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Supporting Information

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Supplementary Information

for

Generation of Aryl Anions by Double Electron Transfer to Aryl Iodides from a Neutral Ground-State Organic Super Electron Donor (SED)

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Section 1. Experimental Materials and Methods

All reactions were performed in flame-dried apparatus under a nitrogen or argon atmosphere using dry and deoxygenated solvents. A glove box (System One Glove Box, Innovative Technology Inc., U.S.A.) was used to handle extremely air-sensitive and moisture-sensitive reagents and reactions under a nitrogen atmosphere (oxygen and moisture levels were maintained at 0-2 ppm at all times). As required, organic solvents were dried and / or distilled prior to use. Tetrahydrofuran, dichloromethane, hexane, diethyl ether and toluene were dried and deoxygenated with a Pure-Solv 400 solvent purification system by Innovative Technology Inc., U.S.A. and the moisture content of the solvents was constantly monitored by employing standard methods by Karl Fischer coulometer (METTLER TOLEDO DL39). Anhydrous DMF was purchased commercially from Sigma-Aldrich Chemical Company and the residual moisture content in it (34 to 100 ppm of H_2O level) was analysed using standard methods by Karl Fischer coulometer (METTLER TOLEDO DL39). A commercial sample of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (abbreviated as DMPU) was distilled over CaH_2 prior to use. Organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4) or anhydrous magnesium sulfate ($MgSO_4$).

Flash chromatography was performed using silica gel 60 (200-400 mesh). Thin layer chromatography (TLC) was performed using aluminium sheets of silica gel 60 F_{254} and was visualized under Mineralight UVGL-58 lamp (254 nm). The plates were developed with aqueous potassium permanganate solution, methanolic phosphomolybdic acid (10-20% w/v), acidic *p*-anisaldehyde (10% v/v) or acidic methanolic vanillin solutions.

High performance liquid chromatography (HPLC) was performed using Gilson Model 302 pump, Gilson 802C manometric module, Milton Roy Spectrometer detector (? = 257 nm) and a Kromasil Silica column (semi-preparative: 10 µm pore size, 100 Å particle size, 250 × 10.0 mm dimension) at a flowrate of 2 ml/min.

All Gas Chromatography Mass Spectrometry (GC-MS) was performed on Thermo Finnigan PolarisQ Ion Trap Mass Spectrometer/Trace GC instrument with ZB-5 column (30 metres), at

1ml/min He gas flow rate and temperature range of 50 to 320 ^{o}C with an increment of 10 to 20 ^{o}C/min.

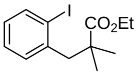
High and low resolution mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre, Swansea on a JLZX 102, VGZAB-E or a VG micromass instrument. The spectra were recorded using electron impact (EI), chemical ionization (CI), fast atom bombardment (FAB) or electrospray ionization (ESI) techniques as stated for each compound.

All Proton NMR (^{1}H) spectra were recorded at 400.13 MHz on a Bruker DPX 400 spectrometer. Carbon NMR (^{13}C) spectra were recorded at 100.62 MHz on the same instrument. The chemical shifts (*d*) are quoted in parts per million (ppm). Multiplicities are abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br., broad. The coupling constants (*J*) are measured in Hertz (Hz). Infra-red spectra were recorded on Perkin Elmer Spectrum One FT-IR spectrometer and are reported in frequency of absorption (cm^{-1}). Assays of sodium levels were evaluated by AAnalyst 200 Atomic Absorption Spectrometer, PerkinElmer instruments, Ltd. Melting points (mp) were carried out on Reichert melting point apparatus or Gallenkamp melting point apparatus and are uncorrected.

All electrochemical experiments were perfomed inside a glove box under a nitrogen atmosphere at 21 ± 1 ^{o}C. Cyclic voltammograms were recorded using an Autolab PGSTAT30 potentiostat /galvanostat with a scan rate of 50 mV/s. A three-electrode system was employed consisting of a platinum working electrode, a platinum wire auxiliary electrode and a Ag/AgCl/KCl(sat) double-junction electrode as the reference electrode. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate of 98% purity was purchased from Sigma-Aldrich Chemical Company and was dried *in vacuo* prior to use. Half-wave potentials ($E_{1/2}$) were calculated as an average of the cathodic and anodic peak potentials. The difference between anodic and cathodic peak potentials (mV) is given in parenthesis. The irreversible (ir) peak potentials are denoted as E_p and are given as the peak for the [cathodic] wave. Calibration was performed with ferrocene $E_{1/2}$ (DMF) = 0.5454 V, (10.3526 mM), Bu_4NPF_6 (49.879 mM). Unless otherwise mentioned, the redox potentials for each of the compounds were reported as an average of five runs.

Procedures for the Preparation of the Substrates **9**, **15** and **18**:

Ethyl 2-(2-iodobenzyl)-2-methylpropanoate 9 (Based on the general procedure in the literature[1])

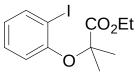


9

Ethyl isobutyrate (6.970 g, 60.0 mmol, 3.0 eq) was charged into a dry 250 ml round bottomed flask fitted with a rubber septum and a magnetic stirbar, dissolved in dry THF (125 ml) and cooled to –78 ^{o}C under an argon atmosphere. To this solution was added lithium diisopropylamide (30.0 ml of 2 M solution in THF/*n*-heptane/ethyl benzene, 60.0 mmol, 3.0 eq) dropwise over 5 min, followed by addition of DMPU [5.127 g, 40.0 mmol, 2.0 eq, freshly distilled (146-147 ^{o}C/44 mm Hg) over CaH_2 prior to use] and stirred at –78 ^{o}C under an argon atmosphere. After 1 h, a solution of 2-iodobenzyl bromide (5.939 g, 20.0 mmol, 1.0 eq) in dry THF (25 ml) was added using a cannula and the reaction mixture was stirred under an argon atmosphere at –78 ^{o}C for 1 h, warmed to r.t. and continued to stir for an additional 3 h at r.t. The reaction mixture was then quenched by addition of saturated ammonium chloride solution (10 ml) at 0 ^{o}C, warmed to r.t. and much of the solvent was removed under reduced pressure. The contents were extracted with diethyl ether (200 ml) and saturated ammonium chloride solution (100 ml). The organic layer was washed with saturated brine solution (3 × 300 ml) in a separating funnel, separated, dried over anhydrous sodium sulfate and evaporated to dryness to obtain a brown oil. The crude product was purified by flash chromatography on silica gel [petroleum ether (40 – 60 ^{o}C)/dichloromethane = 3:7 to 1:1] to yield a clear colorless oil. Further purification of the oil by vacuum distillation (119-121 ^{o}C/0.6 mbar pressure) afforded pure *ethyl 2-(2-iodobenzyl)-2-methylpropanoate* **9** (6.344 g, 95%) as a clear colorless oil [Found: $(M+NH_4)^+$ (ESI), 350.0605. $C_{13}H_{17}IO_2$ requires $(M+NH_4)^+$, 350.0611]; n_{max}(Neat film, NaCl)/cm^{-1} 2978, 1725, 1466, 1185, 1132, 1010, 747; ^{1}H NMR (400 MHz, $CDCl_3$) *d*

1.29 (9H, s and t, *J* 7.1, 2 × CH_3 and CH_2CH_3), 3.18 (2H, s, $ArCH_2$), 4.19 (2H, q, *J* 7.1, OCH_2CH_3), 6.91 (1H, ddd, *J* 7.9, 7.4, 1.7, ArH), 7.18 (1H, dd, *J* 7.7, 1.7, ArH), 7.27 (1H, ddd, *J* 7.7, 7.4, 1.2, ArH), 7.88 (1H, dd, *J* 7.9,1.2, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) ***d*** 14.7 (CH_3), 25.7 (2 × CH_3), 44.8 (C), 49.2 (CH_2), 61.1 (CH_2), 103.6 (C), 128.5 (CH), 128.7 (CH), 130.7 (CH), 140.4 (CH), 142.0 (C), 178.0 (C); *m/z* (CI) 350 [$(M+NH_4)^+$, 100%], 333 (5), 224 (20), 205 (9). E_p (DMF) = –2.100 V (ir) vs. Ag/AgCl/KCl (sat), averaged over 5 runs; Conditions: **7** (26.205 mM), Bu_4NPF_6 (50.059 mM), Pt working and counter electrodes, 50 mV/s.

Ethyl 2-(2-iodophenoxy)-2-methylpropanoate 15 (Based on the general procedure in the literature[2])

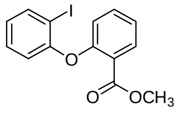


15

2-Iodophenol (4.0 g, 18.18 mmol, 1.0 eq), 1,1,1-trichloro-2-methyl-2-propanol hemihydrate (6.78 g, 36.36 mmol, 2.0 eq) and sodium hydroxide (5.8 g, 145 mmol, 8.0 eq) were dissolved in acetone (200 ml) and the mixture was stirred overnight at r.t. The solvent was then removed *in vacuo*, and the residue was dissolved in water (250 ml). The aqueous layer was extracted with diethyl ether (3 × 200 ml) and acidified with concentrated hydrochloric acid. The aqueous layer was then extracted with diethyl ether (3 × 200 ml), and the combined organic layers were dried over anhydrous sodium sulfate, filtered and evaporated. The residue was dissolved in ethanol (100 ml) and thionyl chloride (2.65 ml, 36.36 mmol, 2.0 eq) was added dropwise at r.t. The mixture was then heated at reflux for 6 h and subsequently concentrated under reduced pressure. The residue was purified by Kugelrohr distillation (150 °C, 1 mbar) to afford *ethyl 2-(2-iodophenoxy)-2-methylpropanoate* **15** (4.6 g, 76%) as a slightly yellow liquid [Found: $(M+NH_4)^+$ (ESI) 352.0407. $C_{12}H_{15}IO_3$ requires $(M+NH_4)^+$, 352.0404]; n_{max}(Neat film, NaCl)/cm^{-1} 3061, 2987, 2938, 1735, 1580, 1468; ^{1}H NMR (400 MHz, $CDCl_3$) ***d*** 1.33 (3H, t, *J* 7.1, CH_3), 1.72 (6H, s, 2 × CH_3), 4.32 (2H, q, *J* 7.1, CH_2), 6.78-6.85 (2H, m, ArH), 7.23-7.29 (1H, m, ArH), 7.85 (1H, dd, *J* 7.8, 1.1, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) ***d*** 14.2

(CH_3), 25.5 (2 × CH_3), 61.6 (CH_2), 81.0 (C), 91.3 (C), 117.8 (CH), 124.1 (CH), 129.1 (CH), 139.8 (CH), 155.2 (C), 174.2 (C); *m/z* (EI) 334 ($M^{+\bullet}$, 12%), 261 (26), 220 (100), 134 (23), 87 (49), 76 (44), 59 (67). E_p (DMF) = –2.2993 V (ir) vs. Ag/AgCl/KCl(sat), averaged over 4 runs; Conditions: **17** (24.91 mM), Bu_4NPF_6 (50.07 mM), Pt working and counter electrodes, 50 mV/s.

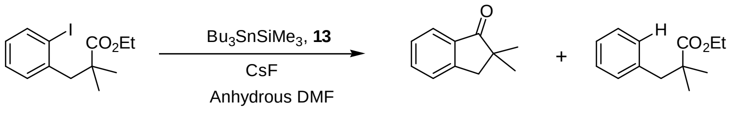
Methyl 2-(2-iodophenoxy)benzoate 18 (Based on general procedure in literature[3-5])



18

Methyl 2-iodobenzoate (4 g, 15.3 mmol, 1.0 eq) and 2-iodophenol (3.36 g, 15.3 mmol, 1.0 eq) were dissolved in pyridine (30 ml) under an argon atmosphere. Cesium carbonate (5.48 g, 16.79 mmol, 1.1 equiv.), copper (I) oxide (400 mg, 2.8 mmol, 0.18 eq) and 4 Å molecular sieves (0.050 g) were added to this mixture under an argon atmosphere. The reaction mixture was heated to 110 °C for 48 h under argon. After allowing to cool to r.t., the mixture was poured into ethyl acetate (200 ml) and water was added (200 ml). The aqueous layer was extracted with ethyl acetate (150 ml) and the combined organic layer was washed with hydrochloric acid (2 M, 5 × 200 ml), followed by sodium hydroxide solution (2 M, 5 × 200 ml) and saturated brine solution (200 ml). After drying over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography (eluant: toluene/dichloromethane/petroleum ether = 1:1:3), followed by Kugelrohr distillation (impurity removed at 150 °C, 2 mbar) to give *methyl 2-(2-iodophenoxy)benzoate* **18** (1.19 g, 22%) as a colorless liquid [Found: $(M+NH_4)^+$ (ESI), 372.0092. $C_{14}H_{11}IO_3$ requires $(M+NH_4)^+$, 372.0091]; n_{max}(Neat film, NaCl)/cm^{-1} 3062 , 2998, 2949, 1732, 1603, 1465, 1452; ^{1}H NMR (400 MHz, $CDCl_3$) *d* 3.81 (3H, s, CH_3), 6.73 (1H, dd, *J* 8.2, 1.4, ArH), 6.85 (1H, ddd, *J* 7.6, 7.6, 1.4, ArH), 6.94 (1H, dd, *J* 8.2, 1.0, ArH), 7.21-7.27 (2H, m, ArH), 7.47-7.51 (1H, m, ArH), 7.87 (1H, dd, *J* 7.9, 1.6 ArH), 7.96 (1H, dd, *J* 7.9, 1.8 ArH); ^{13}C NMR (100 MHz, $CDCl_3$) *d* 52.7 (CH_3), 88.2 (C), 118.1 (CH), 121.1 (CH), 123.5 (C), 124.4 (CH), 125.3 (CH), 130.0 (CH), 132.6 (CH), 134.1 (CH), 140.3 (CH), 155.8 (C), 157.5 (C), 166.4 (C); *m/z* (EI) 354 ($M^{+\bullet}$, 7%), 227 (100), 196 (48), 168 (47), 139 (36), 63 (38). $E_{1/2}$(DMF) = –2.1320 V (ir) and –2.1629 V** (0.1538 V) vs. Ag/AgCl/KCl(sat), averaged over 5 runs; Conditions: **18** (25.395 mM), Bu_4NPF_6 (50.33 mM), Pt working and counter electrodes, 50 mV/s. [**The reversible peak tallied with that seen in cyclic voltammogram of compound **20**.]

Anionic Cyclization of ethyl 2-(2-iodobenzyl)-2-methylpropanoate 9 by $Bu_3SnSiMe_3$ / CsF or TASF Method (Based on general procedure from literature[6])



9 **10** **11**

Representative Procedure:

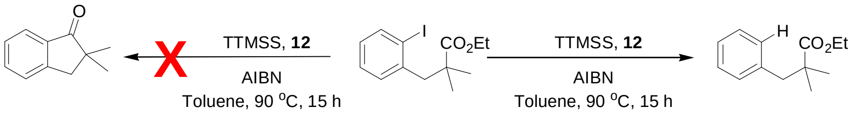
Cesium fluoride (0.205 g, 1.35 mmol, 2.5 eq) was added to a 0.15 M solution of freshly distilled sample of ethyl 2-(2-iodobenzyl)-2-methylpropanoate **13** (0.179 g, 0.54 mmol, 1.0 eq) in anhydrous DMF [3.6 ml, 34.1 (± 1.01) ppm of H_2O level as determined by Karl Fischer Coulometer prior to start of the reaction] under a nitrogen atmosphere inside a glove box. The reaction vessel was transported outside the glove box and purged with a stream of argon gas. The reaction mixture was stirred and heated at 100 °C followed by addition of trimethyl(tributylstannyl)silane (0.392 g, 1.08 mmol, 2.0 eq, previously handled and weighed inside a glove box) under an argon atmosphere. The mixture was stirred at 100 °C for 2.5 h under an argon atmosphere, after which it was cooled to r.t. and quenched with 10% NH_4OH solution (1 ml). The mixture was then extracted with diethyl ether (75 ml) and washed with 10% NH_4OH solution (50 ml). The aqueous layer was separated and washed with additional diethyl ether (2 × 50 ml). The combined organic phases were washed with saturated brine solution (5 × 100 ml), separated, dried over anhydrous sodium sulfate, filtered and evaporated to dryness under reduced pressure to afford a pale-yellow oil. This was purified by flash chromatography on silica gel (eluant: hexane to dichloromethane/hexane = 3:7) to afford ethyl 2-

benzyl-2-methylpropanoate[7] **11** (0.016 g, 14%) as a clear colorless oil and 2,2-dimethyl-1-indanone[8-10] **10** (0.059 g, 68%) as a colorless semi-solid.

2,2-Dimethyl-1-indanone 10:[8-10] [Found: $(M+H)^+$ (ESI), 161.0959. $C_{11}H_{12}O$ requires $(M+H)^+$, 161.0961]; n_{max}(CHCl$_3$, NaCl)/cm^{-1} 2961, 2926, 2867, 1716, 1610, 1467, 1380, 1290, 1206, 992, 939, 798, 737; ^{1}H NMR (400 MHz, CDCl$_3$) ***d*** 1.24 (6H, s, 2 × CH$_3$), 3.01 (2H, s, CH$_2$), 7.32-7.40 (1H, m, ArH), 7.41-7.48 (1H, m, ArH), 7.55-7.65 (1H, m, ArH), 7.72-7.83 (1H, m, ArH); ^{13}C NMR (100 MHz, CDCl$_3$) ***d*** 25.8 (2 × CH$_3$), 43.4 (CH$_2$), 46.0 (C), 125.0 (CH), 127.1 (CH), 127.9 (CH), 135.3 (CH), 135.9 (C), 152.7 (C), 211.8 (C); GC-MS retention time 11.84 min, *m/z* (EI) 160 ($M^{+\bullet}$, 32%), 145 (100), 142 (26), 131 (9), 117 (29), 115 (36), 103 (3), 91 (11), 77 (4), 65 (5), 63 (6), 51 (5). The spectroscopic data of the indanone **10** were identical with those reported in the literature.[8-10] $E_{1/2}$(DMF) = −1.9783 V (0.1675 V) vs. Ag/AgCl/KCl(sat), averaged over 2 runs; Conditions: **10** (25.56 mM), Bu$_4$NPF$_6$ (49.917 mM), Pt working and counter electrodes, 50 mV/s.

Ethyl 2-benzyl-2-methylpropanoate 11: [Found: $(M+NH_4)^+$ (ESI), 224.1645. $C_{13}H_{18}O_2$ requires $(M+NH_4)^+$, 224.1645]; n_{max}(Neat film, NaCl)/cm^{-1} 2979, 1728, 1472, 1188, 1124, 1029, 741, 702; ^{1}H NMR (400 MHz, CDCl$_3$) ***d*** 1.22 (6H, s, 2 × CH$_3$), 1.27 (3H, t, *J* 7.1, CH$_2$C*H*$_3$), 2.90 (2H, s, ArCH$_2$), 4.15 (2H, q, *J* 7.1, OC*H*$_2$CH$_3$), 7.12-7.18 (2H, m, ArH), 7.20-7.33 (3H, m, ArH); ^{13}C NMR (100 MHz, CDCl$_3$) ***d*** 14.4 (CH$_3$), 25.2 (2 × CH$_3$), 43.7 (C), 46.5 (CH$_2$), 60.6 (CH$_2$), 126.6 (CH), 128.1 (CH), 130.4 (CH), 138.2 (C), 177.6 (C); *m/z* (CI) 224 [$(M+NH_4)^+$, 100%], 207 (10), 123 (2), 108 (4), 91 (3), 52 (10).

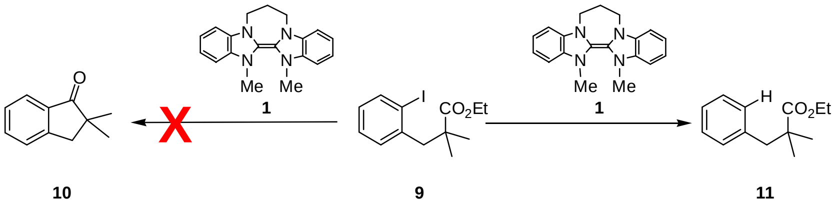
Reduction of ethyl 2-(2-iodobenzyl)-2-methylpropanoate 9 by TTMSS/AIBN (Based on general procedure in literature[11])



10 **9** **11**

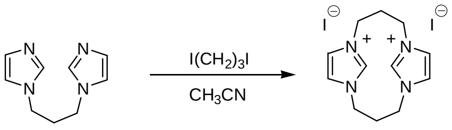
A 50 ml three-necked round bottomed flask equipped with a magnetic stirring bar and a water condenser was flame-dried in vacuo, backfilled with dry argon gas and loaded with freshly distilled ethyl 2-(2-iodobenzyl)-2-methylpropanoate **9** (0.199 g, 0.60 mmol, 1.0 eq) and dry toluene (15 ml, deoxygenated). The solution was degassed by purging with a stream of argon gas for 30 min. and then was heated under reflux at 90 °C. A degassed solution of tris(trimethylsilyl)silane (TTMSS) **12** (0.179 g, 0.72 mmol, 1.2 eq) and azo*bis*isobutyronitrile (AIBN) (0.138 g, 0.84 mmol, 1.4 eq) in dry toluene (14.2 ml, deoxygenated) was loaded into a syringe and added dropwise to the reaction mixture using a syringe pump (flow rate of 3.54 cc/hr) for 4 h under an argon atmosphere. The mixture was stirred and continued to heat under reflux at 90 °C for additional 11 h (15 h in total). The reaction mixture was then cooled to r.t. and evaporated to dryness under reduced pressure to obtain a pale yellow oil. Purification of the crude material by flash chromatography on silica gel (eluant: hexane to dichloromethane/hexane = 1:4) provided a colorless clear oil. Subsequent purification of the oil by HPLC (semi-preparative, retention time 13.6 min) with ethyl acetate/hexane (1:24) as the eluant afforded pure ethyl 2-benzyl-2-methylpropanoate[7] **11** (0.087 g, 70%) as a clear colorless oil. The physical characteristics and spectroscopic data of the ester **11** were identical with those of the same compound reported earlier in this section.

Reduction of ethyl 2-(2-iodobenzyl)-2-methylpropanoate 9 by Tetraazafulvalene 1 (Based on general procedure in literature[12])



A 25 ml Schlenk flask fitted with a magnetic stirbar was flame-dried under vacuum, backfilled with dry argon, charged with 1,1'-dimethyl-3,3'-(trimethylene)bis(benzimidazolium) diiodide[12] (1.401 g, 2.5 mmol, 2.5 eq) and dried *in vacuo* at 120 °C for 2 h. The salt was cooled to r.t., purged with argon gas and dissolved in degassed anhydrous DMF (15 ml). This solution was added dropwise using a cannula to a 35 ml centrifuge tube containing sodium hydride [(0.200 g of 60% NaH dispersed in mineral oil, 5.0 mmol, 5.0 eq), washed with dry hexane (4 × 15 ml) prior to use] at 0 ^{o}C under an argon atmosphere. The reaction mixture was warmed to r.t. and stirred under an argon atmosphere for 1.5 h. The tube was sealed completely under argon and was subsequently centrifuged (3×10^3 r.p.m., 10 min) and the clear yellowish-orange supernatant liquid was carefully transferred into a flask fitted with a water condenser (the apparatus was previously flame dried in vacuum and filled with argon) containing a dry sample of ethyl 2-(2-iodobenzyl)-2-methylpropanoate **9** (0.332 g, 1.0 mmol, 1.0 eq) under an argon atmosphere. The reaction mixture was then heated under reflux at 100-120 ^{o}C for 14 h under an argon atmosphere. The mixture turned dark reddish-brown, was cooled to r.t. and extracted with diethyl ether (100 ml) and saturated brine solution (100 ml). The aqueous layer was separated and washed with additional diethyl ether (2 × 50 ml). The combined organic phases were washed with saturated brine solution (5 × 150 ml), separated, dried over anhydrous sodium sulfate, evaporated to dryness to obtain a brownish orange semi-solid. The crude material was purified by flash chromatography on silica gel (eluant: dichloromethane/hexane = 3 :7 to 1:1) to afford pure ethyl 2-benzyl-2-methylpropanoate[7] **11** (0.139 g, 67%) as a clear colorless oil. The physical characteristics and spectroscopic data of the ester **11** were identical with those of the same compound reported earlier in this section.

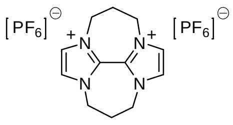
Preparation of the 1,1':3,3'-Bis(trimethylene)bis(imidazolium) diiodide 21



A dry five litre three-necked flask, equipped with a mechanical stirrer and a condenser was charged with acetonitrile (4 litres), 1-[3-(1*H*-imidazol-1-yl)propyl]-1*H*-imidazole[13] (2.002 g, 11.36 mmol, 1.0 eq) and 1,3-diiodopropane (3.361 g, 11.36 mmol, 1.0 eq). The mixture was heated to reflux for 24 h, and then another batch of starting materials (of same quantities) were added. One batch of starting materials (of same quantities) were added every 24 h. White precipitate appeared gradually.

After 20 days, a total of 1-(3-(1*H*-imidazol-1-yl)propyl)-1*H*-imidazole (40.040 g, 227.2 mmol) and 1,3-diiodopropane (67.226 g, 227.2 mmol) had been added. The mixture was further heated to reflux for additional four days. The hot solution was decanted and acetonitrile was removed. The resulting solid was recrystallized from methanol to afford *1,1':3,3'-bis(trimethylene)bis(imidazolium) diiodide* **21** (55 g, 51%) as white needles, mp 284 ºC (dec.) [Found: $(M–I)^+$ (ESI), 345.0569. $C_{12}H_{18}I_2N_4$ requires $(M–I)^+$, 345.0571]; n_{max}(disc, KBr)/cm^{-1} 3051, 3032, 1560, 1454, 1166; ^{1}H NMR (400 MHz, d$_6$-DMSO) *d* 2.29-2.41 (2H, m, CH_2), 2.42-2.56 (2H, m, together with DMSO peak, CH_2), 4.43-4.48 (4H, m, 2 × CH_2), 4.58-4.65 (4H, m, 2 × CH_2), 7.65 (4H, s, ArH), 9.07 (2H, s, 2 × N=CH); ^{13}C NMR (100 MHz, d$_6$-DMSO) *d* 28.6 (CH_2), 49.2 (CH_2), 124.0 (CH), 138.9 (CH); *m/z* (ESI) 345 [$(M-I)^+$, 9%), 217 [$(M-HI)^+$, 65], 109.0 [$\{(M-2I)/2\}^+$, 100].

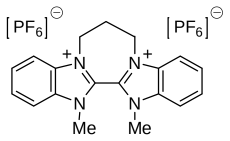
1,1':3,3'-Bis(trimethylene)-2,2'-biimidazolium dihexafluorophosphate 24



24

Dry 1,1':3,3'-bis(trimethylene)bis(imidazolium) diiodide **21** (0.991 g, 2.1 mmol, 1.0 eq) was suspended in dry DMF (5 ml, deoxygenated) and dry toluene (20 ml, deoxygenated) in a dry centrifuge tube (previously flame dried *in vacuo* and filled with argon gas) under an argon atmosphere. KHMDS (9.4 ml of 0.45 M soln. in toluene, 4.2 mmol, 2.0 eq) was added to the reaction mixture and was stirred for 1 h at r.t. under an argon atmosphere. The mixture turned to deep orange, and the tube was sealed completely under an argon atmosphere and centrifuged. The clear orange supernatant solution was carefully transferred using a cannula to a dry flask containing a solution of iodine (1.066 g, 4.2 mmol, 2 eq) in dry diethyl ether (50 ml, deoxygenated) under an argon atmosphere. A brown precipitate formed and was filtered off. The crude solid was dissolved in 50 ml of a 1 : 1 mixture of methanol and water and an aqueous solution of $NaPF_6$ (10 ml, saturated) was added. The solution was heated at reflux for 2 h. When the solution had cooled to r.t., the solid was filtered and washed with water (10 ml). The product *1,1':3,3'-bis(trimethylene)-2,2'-biimidazolium dihexafluorophosphate* **24** (0.722 g, 68%) was collected as a slightly yellow solid, mp 245 °C (dec.) [Found: $[\{M\text{–}(2PF_6)\}\text{–}H]^+$ (ESI), 215.1291. $C_{12}H_{16}N_4P_2F_{12}$ requires $(\{M\text{-}(2PF_6)\}\text{-}H)^+$, 215.1291]; n_{max}(disc, KBr)/cm^{-1} 3161, 1568, 1504, 835; ^{1}H NMR (400 MHz, d$_6$-DMSO) *d* 2.56 (4H, quintet, *J* 6.0, 2 × CH_2), 4.61 (8H, t, *J* 6.0, 4 × CH_2), 8.12 (4H, s, ArH); ^{13}C NMR (100 MHz, d$_6$-DMSO) *d* 26.5 (CH_2), 50.5 (CH_2), 127.0 (CH), 130.8 (C), *m/z* (ESI) 361 [$(M\text{-}PF_6)^+$, 90%], 175 (50), 108 [$(M\text{-}2PF_6)^{2+}$, 100]. $E_{1/2}$(DMF) = –1.1139 V (0.1526 V) vs. Ag/AgCl/KCl(sat), averaged over 5 runs; Conditions: **25** (10.03 mM), Bu_4NPF_6 (49.835 mM), Pt working and counter electrodes, 50 mV/s.

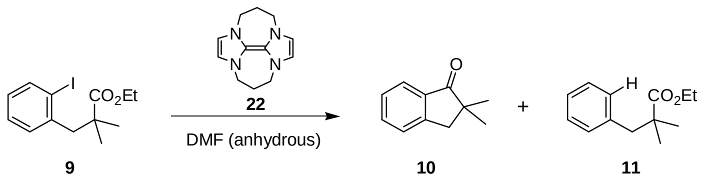
1,1'-Dimethyl-3,3'-(trimethylene)-2,2'-bibenzimidazolium dihexafluorophosphate 8



Following an experimental procedure identical to that described previously for the preparation of 1,1':3,3'-bis(trimethylene)-2,2'-biimidazolium dihexafluorophosphate **24**, a suspension of 1,1'-dimethyl-3,3'-(trimethylene)bis(benzimidazolium) diiodide[12] (1.008 g, 1.8 mmol, 1.0 eq) in anhydrous DMF (5 ml, deoxygenated) and dry toluene (20 ml, deoxygenated) was reacted with KHMDS (11.6 ml of 0.31 M solution in toluene, 2.0 eq) at r.t. for 1 h and the clear orange supernatant liquid was reacted with iodine (0.914 g, 3.6 mmol, 2 eq). The resulting solid was later heated at reflux with an aqueous $NaPF_6$ solution (10 ml, saturated) in 50 ml of a 1 : 1 mixture of methanol and water for 2 h to yield *1,1'-dimethyl-3,3'-(trimethylene)-2,2'-bibenzimidazolium dihexafluorophosphate*, **8** (0.353 g, 33 %) as a slightly yellow solid, mp 307 °C (dec.); n_{max}(disc, KBr)/cm^{-1} 3117, 1610, 1558, 1521, 1489, 1466, 834; ^{1}H NMR (400 MHz, d$_6$-DMSO) *d* (400 MHz, DMSO) 2.70-2.90 (2H, m, CH_2), 4.37 (6H, s, 2 × CH_3), 4.52-4.61 (2H, m, CH_2), 5.25-5.32 (2H, m, CH_2), 7.96-8.03 (2H, m, ArH), 8.28-8.34 (1H, m, ArH), 8.38-8.42 (1H, m, ArH); ^{13}C NMR (100

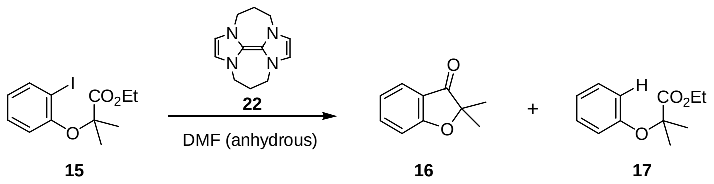
MHz, d_6-DMSO) *d* 30.1 (CH_2), 35.5 (CH_3), 42.9 (CH_2), 114.3 (CH), 115.0, (CH), 129.3 (CH), 129.4 (CH), 132.6 (C), 133.5 (C), 133.9 (C); *m/z* (ESI) 449 [(M-PF_6)$^+$, 15%), 337 (14), 321, (10), 263 (16) 152 [(M-2PF_6)$^{2+}$, 100]. $E_{1/2}$(DMF) = –0.64 V, -0.76 V vs. Ag/AgCl/KCl(sat), averaged over 5 runs; Conditions: 1,1'-Dimethyl-3,3'-(trimethylene)-2,2'-bibenzimidazolium dihexafluorophosphate **8** (9.85 mM), Bu_4NPF_6 (49.633 mM), Pt working and counter electrodes, 50 mV/s.

Cyclization of Ethyl 2-(2-iodobenzyl)-2-methylpropanoate 9 by Electron Donor 22



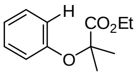
Anhydrous DMF (1 ml, deoxygenated) was added to a dry sample of ethyl 2-(2-iodobenzyl)-2-methylpropanoate **9** (0.250 g, 0.753 mmol, 1.0 eq) in a dry flask under an argon atmosphere. The reaction mixture was deoxygenated with argon gas for 20 min. and transferred into a glove box under a nitrogen atmosphere (oxygen and moisture levels were maintained at 0-2 ppm at all times). Tetraazafulvalene **22** (0.326 g, 1.506mmol, 2.0 eq) was weighed into a dry round-bottomed flask inside the glove box under nitrogen and dissolved in anhydrous DMF (5 ml, deoxygenated). The solution of ethyl 2-(2-iodobenzyl)-2-methylpropanoate **9** was added to the solution of the tetraazafulvalene **22** inside the glove box under a nitrogen atmosphere and the reaction mixture turned deep red in color. After stirring the reaction mixture for 2 h at r.t. inside the glove box, the mixture was diluted with water (50 ml) and extracted with diethyl ether (3 × 20 ml). The combined organic extracts were then washed with saturated brine solution (4 × 20 ml), separated, dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluant: diethyl ether/petroleum ether = 1:19) to give ethyl 2-benzyl-2-methylpropanoate[7] **11** (0.109 g, 70%) as a colorless clear oil and 2,2-dimethyl-1-indanone[8-10] **10** (0.019 g, 16%) as a colorless semi-solid. The spectroscopic data of the compounds **10** and **11** were identical with those reported earlier in this section.

Cyclization of ethyl 2-(2-iodophenoxy)-2-methylpropanoate 15 by Electron Donor 22



Following the general procedure described for the cyclization of ethyl 2-(2-iodobenzyl)-2-methylpropanoate **9** by electron-donor **22**, a dry sample of ethyl 2-(2-iodophenoxy)-2-methylpropanoate **15** (0.106 g, 0.317 mmol, 1.0 eq) dissolved in anhydrous DMF (15 ml, deoxygenated) was reacted with tetraazafulvalene **22** (0.103 g, 0.476 mmol, 1.5 eq) inside a glove box under a nitrogen atmosphere at r.t. for 18 h. After workup, the crude material was purified by column chromatography on silica gel (eluant: ethyl acetate/petroleum ether = 1:4, then dichloromethane) to afford a colorless oil (0.0401 g) containing an inseparable mixture of ethyl 2-methyl-2-phenoxypropanoate[2] **17** (21% NMR yield) and 2,2-dimethyl-benzofuran-3-one[14] **16** (51% NMR yield). The NMR yields of the products **16** and **17** were determined from standardized ^{1}H NMR spectroscopic analysis of 1 ml solution of the total amount of the isolated mixture of **16** and **17** in $CDCl_3$ along with diphenylmethane (0.01727 g, 0.1026 mmol) as an internal standard. The ^{1}H NMR chemical shifts and the ratio of the corresponding integrals attributed to each component of the mixture were in accordance with ^{1}H NMR spectroscopic data of the authentic samples of each of the compounds **16**, **17** and diphenylmethane (for spectroscopic data see below).

Ethyl 2-methyl-2-phenoxypropanoate[2] 17

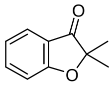


17

Colorless liquid [Found: $(M+NH_4)^+$ (ESI), 226.1440. $C_{12}H_{16}O_3$ requires $(M+NH_4)^+$, 226.1438]; n_{max}(Neat film, NaCl)/cm^{-1} 3064, 2989, 2940, 1733, 1580, 1495; ^{1}H NMR (400 MHz, $CDCl_3$) *d* 1.28

(3H, t, *J* 7.1, CH_3), 1.64 (6H, s, CH_3), 4.27 (2H, q, *J* 7.1, CH_2), 6.88-6.90 (1H, m, ArH), 6.99-7.03 (1H, m, ArH), 7.25-7.30 (2H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) *d* 14.2 (CH_3), 25.5 (CH_3), 61.5 (CH_2), 79.1 (C), 119.2 (CH), 122.2 (CH), 129.9 (CH), 155.6 (C), 174.4 (C); *m/z* (EI) 208 ($M^{+\bullet}$, 99 %), 135 (100), 94 (56), 66 (14).

2,2-Dimethyl-benzofuran-3-one[14] 16



16

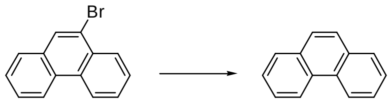
Colorless liquid; n_{max}(Neat film, NaCl)/cm^{-1} 2973, 2918, 1721, 1615, 1464; ^{1}H NMR (400 MHz, $CDCl_3$) *d* 1.48 (6H, s, 2 × CH_3), 7.06-7.10 (2H, m, ArH), 7.61 (1H, dd, *J* 7.2, 1.3, ArH), 7.64-7.69 (1H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) *d* 23.2 (CH_3), 88.1 (C), 113.8 (CH), 119.8 (C), 121.9 (CH), 125.1 (CH), 138.3 (CH), 171.1 (C), 204.6 (C); *m/z* (EI) 162 ($M^{+\bullet}$, 100 %), 147 (54), 91 (14).

Reaction between tetraazafulvalene 1 and 9-bromophenanthrene 25

A suspension of 1,3-*bis*[3-methyl-3*H*-benzimidazolium]propane diiodide, (840 mg, 1.50 mmol, 5.0 equiv.) in *N,N*-dimethyl formamide (10 ml) was purged with argon. A solution of 0.44 M potassium *bis*(trimethylsilyl)amide (6.80 ml, 3.00 mmol, 10.0 equiv.) was added drop-wise and the reaction mixture was stirred for 1 h. A purged solution of 9-bromophenanthrene **25** (77 mg, 0.3 mmol, 1.0 equiv.) in *N,N*-dimethylformamide (5 ml) under argon was added and the reaction mixture heated at 100^{o}C for 18 h. The cooled reaction mixture was poured into diethyl ether (50 ml) and water (50 ml). The aqueous phase was extracted with further diethyl ether (2 x 50 ml) and the combined organic phases were washed with water (2 x 75 ml) and then saturated brine solution (75 ml). The organic phase was then dried over sodium sulfate, filtered and evaporated. The residue was purified by column chromatography (95 : 5 petroleum ether - ethyl acetate) to afford a mixture (42 mg) of phenanthrene **26** (4mg, 7%) and 9-bromophenanthrene **25** (38 mg, 49%) that could not be separated; NMR spectra and GCMS data were assigned based on their identity with authentic materials. ^{1}H

NMR (400 MHz, CDCl$_3$) 7.50-7.76 (4H, m, 4 x ArH, **26**) and (4H, m, 4 x ArH **25**), 7.81-7.83 (2H, m, ArH, **26**) and (1H, m, ArH, **25**), 7.90 (2H, dd, *J* 7.6, 1.5, 2 x ArH, **26**), 8.13 (1H, s, ArH, **25**), 8.39 (1H, m, ArH, **25**), 8.66-8.72 (2H, m, 2 x ArH, **26**) and (2H, m, 2 x ArH **25**); *GC-MS* (RT 19.29-19.49 min, **26**) (EI) 178 (M$^+$, 100%) and 152 (20), (RT 23.32-23.45 min, **25**) (EI) 258 (M$^+$, 100%), 256 (M$^+$, 100%), 177 (70) and 176 (50).

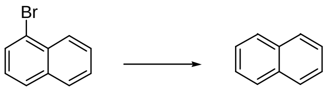
Reaction between tetraazafulvalene 22 and 9-bromophenanthrene 25



25 **26**

A solution of 1,1':3,3'-*bis*(trimethylene)*bis*(imidazolium) diiodide **21** (212 mg, 0.45 mmol, 1.5 equiv.) in *N,N*-dimethyl formamide (10 ml) was purged with argon. This solution was added to washed sodium hydride (96 mg, 2.40 mmol, 8.0 equiv.) under argon and stirred for 1 h. The suspension was centrifuged and the supernatant solution only was added to a solution of 9-bromophenanthrene **25** (77 mg, 0.3 mmol, 1.0 equiv.) in *N,N*-dimethyl formamide (5 ml). The reaction mixture was heated at 100^{o}C for 2 h. The reaction mixture was then cooled and poured into diethyl ether (30 ml) and water (30 ml). The aqueous phase was extracted with further diethyl ether (2 x 30 ml) and the combined organic phases were washed with water (2 x 50 ml) and then saturated brine solution (50 ml). The organic phase was then dried over sodium sulfate, filtered and evaporated. The residue was purified by column chromatography (petroleum ether) to afford phenanthrene **26** as a white solid (51 mg, 96%); mp 98-99 ^{o}C (lit.,[15] 98-100 ^{o}C) ?$_{max}$ (KBr)/cm^{-1} 3053 (Ar-H), 2923 (Ar-H), 2853 (Ar-H), 1454 (Ar), 817 (Ar) and 732 (Ar); ^{1}H NMR (400 MHz, CDCl$_3$) *d* 7.61-7.71 (4H, m, 4 x ArH), 7.78 (2H, s, 2 x ArH), 7.93 (2H, dd, *J* 7.6, 1.5, 2 x ArH) and 8.72 (2H, d, *J* 8.0, 2 x ArH); ^{13}C NMR (100 MHz, CDCl$_3$) *d* 122.9 (CH), 126.8 (2 x CH), 127.1 (CH), 128.8 (CH), 130.5 (C) and 132.3 (C); *m/z* (EI) 178 (M$^+$, 100%) and 152 (20).

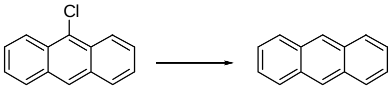
Reaction between tetraazafulvalene 22 and 1-bromonaphthalene 28.



27 **28**

A solution of 1,1':3,3'-*bis*(trimethylene)*bis*(imidazolium) diiodide **21** (212 mg, 0.45 mmol, 1.5 equiv.) in *N,N*-dimethyl formamide (10 ml) was purged with argon. This solution was added to washed sodium hydride (96 mg, 2.40 mmol, 8.0 equiv.) under argon and stirred for 1 h. The suspension was centrifuged and the supernatant solution only was added to a solution of 1-bromonaphthalene 2.165 (0.04 ml, 0.3 mmol, 1.0 equiv.) in *N,N*-dimethyl formamide (5 ml). The reaction mixture was heated at 100^{o}C for 18 h. The reaction mixture was then cooled and poured into diethyl ether (30 ml) and water (30 ml). The aqueous phase was extracted with further diethyl ether (2 x 30 ml) and the combined organic phases were washed with water (2 x 75 ml) and then saturated brine solution (75 ml). The organic phase was then dried over sodium sulfate, filtered and evaporated. The residue was purified by column chromatography (petroleum ether) to afford naphthalene **28** as a white solid (33 mg, 86%); mp 80-81 ^{o}C (lit.,[15] 80-82 ^{o}C); ?$_{max}$ (KBr)/cm^{-1} 3048 (Ar-H), 2924 (Ar-H), 1593 (Ar) and 1509 (Ar); ^{1}H NMR (400 MHz, CDCl$_3$) *d* (CDCl$_3$) 7.50 (4H, dd, *J* 6.3, 3.2, 4 x ArH) and 7.87 (4H, dd, *J* 6.3, 3.2, 4 x ArH); ^{13}C NMR (100 MHz, CDCl$_3$) *d* 126.0 (CH), 128.1 (CH) and 133.7 (C); *m/z* (EI) 128 (M^{+}, 100%) and 102 (10).

Reaction between tetraazafulvalene 23 and 9-chloroanthracene 29.

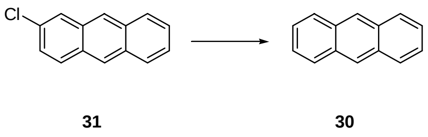


29 **30**

A solution of 1,1':3,3'-*bis*(trimethylene)*bis*(imidazolium) diiodide **21** (212 mg, 0.45 mmol, 1.5 equiv.) in *N,N*-dimethyl formamide (10 ml) was purged with argon. This solution was added to washed sodium hydride (96 mg, 2.40 mmol, 8.0 equiv.) under argon and stirred for 1 h. The suspension was centrifuged and the supernatant solution only was added to a solution of 9-

chloroanthracene **29** (64 mg, 0.3 mmol, 1.0 equiv.) in *N*,*N*-dimethyl formamide (5 ml). The reaction mixture was heated at 100^{o}C for 2 h. The reaction mixture was then cooled and poured into diethyl ether (30 ml) and water (30 ml). The aqueous phase was extracted with further diethyl ether (2 x 30 ml) and the combined organic phases were washed with water (2 x 50 ml) and then saturated brine solution (50 ml). The organic phase was then dried over sodium sulfate, filtered and evaporated. The residue was purified by column chromatography (petroleum ether) to afford anthracene **30** as a white solid (53 mg, 99%); mp 214-215 ^{o}C (lit.[15] 210-211 ^{o}C); $?_{max}$ (KBr)/cm^{-1} 3048 (Ar-H) and 1620 (Ar); ^{1}H NMR (400 MHz, CDCl$_3$) *d* 7.48 (4H, dd, *J* 6.5, 3.2, 4 x ArH), 8.02 (4H, dd, *J* 6.5, 3.2, 4 x ArH) and 8.44 (2H, s, 2 x ArH); ^{13}C NMR (100 MHz, CDCl$_3$) *d* (CDCl$_3$) 125.6 (CH), 126.4 (CH), 128.4 (CH) and 131.9 (C); *m/z* (EI) 178 (M$^+$, 100%), 176 (30) and 152 (20).

Reaction between tetraazafulvalene 23 and 2-chloroanthracene 31.



A solution of 1,1':3,3'-*bis*(trimethylene)*bis*(imidazolium) diiodide **22** (212 mg, 0.45 mmol, 1.5 equiv.) in *N*,*N*-dimethyl formamide (10 ml) was purged with argon. This solution was added to washed sodium hydride (96 mg, 2.40 mmol, 8.0 equiv.) under argon and stirred for 1 h. The suspension was centrifuged and the supernatant solution only was added to a solution of 2-chloroanthracene **31** (64 mg, 0.3 mmol, 1.0 equiv.) in *N*,*N*-dimethyl formamide (5 ml). The reaction mixture was heated at 100^{o}C for 18 h. The reaction mixture was then cooled and poured into diethyl ether (30 ml) and water (30 ml). The aqueous phase was extracted with further diethyl ether (2 x 30 ml) and the combined organic phases were washed with water (2 x 75 ml) and then saturated brine solution (75 ml). The organic phase was then dried over sodium sulfate, filtered and evaporated. The residue was purified by column chromatography (petroleum ether) to afford anthracene **30** as a white solid (52 mg, 97%); the data agreed with those given above.

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15. Aldrich Chemical Suppliers Catalogue.

Section 2. Computational Methods

Computational Methods

Density functional theory[1,2] (DFT) was employed to calculate the reorganization energies for the donor compounds **1** and **22**, undergoing electron transfer with the model acceptor compound iodobenzene (**IB**). All structures were optimized with the gradient corrected BP86 functional,[3-5] in order to take advantage of the resolution-of-the-identity (RI)-DFT approach,[6] as implemented in TURBOMOLE.[7-10] Calculations involving the iodine atom employed a large-core, quasi-relativistic, effective core potential[11] with the associated (16s11p6d)/[9s6p1d] valence basis set, all other atoms were described with the def2-TZVP basis set.[12]

In order to obtain a more realistic description of the relative energies of the cationic, anionic and neutral species of the molecules single point calculations of the gas phase optimized structures were performed using a dielectric continuum model of the solvent. For the single point calculations the B3LYP functional[3,4,13-16] was used in conjunction with the 6-311++G(d,p) basis set.[17-19] The Gaussian03 program[20] was used for the solvent phase calculations, making use of the polarizable continuum model[21] with a dielectric constant of 38.3 used to describe the DMF solvent. The single point energy calculations in the solvent phase were used to obtain the energies used in the calculation of the internal reorganization energy (λ_i).

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