J = 2.5 Hz, 6 Hz, ArH); 6.63 (1H, d, J = 2.5 Hz, ArH); 7.93 (1H, d, J = 6 Hz, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 39.5 (NCH_3), 106.4 (CH), 109.4 (CH), 143.2 (C), 149.5 (CH), 156.0 (C); m/z (CI^+) 202 ($[M + H]^+$, ^{79}Br, 63%), 204 ($[M + H]^+$, ^{81}Br, 4%), 123 (100). Data were consistent with precedent.[42]

Preparation of *1,4-bis-(4-dimethylamino-2-pyridyl)butane-1,4-dione* 22, with *1-(4-dimethylamino-2-pyridyl)-5,5-dimethylhexane-1,4-dione* 23 as by-product

To a solution of 2-bromo-4-dimethylaminopyridine **21** (300 mg, 1.49 mmol, 2.05 eq.) in dry THF (20 mL) at −78 °C under argon was added *t*-BuLi (2.01 mL, 3.02 mmol, 4.15 eq.) dropwise using argon pressure. The reaction was stirred for 60 min and a solution of *N*,*N*′-dimethoxy-*N*,*N*′-dimethylsuccinamide (149 mg, 0.73 mmol, 1 eq.) in THF (10 mL) was added dropwise using argon pressure. The reaction was then left to warm to room temperature overnight. After quenching the reaction by dropwise addition of water (5 mL), THF was removed under reduced pressure. The red residue was dissolved in DCM (40 mL) and washed with water (2 × 20 mL), sat. $NaHCO_{3(aq)}$ (1 × 20 mL), brine (1 × 20 mL) and dried over Na_2SO_4. The crude solution was concentrated under reduced pressure and purified by column chromatography (1% Et_3N–EtOAc). Since the product is insoluble in EtOAc, the crude material was washed with EtOAc in a sinter funnel to remove unreacted 4-dimethylaminopyridine. The yellow solid was then dried under reduced pressure to afford *1,4-bis-(4-dimethylamino-2-pyridyl)butane-1,4-dione* **22** (5.3 g, 49%) as a yellow powder; m.p. 165–167 °C; [Found: (EI^+) (M^+) 326.2; $C_{18}H_{22}N_4O_2$ requires M^+, 326.2]; ν_{max}(film)/cm^{-1} 2924, 1692, 1600, 1509, 1432, 1377, 1226, 985, 810; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.04 (12H, s, NCH_3), 3.64 (4H, s, CH_2), 6.63 (2H, dd, J = 2.5 Hz, 6 Hz, ArH), 7.31 (2H, d, J = 2.5 Hz, ArH), 8.31 (2H, d, J = 6 Hz, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 32.5 (CH_2), 39.2 (NCH_3), 104.9 (CH), 109.2 (CH), 149.1 (CH), 153.7 (C), 155.1 (C), 201.6 (C); m/z (EI^+) 326 ($[M^+]$, 100%), 327 (21), 328 (5). *1-(4-Dimethylamino-2-pyridyl)-5,5-dimethylhexane-1,4-dione* **23** (623 mg, 6.5%) was also separately isolated as a yellow oil [Found: (ESI^+) $(M + H)^+$ 263.1757; $C_{15}H_{22}N_2O_2$ requires MH, 263.1754]; ν_{max}(film)/cm^{-1} 2966, 1698, 1601, 1540, 1509, 1432, 1376, 1224, 1054, 985, 947, 818, ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.14 (9H, s, CH_3), 2.86 (2H, t, J = 6 Hz, CH_2), 2.95 (6H, s, NCH_3), 3.39 (2H, t, J = 6 Hz, CH_2), 6.53 (2H, dd, J = 2.5 Hz, 6 Hz, ArH), 7.17 (2H, d, J = 2.5 Hz, ArH), 8.20 (2H, d, J = 6 Hz, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 26.6 (CH_3), 30.8 (CH_2), 32.0 (CH_2), 39.1 (NCH_3), 43.9 (C), 104.6 (CH), 109.2 (CH), 149.0 (CH), 153.5 (C), 154.8 (C), 201.6 (C), 214.4 (C); m/z (ESI^+) 263 ($[M + H]^+$, 100%), 264 (16), 265 (5).

Preparation of *N-ethyl-2,5-bis-(4-dimethylamino-2-pyridyl)-pyrrole* 24

To a solution of *1,4-bis-(4-dimethylamino-2-pyridyl)butane-1,4-dione* **22** (1.56 g, 4.79 mmol, 1 eq.) in methanol (10 mL) was added freshly distilled ethylamine$_{(aq)}$ (20 mL, excess). The reaction was stirred at room temperature overnight and concentrated under reduced pressure. The residue was purified by column chromatography (EtOAc to 2% Et_3N–EtOAc) and washed in a sinter funnel with diethyl ether to remove further impurities to afford *N-ethyl-2,5-bis-(4-dimethylamino-2-pyridyl)-pyrrole* **24** (1.26 g, 79%) as a light brown semi-solid; [Found: (ESI^+) $(M + H)^+$ 336.2185, $C_{20}H_{25}N_5$ requires MH, 336.2183]; ν_{max}(KBr)/cm^{-1} 3091, 2978, 2927, 2814, 1593, 1542, 1501, 1443, 1370, 1325, 1278, 1224, 989, 804, 770; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.04 (3H, t, J = 7 Hz, CH_3), 3.04 (12H, s, NCH_3), 4.80 (2H, q, J = 7 Hz, CH_2), 6.42 (2H, dd, J = 2.5 Hz, 6 Hz, ArH), 6.76 (2H, d, J = 2.5 Hz, ArH), 8.27 (2H, d, J = 6 Hz, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 16.6 (CH_3), 39.2 (NCH_3), 40.7 (CH_2), 104.7 (CH), 105.9 (CH), 110.6 (CH), 136.0 (C), 144.0 (CH), 153.0 (C), 154.8 (C); m/z (ESI^+) 336 ($[M + H]^+$, 100%), 337 (20), 338 (3).

EPR measurements

Deoxygenated dry DMF (15 mL) was added under a flow of argon to an oven-dried 25 mL round-bottomed flask containing sodium amalgam (prepared from 50 mg of sodium in 5 g of mercury) and the donor precursor diiodide salt (69.7 mg, 0.113 mmol, 1 eq.). The deep purple reaction mixture was stirred at room temperature under fast argon flow for 3 h. Three test aliquots of this 0.0075 M solution were transferred into an oven dried syringe needle and the centre of a freshly created stream of this air-sensitive solution was immediately drawn from inside the tip of the syringe needle into a 1 mm diameter glass capillary (with a sample height of around 5 cm) before being sealed at the open end by flame-gun. This was repeated a fourth time until there was great confidence that no oxygen was present in the sample solution (which maintained a deep purple colour). ESR data were then obtained for this sample, which showed a signal with *g*-factor 2.0035).

To an oven-dried 25 mL round bottom flask containing diphenylpicrylhydrazyl (DPPH, 44.5 mg, 0.113 mmol, 1 eq.) was added deoxygenated dry DMF (15 mL) and a sample of this 0.0075 M solution was transferred into a 1 mm capillary in an identical manner to that mentioned above so that a reference ESR signal could be obtained (*g*-factor 2.0035). Comparison of the signal intensities indicated a concentration of 9×10^7 M, corresponding to 0.012 M conversion of the donor to the radical cation within that solution.

Preparation of *N-ethyl-2,5-bis-(N′-methyl-4-dimethylamino-2-pyridinium iodide)pyrrole* 25

Methyl iodide (12 mL, 192 mmol, 15 eq.) was added dropwise to a solution of *N-ethyl-2,5-bis-(4-dimethylamino-2-pyridyl)-pyrrole* **24** (4.30 g, 12.8 mmol, 1 eq.) in acetonitrile (80 mL) was under argon. The solution was refluxed and the suspension formed was left stirring overnight. The suspension was cooled to room temperature, diethyl ether (100 mL) was added and the solid was filtered *via* suction and washed with diethyl ether several times to afford *N-ethyl-2,5-bis-(N′-methyl-4-dimethylamino-2-pyridinium iodide)pyrrole* **25** (7.50 g, 95%) as a light brown powder; m.p. (dec.) $T > 250$ °C; [Found: (NSI^+) $(M - 2I)^{2+}$ 182.6281 $C_{22}H_{31}N_5$ $(M - 2I)^{2+}$ requires 182.6284]; ν_{max}(KBr)/cm^{-1} 2924, 1674, 1567, 1382, 1314, 1059; ^{1}H-NMR (500 MHz, DMSO-d_6) δ 0.91 (3H, t, J = 7 Hz, CH_3), 3.23 (12H, s, NCH_3), 3.74 (6H, s, NCH_3), 3.82 (2H, bs, CH_2), 6.69 (2H, s, ArH), 7.11 (2H, d, J = 3 Hz, ArH), 7.15 (2H, dd, J = 3 Hz, 7.5 Hz, ArH), 8.42 (2H, d, J = 7.5 Hz, ArH); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 16.7 (CH_3), 40.5 (NCH_3), 41.1 (CH_2), 43.3 (NCH_3), 107.9 (CH), 111.6 (CH), 113.7 (CH), 126.4 (C), 144.2 (C), 145.2 (CH), 156.4 (C), m/z (NSI^+) 182 ($[M - 2I]^{2+}$, 100%), 337 (42), 492 (29), 651 (13).

Preparation of *N*-methyl-1-naphthamide 29

The general procedure for electron transfer reactions was applied to *N*-methoxy-*N*-methyl-1-naphthamide (116 mg, 0.54 mmol, 1 eq.) using pyrrole salt **25** (500 mg, 0.81 mmol, 1.5 eq.). The reaction was stirred at room temperature and the crude material was purified by column chromatography (5% EtOAc–DCM) to give *N*-methyl-1-naphthamide **29** (102 mg, 96%) as a white crystalline solid m.p. 159–161 °C (lit.:[43] 159–160 °C); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.08 (3H, d, J = 4.9 Hz, CH_3), 6.05 (1H, bs, NH), 7.42–7.47 (1H, m, ArH), 7.51–7.60 (3H, m, ArH), 7.85–7.92 (2H, m, ArH), 8.29–8.31 (1H, m, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 26.8 (CH_3), 124.7 (CH), 124.9 (CH), 125.5 (CH), 126.4 (CH), 127.1 (CH), 128.3 (CH), 130.1 (C), 130.5 (CH), 133.7 (C), 134.7 (C), 170.3 (C).

Preparation of *N*-phenyl-*N*-benzyl-4-methylbenzenesulfonamide 30

An oven-dried flask containing *N*-benzylaniline (2.01 g, 11.0 mmol, 1 eq.) and NaH (60% dispersed in mineral oil, 526 mg, 13.2 mmol, 1.2 eq.) under flow of argon, was washed with dry hexane (3 × 20 mL) prior to addition of dry THF (100 mL). To this was added a solution of tosyl chloride (2.10 g, 11.0 mmol, 1 eq.) in THF (30 mL). Solution was stirred at room temperature overnight. THF was removed under reduced pressure and partitioned between EtOAc and 1 M $HCl_{(aq)}$. The organic phase was washed with $NaHCO_{3(aq)}$ (1 × 100 mL), brine (1 × 100 mL) and dried over Na_2SO_4. The crude solution was concentrated under reduced pressure and recrystallised in DCM–hexane to afford *N*-phenyl-*N*-benzyl-4-methylbenzenesulfonamide **30** (3.38 g, 91%) as a white solid; m.p. 138–140 °C (lit.[16] 139–140 °C); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.45 (3H, s, CH_3), 4.73 (2H, s, CH_2), 6.98–7.00 (2H, m, ArH), 7.20–7.23 (8H, m, ArH), 7.27–7.29 (2H, m, ArH), 7.55–7.56 (2H, m, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3), 54.7 (CH_2), 127.6 (CH), 127.8 (CH), 128.4 (CH), 128.5 (CH), 128.8 (CH), 129.0 (CH), 129.5 (CH), 135.7 (C), 136.0 (C), 139.0 (C), 143.5 (C). Data were consistent with those previously published.[16]

Preparation of *N*-benzylaniline 31

The general procedure for electron transfer reactions was applied to *N*-phenyl-*N*-benzyl-4-methylbenzenesulfonamide **30** (90.8 mg, 0.27 mmol, 1 eq.) using pyrrole salt **25** (500 mg, 0.81 mmol, 3 eq.). The reaction was heated to 100 °C and the crude material was purified by column chromatography (20% EtOAc–Pet. Ether) to give *N*-benzylaniline **31** (33 mg, 68%) as a white solid; m.p. 35–37 °C (lit.[7] 35–38 °C); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.08 (1H, bs, NH), 4.35 (2H, s, CH_2), 6.65–6.67 (2H, m, ArH), 6.74 (1H, t, J = 7 Hz, ArH), 7.12–7.21 (2H, m, ArH), 7.29–7.30 (1H, m, ArH), 7.34–7.40 (4H, m, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 48.7 (CH_2), 112.0 (CH), 118.1 (CH), 128.5 (CH), 128.7 (CH), 129.1 (CH), 129.7 (CH), 139.8 (C), 148.4 (C); Data consistent with those previously published.[35]

Preparation of 1-(toluene-4-sulfonyl)-1*H*-indole 32

An oven-dried flask containing indole (5 g, 42 mmol, 1 eq.) and NaH (60% dispersed in mineral oil, 2.05 g, 51 mmol, 1.2 eq.) under flow of argon, was washed with dry hexane (3 × 50 mL) prior to addition of dry THF (200 mL). To this was added a solution of tosyl chloride (8.14 g, 42 mmol, 1 eq.) in THF (50 mL). The solution was stirred at room temperature overnight. THF was removed under reduced pressure and partitioned between EtOAc and 1 M $HCl_{(aq)}$. The organic phase was washed with $NaHCO_{3(aq)}$ (1 × 100 mL), brine (1 × 100 mL) and dried over Na_2SO_4. The crude solution was concentrated under reduced pressure and recrystallised in DCM–hexane to afford 1-(toluene-4-sulfonyl)-1*H*-indole **32** (10.9 g, 94%) as a white solid m.p. 82–84 °C (lit.:[16] 83–84 °C); ^{1}H-NMR (500 MHz, DMSO-d_6) δ 2.29 (3H, s, CH_3), 6.81–6.83 (1H, m, ArH), 7.22–7.25 (1H, m, ArH), 7.31–7.37 (3H, m, ArH), 7.58–5.60 (1H, m, ArH), 7.77–7.78 (1H, m, ArH), 7.83–7.85 (2H, m, ArH), 7.91–7.93 (1H, m, ArH); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 20.5 (CH_3), 108.7 (CH), 113.5 (CH), 120.2 (CH), 123.5 (CH), 125.2 (CH), 126.3 (CH), 130.6 (CH), 131.0 (C), 134.8 (C), 135.1 (C), 145.1 (C).

Preparation of 1*H*-indole 33

The general procedure for electron transfer reactions was applied to 1-(toluene-4-sulfonyl)-1*H*-indole **32** (73 mg, 0.27 mmol, 1 eq.) using pyrrole salt **25** (500 mg, 0.81 mmol, 3 eq.). The reaction was heated to 100 °C and the crude material was purified by column chromatography (20% EtOAc–Pet. ether) to give 1*H*-indole **33** (27 mg, 87%) as a white solid; m.p. 52–53 °C (lit.[16] 51–54 °C); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.64–6.65 (1H, m, ArH), 7.19–7.31 (3H, m, ArH), 7.41–7.43 (1H, m, ArH), 7.74–7.76 (1H, m, ArH), 8.01 (1H, bs, NH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 102.6 (CH), 111.3 (CH), 119.9 (CH), 120.8 (CH), 122.1 (CH), 124.3 (CH), 127.9 (C), 135.8 (C).

Preparation of *N*,*N*′,*N*′-*tris*(p-toluenesulfonyl)tryptamine 34

To a solution of tryptamine (1.00 g, 6.24 mmol, 1 eq.) in dry THF (100 mL) was added NaH (60% mineral oil, 1.25 g, 31.2 mmol, 5 eq.) and light brown suspension was stirred for 10 min. To this was added a solution of tosyl chloride (4.76 g, 25.0 mmol, 4 eq.) in dry THF (50 mL) *via* cannula and suspension was stirred for 18 h under argon. Reaction was concentrated under reduced pressure and partitioned between EtOAc (100 mL) and 2 M $NaOH_{(aq)}$ (50 mL). Organic layer was washed with brine (50 mL) and dried over Na_2SO_4. The crude solution was concentrated under reduced pressure and purified by column chromatography (10% EtOAc–hexane) to give *N*,*N*′,*N*′-*tris(toluenesulfonyl)tryptamine* **34** (1.53 g, 37%) as a pink foam; [Found: $(NSI)^+$ $(M + NH_4)^+$ 640.1600, $C_{31}H_{34}N_3O_6S_3$ $(M + NH_4)^+$ requires 640.1604]; ν_{max}(KBr)/cm^{-1} 3387, 2941, 2074, 1635, 1566, 1526, 1448, 1390, 1310, 1252, 1206, 1163, 1118, 1050, 924, 811, 624; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.36 (3H, s, CH_3), 2.47 (6H, s, CH_3), 3.09–3.13 (2H, m, CH_2), 3.88–3.92 (2H, m, NCH_2), 7.23–7.35 (9H, m, ArH), 7.60 (1H, d, J = 8.2 Hz, ArH), 7.77 (4H, d, J = 8.4 Hz, ArH), 7.91 (2H, d, J = 8.4 Hz, ArH), 7.98 (1H, d, J = 8.2 Hz, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 21.1 (CH_3), 21.2 (CH_3), 26.1 (CH_2), 48.6 (NCH_2), 113.7 (CH), 118.2 (C), 119.5 (CH), 123.3 (CH), 123.8 (CH), 124.9 (CH), 126.8 (CH), 128.2 (CH), 129.8 (CH), 129.9 (CH), 130.4 (C), 135.1 (C), 135.4 (C), 136.9 (C), 144.9 (C), 145.1 (C). *m*/*z* (ESI^+) 640 $[(M + NH_4)^+$, 100%].

Preparation of 3-(2-(*p*-toluenesulfonylamido)ethyl)indole 35

The general procedure for electron transfer reactions was applied to *N*,*N*,*N*-*tris*(toluenesulfonyl)tryptamine **34** (200 mg, 0.30 mmol, 1 eq.) using pyrrole salt **25** (748 mg, 1.20 mmol, 4 eq.). The reaction was heated to 100 °C and the crude material was purified by column chromatography (30% EtOAc–hexane) to give 3-(2-(*p*-toluenesulfonylamido)ethyl)indole **35** (89 mg, 94%) as a clear oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.41 (3H, s, CH_3), 2.94 (2H, t, J = 6.4 Hz, CH_2), 3.28 (2H, q, J = 6.4 Hz, CH_2), 4.50 (1H, t, J = 6.4 Hz, NH), 6.97 (1H, ArH), 7.06 (1H, t, J = 8 Hz, ArH), 7.18–7.23 (3H, m, ArH), 7.38 (1H, d, J = 8 Hz, ArH), 7.43 (1H, d, J = 8 Hz, ArH), 7.64 (2H, d, J = 8 Hz, ArH), 8.09 (1H, bs, ArNH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 21.5 (CH_3), 25.5 (CH_2), 43.1 (NCH_2), 111.3 (CH), 111.6 (C), 118.5 (CH), 119.5 (CH), 122.3 (CH), 122.4 (CH), 126.9 (C), 127.0 (CH), 129.6 (CH), 136.4 (C), 136.8 (C), 143.3 (C). Data were consistent with those published in literature.[44]

Acknowledgements

We thank Professor John C. Walton and Dr Michael J. Corr for EPR measurements (St. Andrews University), and we thank University of Strathclyde, Scottish Funding Council and BAE Systems for a SPIRIT studentship to HSF. Mass spectrometry data were acquired at the EPSRC UK National Mass Spectrometry Facility at Swansea University.

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