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Supporting Information

n-Doping of bio-inspired electron transporting materials: the influence of charge-transfer complexation

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1. General Experimental.

A Bruker Avance III 400 spectrometer was used to obtain NMR spectra (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz) with chemical shift values given in ppm with reference to tetramethylsilane and these were analysed using MestReNova®. The spin coupling patterns observed in NMR spectra are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m) or a combination of these.

UV-Vis absorption spectra were measured using Shimadzu UV 3600 UV/visible/IR spectrometer. The concentration of **BFG** and **BFA** was kept at 10^{-5} M. Different mole percentages of N-DMBI were added to solution for the doping, and these samples were used for the UV-Vis absorption measurement.

Cyclic voltammetry was performed using a CH Instruments Electrochemical Workstation (CHI 440a), Austin, TX, USA. Solutions of **BFG** and **BFA** and the electrolyte (0.1 M tetrabutylammonium hexafluorophosphate) were prepared to a concentration of ~10^{-4} M in dichloromethane. A glassy carbon working electrode, a Pt wire counter electrode and a coiled Ag wire pseudo-reference electrode were used. The potential was cycled with scan rate of 0.1 V/s. All solutions were purged with N_2 prior to use.

EPR spectra were measured using Bruker ELEXSYS E500 spectrometer. The concentration of undoped and 20mol% **N-DMBI** doped **BFG** and **BFA** were 1.76 x10^{-2} M and 1.97 x10^{-2} M, respectively. Samples were transferred into soda glass capillary tubes of 2 mm diameter, sealed at one end, and filled to a height of 20 mm. The sample was irradiated at 450 nm during data acquisition.

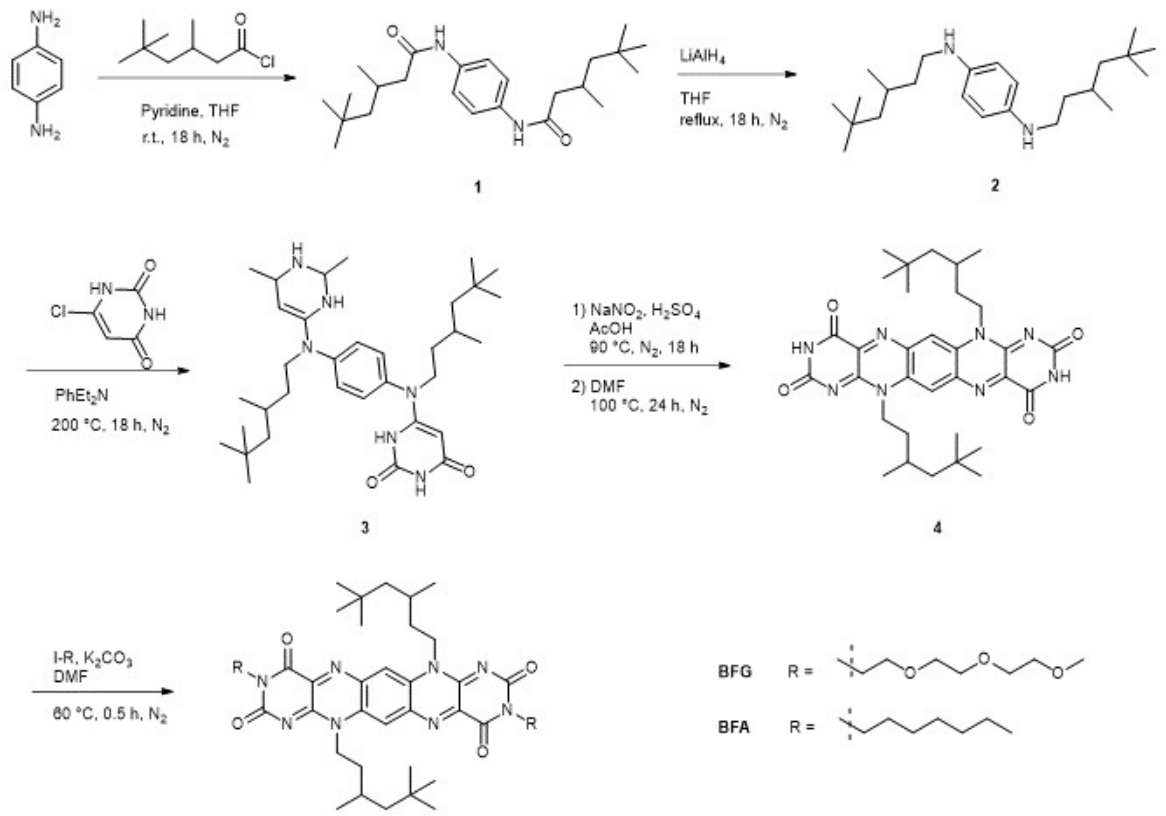

Figure S1. Synthesis of **BFG** and **BFA.**

2. Synthesis of BFG and BFA.

Compound **1**

Under N_2, *p*-phenylenediamine (5.00 g, 46.3 mmol) was dissolved in anhydrous THF (50 ml). Pyridine (7.5 ml, 92.5 mmol) was added, and the mixture was cooled down to 0 °C. 3,5,5-Trimethylhexanoyl chloride (17.2 ml, 92.5 mmol) was added drop-wise, then the resulting mixture was allowed to warm up to room temperature and left to stir for 10 hours. Afterwards, it was poured into water (250 ml) and the suspension was left to stir for 10 minutes. The resulting white precipitate was collected by vacuum filtration, washed with water, and dried under vacuum, affording **1** (17.5 g, 97%) as a pink solid.^{1}H-NMR (500 MHz, DMSO-d6) δ 9.76 (s, 2H), 7.48 (s, 4H), 2.25 – 2.18 (m, 2H), 2.15 – 2.07 (m, 2H), 2.06 – 1.99 (m, 2H), 1.28 (dd, J = 13.9, 3.6 Hz, 2H), 1.08 (dd, J = 13.9, 6.6 Hz, 2H), 0.94 (d, J = 6.6 Hz, 6H), 0.88 (s, 18H). ^{13}C-NMR (125 MHz, DMSO-d6) δ 170.3, 134.6, 119.5, 50.1, 46.2, 30.80, 29. 9, 26.9, 22.6. HRMS (ESI+, m/z): [M+H]+ found 389.3170; calc. for ($C_{24}H_{41}N_2O_2$+) 389.3163.

Compound **2**

Under N_2, compound **1** (5.08 g, 15.0 mmol) was dissolved in anhydrous THF (200 ml) and the mixture was cooled down to 0 °C. Lithium aluminium hydride (4.56 g, 0.120 mol) was added portion-wise, under a steam of N_2, then the resulting mixture was stirred at reflux for 20 hours. The mixture was then cooled down to 0 °C and water (5 ml), 10% aqueous NaOH (5 ml) and water (15 ml) were sequentially added, in a drop-wise fashion. The suspension was filtered under vacuum and the solids were washed with ethyl acetate (200 ml). Water (200 ml) was added to the filtrate and the organic layer was extracted. This was then washed with more water (3 x 150 ml), dried over magnesium sulfate, filtered, and concentrated under vacuum. Compound **2** (4.44 g, 82%) was obtained as a brown oil and used for the next step with no further purification. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 4H), 3.10 – 3.02 (m, 4H), 1.68 – 1.40 (m, 8H), 1.31 – 1.25 (m, 2H), 1.15 – 1.06 (m, 2H), 0.99 (d, J = 6.4 Hz, 6H), 0.92 (s, 18H). HRMS (ESI+, m/z): [M+H]+ found 361.3589; calc. for ($C_{24}H_{45}N_2$+) 361.3577.

Compound **3**

Compound **2** (4.29 g, 11.9 mmol), 6-chlorouracil (2.18 g, 14.8 mmol) and *N,N*-diethylaniline (6 ml) were stirred at 200 °C, under N_2, for 18 hours. The mixture was then allowed to cool to 60 °C, and poured into a mixture of ethanol and diethyl ether (500 ml, 4:1, v:v). The suspension was stirred for 30 minutes and the precipitate was collected by vacuum filtration. This was then recrystallised from acetic acid, affording **3** (1.79 g, 25%) as a pale-yellow solid. ^{1}H-NMR (500 MHz, DMSO-d6) δ 10.45 (s, 2H), 9.67 (s, 2H), 6.66 (s, 4H), 4.59 (s, 2H), 3.62 (bs, 4H), 1.53 – 1.48 (m, 8H), 1.06 (d, 1H), 0.99 (d, 1H), 0.85 (d, J = 6.4 Hz, 6H), 0.81 (s, 18H).

Compound **4**

To a suspension of compound **3** (2.72 g, 4.68 mmol) in glacial acetic acid (60 ml), sodium nitrate (2.39 g, 28.1 mmol) and concentrated sulfuric acid (0.3 ml, 5.62 mmol) were added. The mixture was stirred at 90 °C, under N_2, for 18 hours. The mixture was then allowed to cool to room temperature and poured into a mixture of water and methanol (200 ml, 1:1, v:v). The resulting dark solid was filtered under vacuum and washed with water (50 ml), methanol (50 ml) and diethyl ether (50 ml) sequentially, giving a dark purple powder that was dried under vacuum. This was then added to *N,N*-dimethylformamide (1 L) and the mixture was stirred at 100 °C, under air, for 18 hours. The mixture was then concentrated under vacuum to a minimum amount of solvent. This was then added to methanol (300 ml) while stirring. The resulting dark solid was the filtered under vacuum and washed with methanol until a clear filtrate was obtained. Compound **4** (1.26 g, 44%) was afforded as a dark purple

powder. ^{1}H-NMR* (500 MHz, $CDCl_3$) δ 8.76 (s, 2H), 4.92 – 4.72 (m, 4H), 1.92 – 1.82 (m, 4H), 1.78 - 1.69 (m, 2H), 1.33 (dd, J = 14.1, 3.3 Hz, 2H), 1.26 (dd, J = 14.1, 5.8 Hz, 2H), 1.16 (d, J = 6.2 Hz, 6H), 0.94 (s, 18H). HRMS (ESI+, m/z): [M+H]+ found 603.3405; calc. for ($C_{24}H_{45}N_2$+) 361.3402.
*A drop of TFA-d was added to dissolve the sample as the compound is highly insoluble before adding the peripheral alkyl/glycol chains.

BFG

Compound **4** (0.436 g, 0.724 mmol) and potassium carbonate (0.500 g, 3.62 mmol) were dissolved in anhydrous DMF (100 ml), and stirred at 60 °C for 30 minutes under N_2. 2-[2-(2-Iodoethoxy)ethoxy]ethanol methyl ether (0.992 g, 3.62 mmol) was then added and the resulting mixture was stirred for further 6 hours. The mixture was concentrated under reduced pressure and the residue dissolved in dichloromethane (50 ml). Saturated aqueous ammonium chloride (100 ml) was added, and the organic layer was extracted. The aqueous layer was further extracted with dichloromethane (2 x 50 ml), and the combined organic extracts were washed with water (70 ml) and brine (70 ml), sequentially, dried over magnesium sulfate, filtered and concentrated under vacuum. The crude material was purified by column chromatography (SiO_2, dichloromethane:methanol, 99:1), affording **BFG** (0.344 g, 51%) as a dark purple solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 2H), 4.78 – 4.56 (m, 4H), 4.37 (t, J = 5.6 Hz, 4H), 3.85 (t, J = 5.6 Hz, 4H), 3.74 – 3.70 (m, 4H), 3.65 – 3.60 (m, 8H), 3.53 – 3.49 (m, 4H), 3.33 (s, 6H) 1.90 – 1.77 (m, 4H), 1.75 – 1.67 (m, 2H), 1.41 (dd, J = 14.1, 3.1 Hz, 2H), 1.23 (dd, J = 14.1, 6.4 Hz, 2H), 1.15 (d, J = 6.4 Hz, 6H), 0.96 (s, 18H). ^{13}C-NMR (100 MHz, CDCl3) δ 159.0, 154.7, 148.4, 140.7, 138.6, 130.1, 118.7, 72.1, 70.8, 70.7, 70.1, 67.8, 59.2, 50.9, 44.5, 41.2, 36.0, 31.3, 30.2, 28.5, 22.8. HRMS (ESI+, m/z): [M+H]+ found 895.5304; calc. for ($C_{24}H_{45}N_2$+) 895.5288.

BFA

Compound **4** (0.500 g, 0.830 mmol) and potassium carbonate (0.573 g, 4.16 mmol) were dissolved in anhydrous DMF (100 ml), and stirred at 60 °C for 30 minutes under N2. 1-Iodoheptane (0.992 g, 3.62 mmol) was then added and the resulting mixture was stirred for further 6 hours. The mixture was then concentrated under reduced pressure and the residue dissolved in dichloromethane (50 ml). Saturated aqueous ammonium chloride (100 ml) was added and the organic layer was extracted. The aqueous layer was further extracted with dichloromethane (2 x 50 ml), and the combined organic extracts were washed with water (70 ml) and brine (70 ml), sequentially, dried over magnesium sulfate, filtered and concentrated under vacuum. The crude material was purified by column chromatography (SiO_2, dichloromethane:methanol, 99:1), affording **BFA** (0.391 g, 59%) as a dark purple solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 4.78 – 4.56 (m, 4H), 4.11 (dd, J = 8.6, 6.5 Hz, 4H), 1.90 – 1.68 (m, 10H), 1.49 – 1.18 (m, 20H), 1.15 (d, J = 6.3 Hz, 6H), 0.96 (s, 18H), 0.92 – 0.80 (m, 6H). 13C NMR (101 MHz, CDCl3) δ 158.8, 154.7, 148.3, 140.7, 138.6, 130.1, 118.6, 50.9, 44.5, 36.0, 31.9, 31.3, 30.2, 30.2, 29.1, 28.44, 27.9, 27.1, 22.8, 22.8, 14.2. HRMS (ESI+, m/z): [M+H]+ found 799.5590; calc. For ($C_{46}H_{71}N_8O_4$+) 799.5593.

3. NMR spectra.

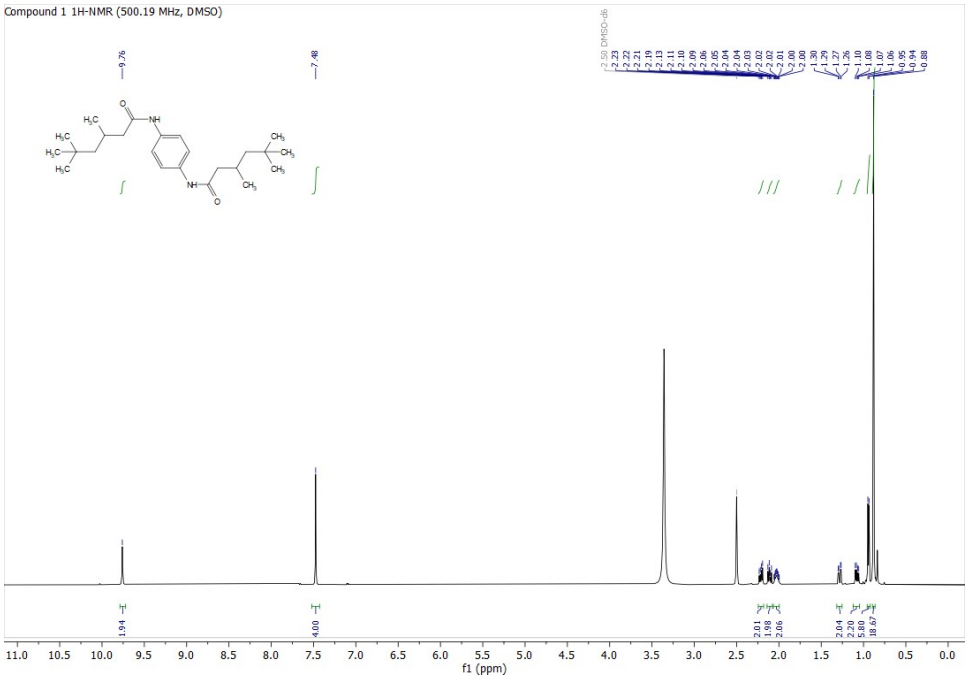

Figure S2. ^{1}H NMR of compound **1** recorded in DMSO-d6.

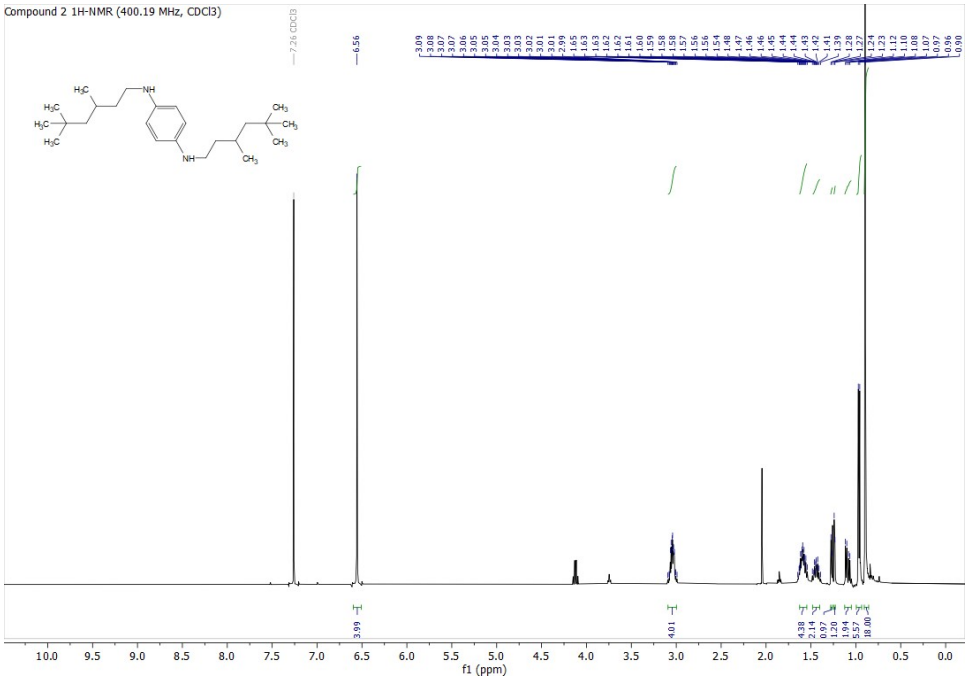

Figure S3. ^{1}H NMR of compound **2** recorded in $CDCl_3$.

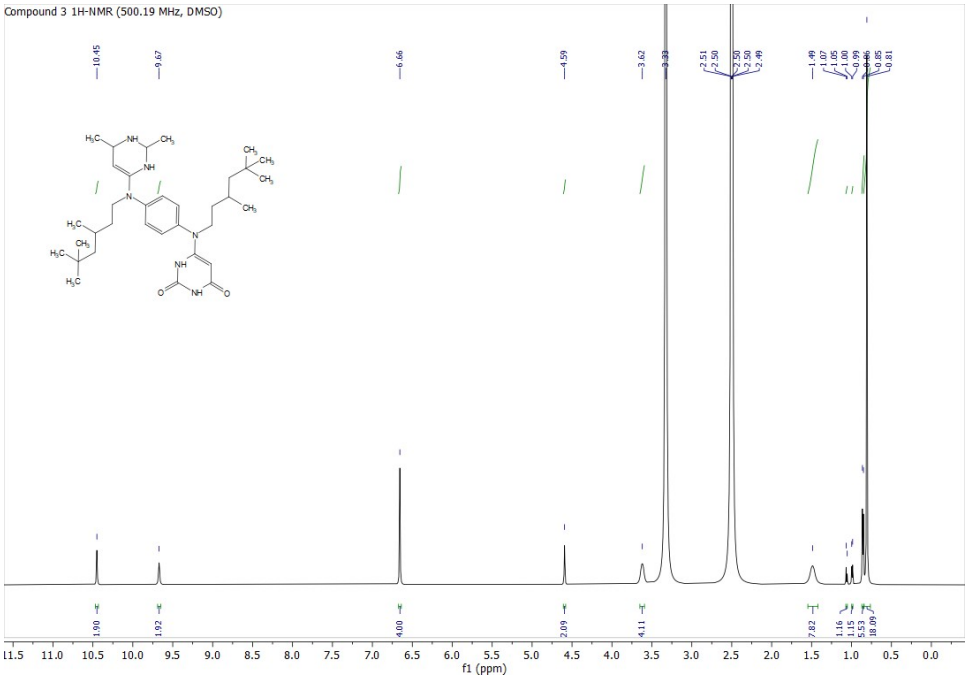

Figure S4. ^{1}H NMR of compound **3** recorded in DMSO-d6.

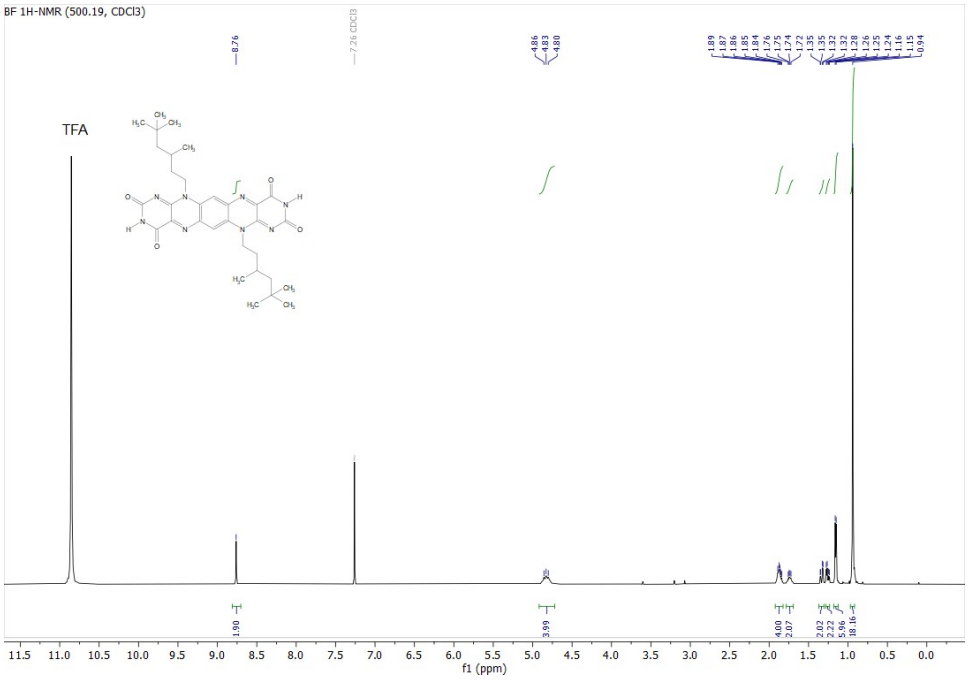

Figure S5. ^{1}H NMR of compound **4** recorded in $CDCl_3$/ TFA.

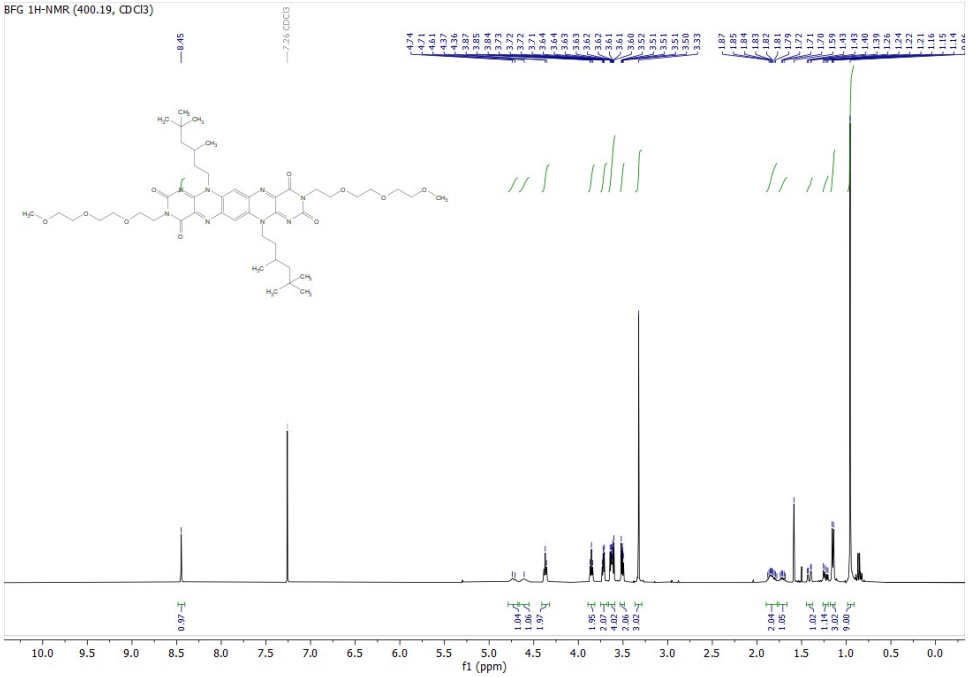

Figure S6. ^{1}H NMR of compound **BFG** recorded in $CDCl_3$.

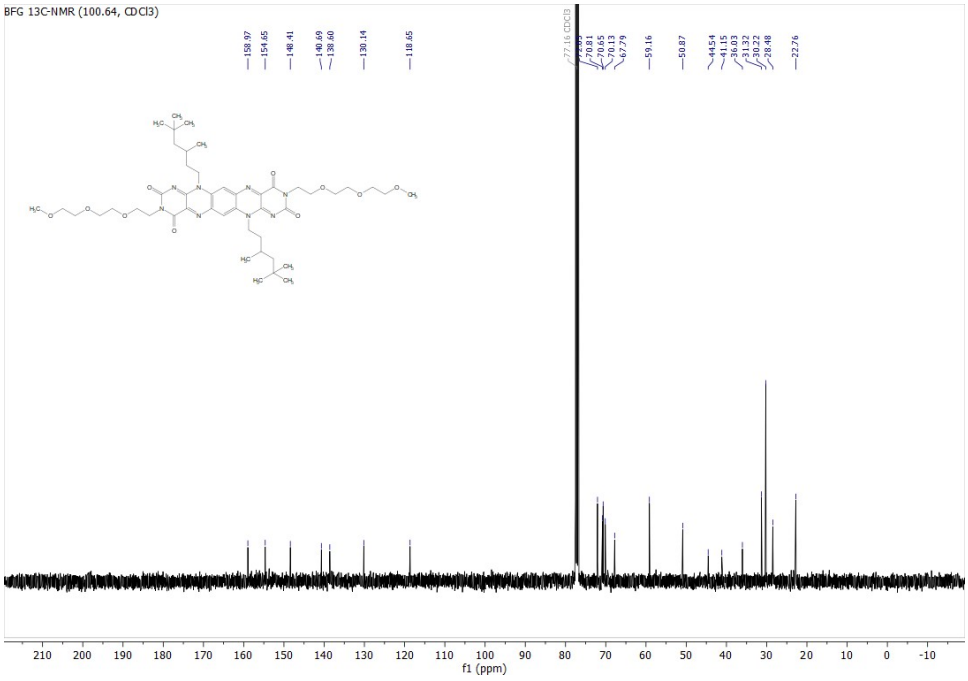

Figure S7. ^{13}C NMR of compound **BFG** recorded in $CDCl_3$/ TFA.

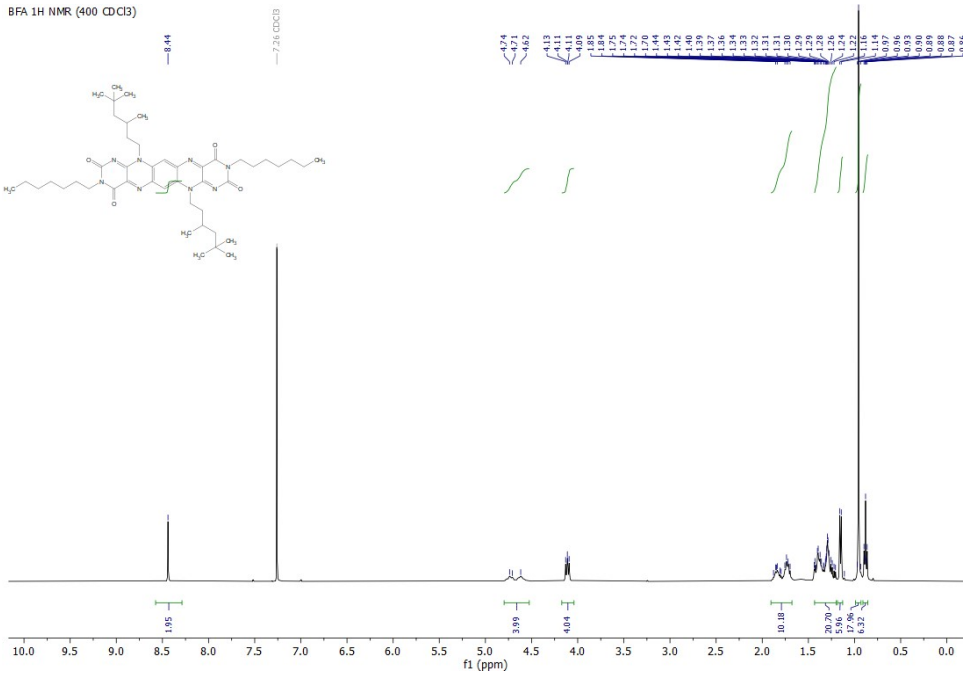

Figure S8. ^{1}H NMR of compound **BFA** recorded in $CDCl_3$.

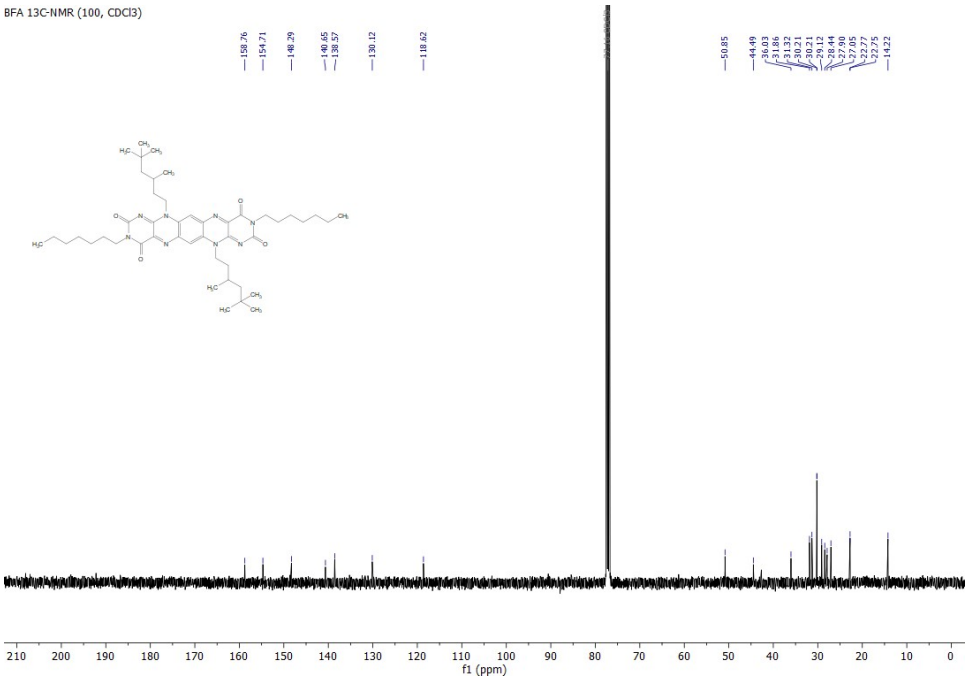

Figure S9. ^{1}H NMR of compound **BFA** recorded in $CDCl_3$.

4. Cyclic voltammetry.

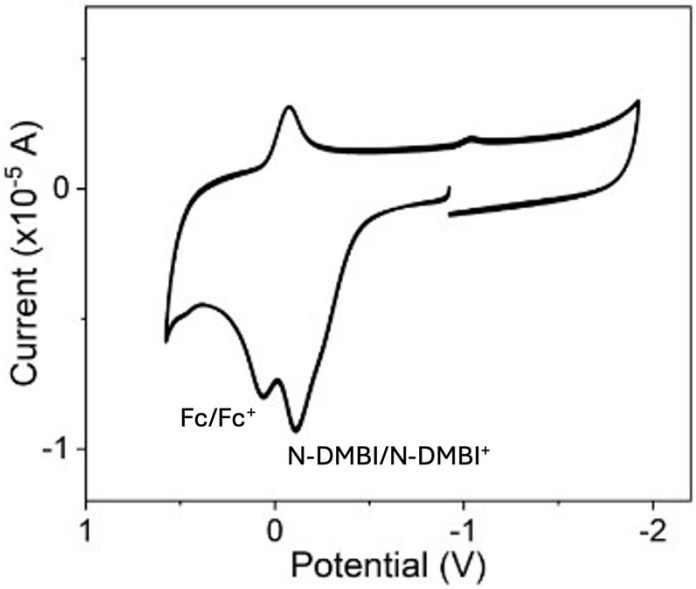

Figure S10. CV measurement of N-DMBI with ferrocene as reference (10^{-3} M in DMF, scan rate 100 mVs^{-1}).

5. UV-Vis spectra.

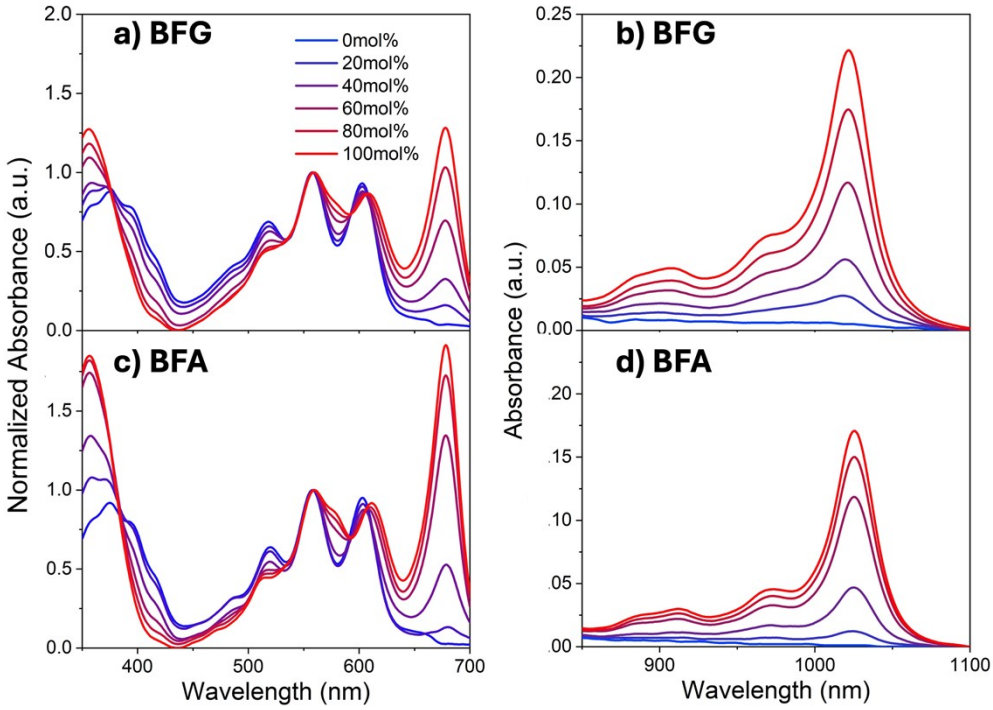

Figure S11. Solution state of UV-Vis absorption spectra for 0 mol% to 100 mol% of **N-DMBI** doping in **BFG** from a) 350 nm to 700 nm; b) 800 nm to 1100 nm; **BFA** from c) 350 nm to 700 nm; d) 800 nm to 1100 nm. The absorption spectra of Figure S10a and S10c have been normalized at 558 nm.

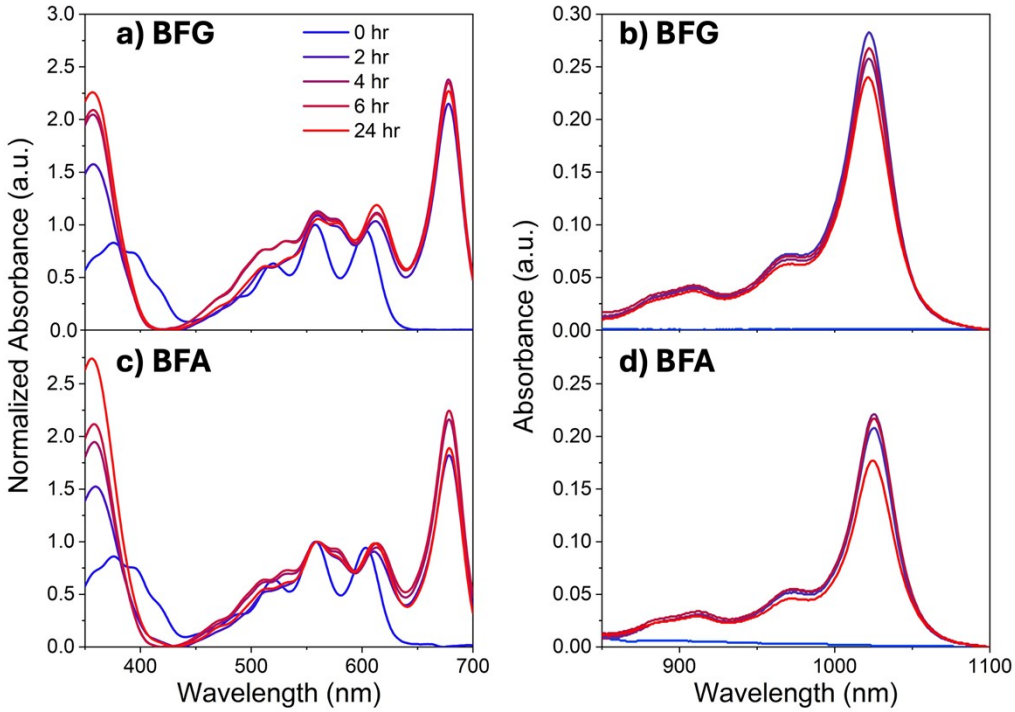

Figure S12. Solution state of UV-Vis Absorption Spectra for reaction time from 0 to 24 hours of 100 mol% N-DMBI doping in **BFG** from a) 350 nm to 700 nm; b) 800 nm to 1100 nm; **BFA** from c) 350 nm to 700 nm; d) 800 nm to 1100 nm. The absorption spectra of Figure S11a and S11c have been normalized at 558 nm.

6. Scanning electron microscopy.

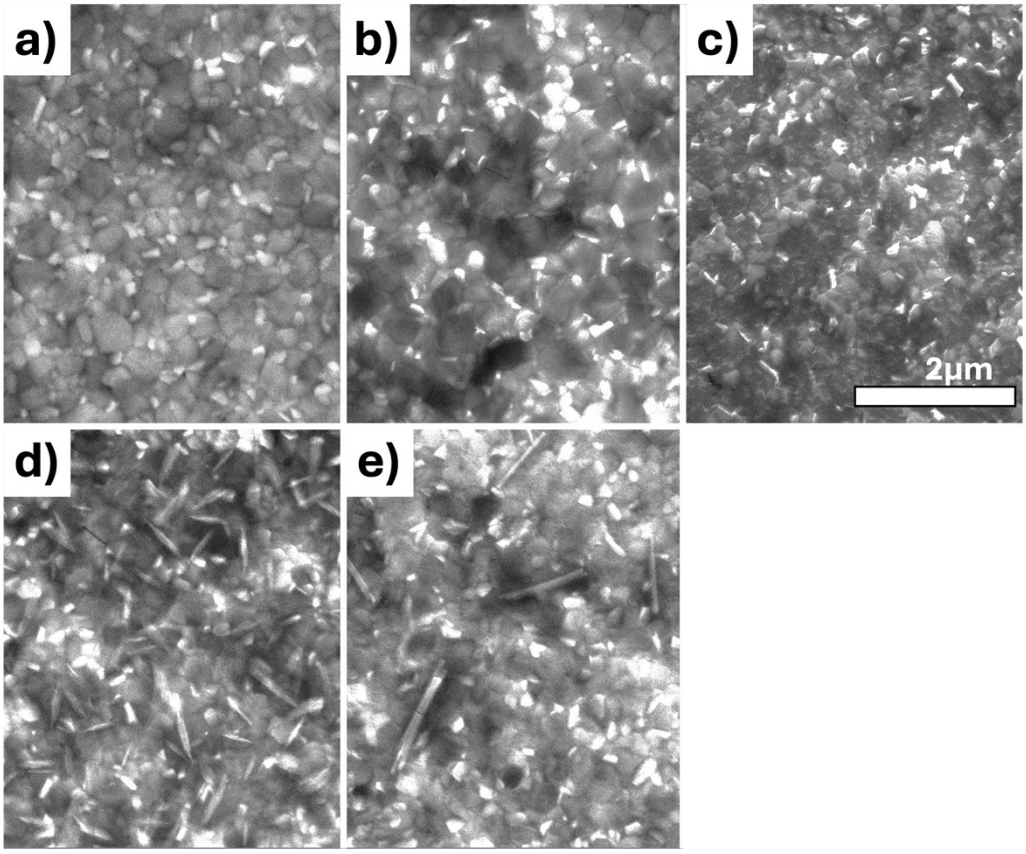

Figure S13. SEM images of a) **PCBM**, b) pristine **BFG**, c) pristine **BFA**, d) doped **BFG** and e) doped **BFA**.

7. Theoretical Calculations.

Density Function Theory (DFT) calculations were performed with Gaussian 09 program.[1] **BFA** and **BFG** were calculated with alkyl or glycol chains truncated (**BF**) to allow more efficient optimisation of the core. All calculations were carried out in the gas phase. The geometries of all species were optimized using B3LYP/6-31G(dp) method. Spin density distributions of radical species were calculated at the spin-unrestricted B3LYP/6-31G(dp) method. The fully optimized structures were confirmed to be true minima by vibrational analysis at the same level of computation, which showed no imaginary frequencies. Excitation energies and oscillator strengths for the optimized structures were calculated with the TD-DFT B3LYP/6-31G(dp) method and used to simulate the UV/vis absorption spectra.

For calculations on dimers and complexes, individual molecules were separated by 4Å with the central aromatic rings aligned parallel. This distance was not fixed, and species were allowed to relax to energy minimum. The basis set superposition error was minimised by carrying out a single point energy calculation on the optimised geometry using the counterpoise adjustment to the B3LYP/6-31G(dp) method. The binding energy was estimated by comparing the free energy of individual species compared to the energy of the complex/dimer.

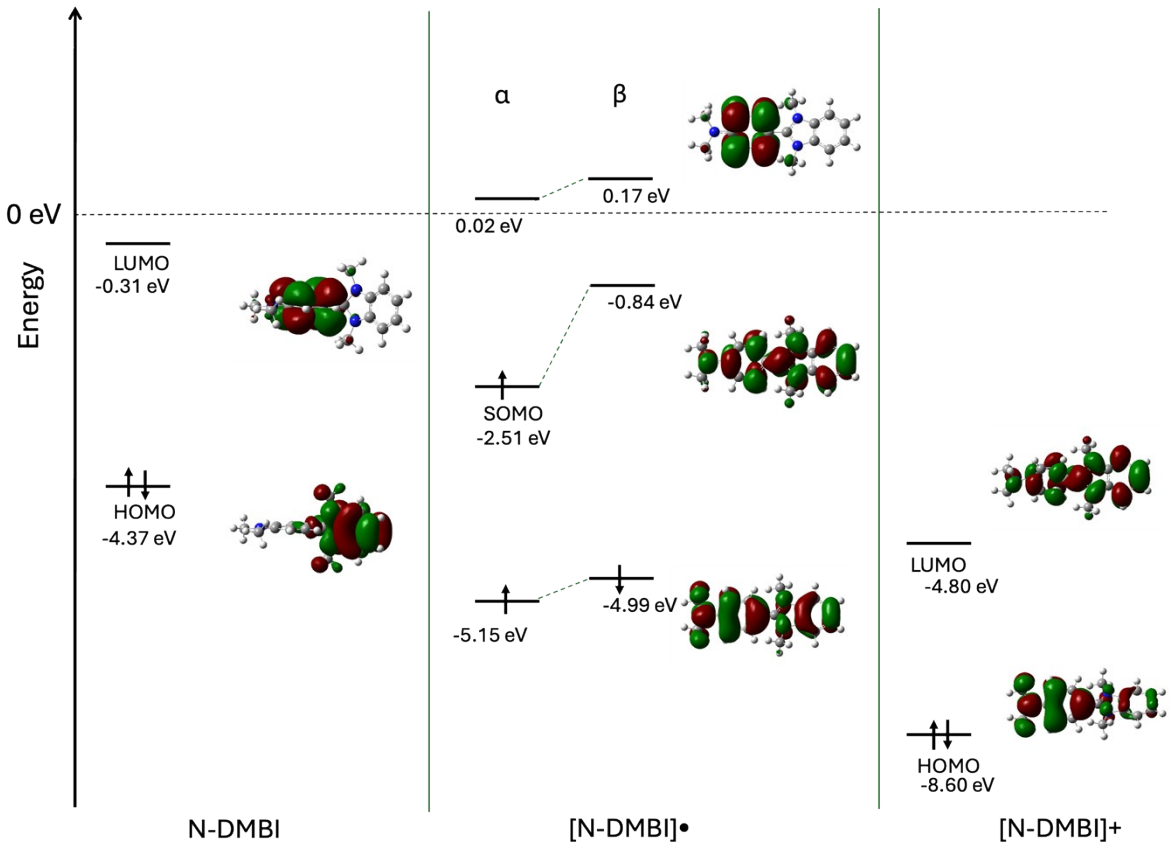

Figure S14. Frontier molecular orbital diagrams and energy levels of **N-DMBI,** [**N-DMBI]•, [N-DMBI]+.**

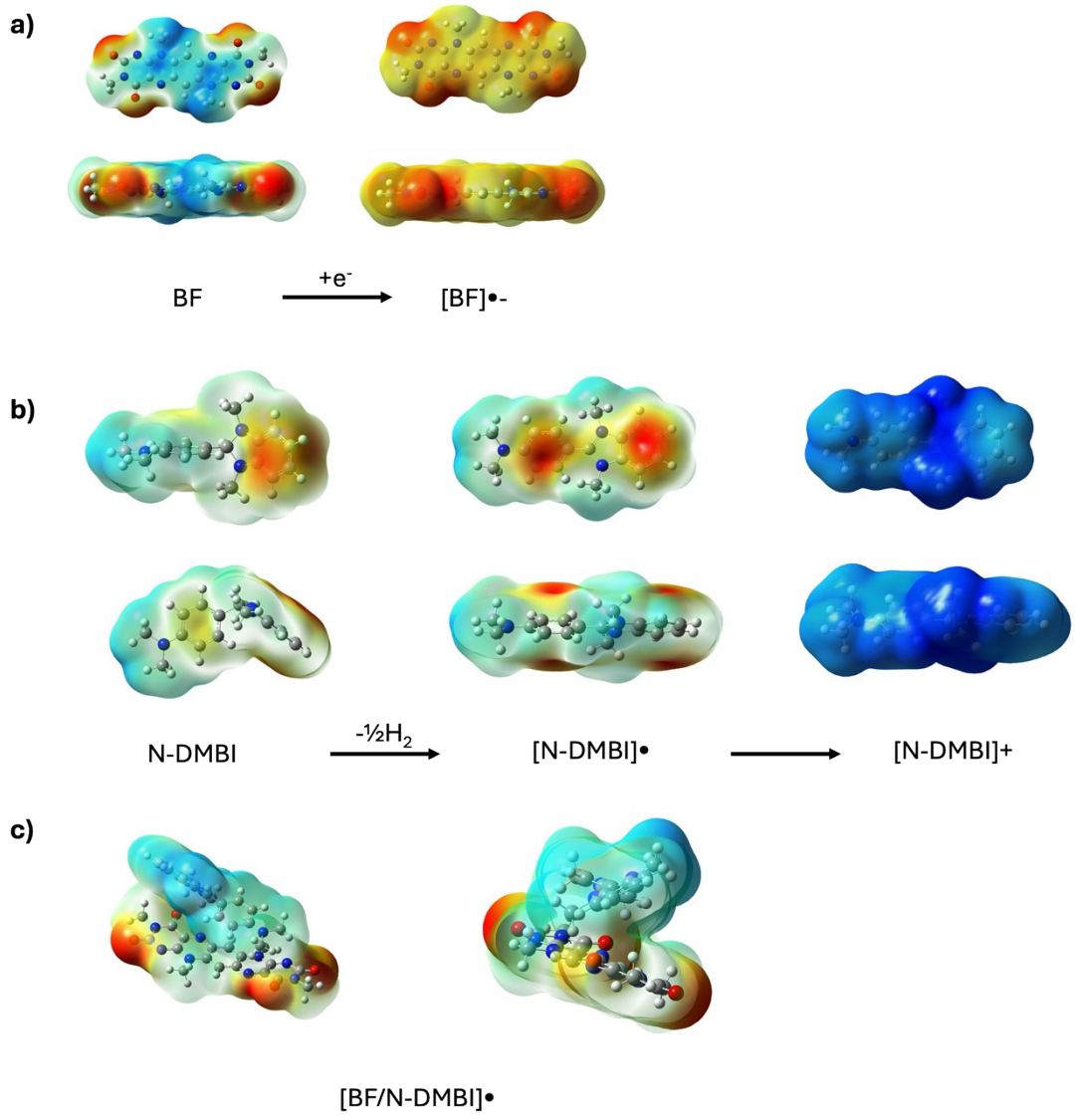

Figure S15. ESP plots of (a) **BF**, **[BF]•-,** (b) **N-DMBI**, [**N-DMBI]•, [N-DMBI]+,** and (c) **[BF/N-DMBI]•** complex (blue = positive, red = negative).

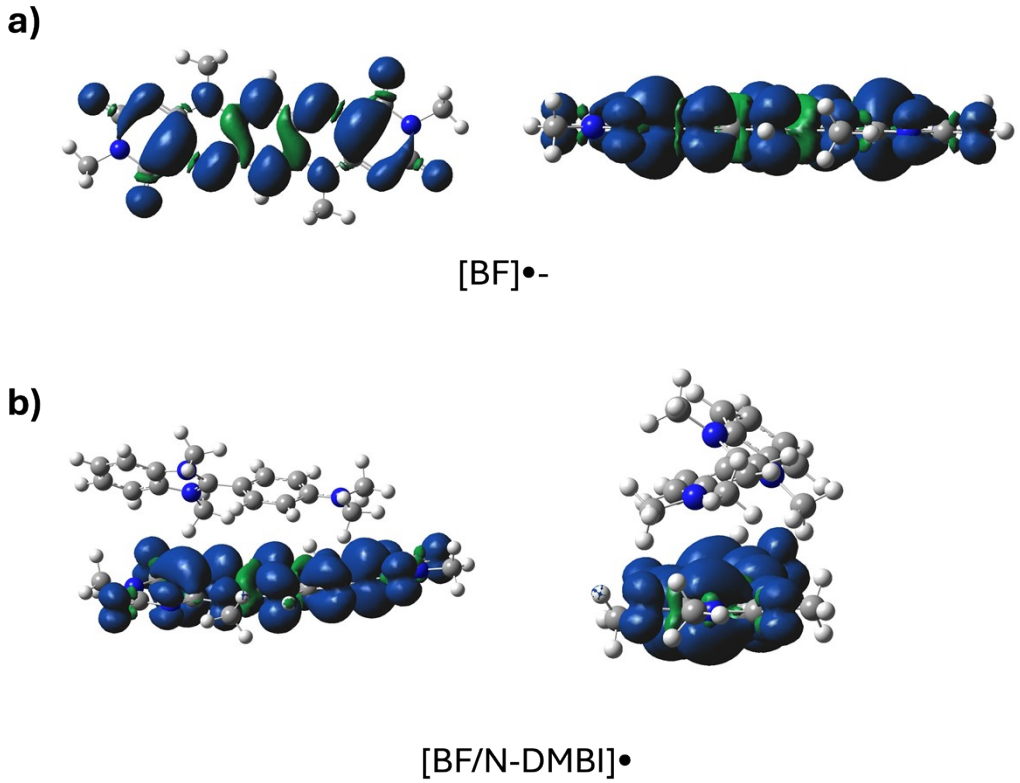

Figure S16. a) Spin density distribution in the radical anion of **[BF]•-** and radical complex **[BF/N-DMBI]•** showing high degree of delocalisation. Iso-density level of 0.0004 electron/bohr.

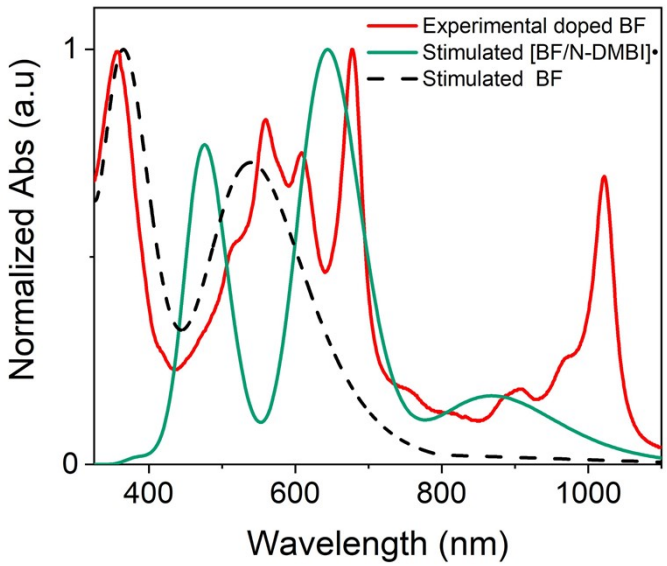

Figure S17. Simulated UV-Vis spectra of neutral of **BF** and **[BF/N-DMBI]•** using TD-DFT and the doped spectrum of **BFG**.

8. Conductivity measurements.

For the measurement of conductivity, both undoped and doped **BFG** and **BFA** were dissolved in chlorobenzene (CB) and prepared on the pattern ITO substrates by spin coating method. The conductivity was calculated by analysing the current-voltage characteristics of thin films. The direct current conductivity of thin film (σ) with units of siemens per meter (S/cm) could be measured by $\sigma = 1/\rho = (l)/(A \cdot R)$ where ρ, l, A and R are resistivity, length of the thin film, cross-sectional area of the thin film and resistance of given thin film, respectively.

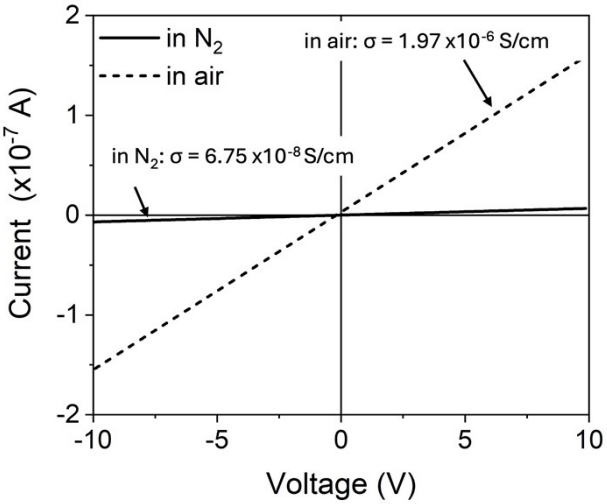

Figure S18. Conductivity measurements of pristine **PCBM** films exposed in N_2 and air.

7. Device fabrication

The ITO glass substrates with pattern were cleaned with 8% decon-90 solution, DI water, acetone, ethanol and DI water. Following this, the substrates were dried with using N_2 and exposed to UV ozone for 20 min. To prepare the hole transporting layer, 3 mg/ml of MeO-2PACz was dissolved in ethanol and heated overnight at 70 °C. MeO-2PACz solution was then spin-coated onto the ITO substrates at 4000 rpm for 30 seconds and annealed at 100 °C for 15 minutes. Subsequently, a 0.2 wt% dispersion of Al_2O_3 nanoparticles (NPs) in isopropanol (IPA) was spin-coated onto the MeO-2PACz layer at 2000 rpm for 30 seconds and dried at 100 °C for 5 minutes. The perovskite precursor solution, composed of 726 mg of PbI_2, 208 mg of FAI, 33 mg of MAI, 19 mg of CsI and 14 mg of $PbCl_2$ in a 1 ml solvent mixture (DMF/DMSO:4/1) was heated overnight at 70 °C. 50 µL of perovskite solution was filtered and dispensed on the substrates, followed by a one-step spin-coating process at 4000 rpm for 40 seconds. During the final 15 seconds of the spin-coating, 200 µL of ethyl acetate (EA) was introduced as an anti-solvent. Subsequently, the substrates were annealed at 100 °C for 30 minutes. A solution of 20 mg/ml of PCBM in CB was prepared and heated at 70 °C overnight. PCBM was spin-coated onto the substrates at 3000 rpm for 30 seconds and annealed at 100 °C for 15 min. To prepare undoped and doped **BFG** and **BFA**, 15 mg of **BFG** and **BFA** were prepared in 1 ml CB. For the doped derivatives, 20 mol% **N-DMBI** was added and the solutions were heated at 70 °C for 3 hours (**BFG**) and 6 hours (**BFA**). These solutions were spin-coated at 2000 rpm for 30 seconds. A hole blocking layer was prepared by 1 mg/ml of bathocuproine (BCP) in IPA and spin-coated it onto the top of the PCBM or bis-flavin layer at 5000 rpm for 30 seconds. Finally, a 100 nm Ag cathode was deposited onto the substrates by thermal evaporation. The performance of perovskite solar cells was measured by illuminating the samples with AM1.5G sunlight provided by WaveLabs SIN-US70 solar simulator with UV and UR range extenders. The aperture area of the metal masks was 0.0098 cm^2.

8. References

1. Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.