# Supporting Information

**Role of structural isomerism in the properties of imine-based organic hole-transporting materials.**

Benjamin Vella,[a,†] Dylan Wilkinson,[a,‡] Son Singh,[b] Stephen Sproules,[a] Soad S. Alzahrani,[c] Abdulrahman G. Alhamzani,[c] Abdul-Wasir Shaka,[a] Shahzada Ahmad,[b,d,e,f] Sondos A. J. Almahmoud,[c,*] Graeme Cooke,[a,*] and Pablo Docampo[a,§*]

a. School of Chemistry, University of Glasgow, University Avenue, Glasgow, G12 8QQ
b. BCMaterials, Basque Center for Materials, Applications, and Nanostructures, UPV/EHU Science Park, 48940, Leioa, Spain
c. Department of Chemistry, College of Science, Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh 11623, Saudi Arabia.
d. IKERBASQUE, Basque Foundation for Science, Bilbao, 48009, Spain
e. New Energy & Optical Materials Lab., Departament de Química Inorgànica i Orgànica and Institut de Química Teòrica i Computacional, Diagonal 645, Universitat de Barcelona, E-08028
f. Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain

## Table of Contents



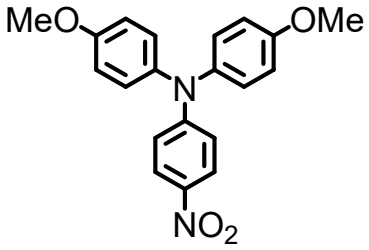
Current affiliations:
† Strathclyde Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, Glasgow, G4 0RE, UK.
‡ RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.
§ BCMaterials, Basque Center for Materials, Applications, and Nanostructures, UPV/EHU Science Park, 48940, Leioa, Spain

# 1 General Experimental

All reagents were purchased from commercial sources and used as received unless stated otherwise. Dry solvents were obtained from a Pure Solv 500 MD™ solvent purification system or purchased from Merck. All reactions were performed under nitrogen atmosphere. Brine, in this context, refers to a saturated solution of sodium chloride. Column chromatography was carried out using 60 Å silica gel purchased from Fluorochem/Doug Discovery®. Merck silica gel (60 Å) covered aluminium plates (F254) were used for thin layer chromatography (**TLC**). $^{1}H$ and $^{13}C$ NMR spectra were acquired using a Bruker AVIII 400 MHz spectrometer. All chemical shift values are reported in ppm relative to tetramethylsilane (**TMS**) and are referenced to the residual solvent peaks. All mass spectra were obtained using a Bruker Microtof-q for electrospray ionisation (**ESI**) measurements. Electrochemical measurements were performed on a CH Instruments Electrochemical Workstation, CHI 440a. Ferrocene was used as an external standard, with the ferrocenium/ferrocene ($Fc^{+}/Fc$) redox couple adjusted to 0.0 V. The solutions were prepared using anhydrous DMF, with the target compound at a concentration of $10^{-4}$ M. Electrochemical grade tetrabutylammonium hexafluorophosphate (**TBAF**) was included as supporting electrolyte at a concentration of 0.1 M. All solutions were purged with $N_2$ gas for 3 minutes prior to recording the electrochemical data. UV-Visible absorption spectra were recorded on a Shimadzu UV-3600 UV–vis–NIR spectrophotometer, using $10^{-5}$ M solutions of the target compounds in dichloromethane. Infrared spectra were obtained using the neat solids in the 4000 – 500 $cm^{-1}$ range using an Agilent Cary 630 FTIR spectrometer (50 scans, 4 $cm^{-1}$ resolution, ATR diamond crystal). Theoretical infrared spectra and frequency calculations were performed using ORCA version 4.2.1 quantum chemistry program package, and the input files were generated using Avogadro 1.2.0 visualisation software using density functional theory (DFT, B3LYP, 6-311G**). Samples used for thermal analysis were thoroughly dried under vacuum for at least 12 hours prior to measurement. A Stuart Scientific SMP10 melting point apparatus was used for determining the melting points of all synthesised materials, and all melting points were uncorrected. TGA was performed using powder samples on a TA Instruments SDT Q600 V8.3 thermogravimetric analyser. DSC was performed on a TA Instruments DSC2A-01781, ensuring that the heating did not exceed 10°C below their decomposition temperature determined from TGA. All the thermal analyses were carried out under $N_2$, at a rate of 10°C per minute.

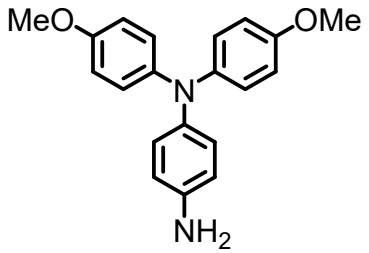
## 1.1 Synthetic procedures

**4,4'-Dimethoxy-4''-nitrotriphenylamine** (**3**)[1]




4-Nitroaniline (410 mg, 2.97 mmol), 1-methoxy-4-iodobezene (1458 mg, 6.23 mmol), copper powder (184.9 mg, 2.91 mmol), potassium carbonate (862.4 mg, 6.24 mmol), and 18-crown-6 (31.7 mg, 0.12 mmol) were dissolved in DMF (5 mL). The mixture was stirred vigorously under reflux (150 °C) for 16 hours. The mixture was allowed to cool to room temperature and was then diluted with ethyl acetate and extracted with $H_2O$ and brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent was then removed under vacuum. The product was further purified by column chromatography (30% diethyl ether/petroleum ether), and then recrystallised from isopropanol to yield red crystals of the pure product (690 mg, 67%). Mpt. 132 – 134 °C (lit.[2,3] 125 – 129 °C). $R_f$ = 0.37 (30% diethyl ether/petroleum ether). $^1$H-NMR ($CDCl_3$, 400MHz) δ = 7.93 (dt, *J* = 9.36, 3.28 Hz, 2H), 7.07 (dt, *J* = 8.96, 2.24 Hz, 4H), 6.84 (dt, *J* = 9.00, 2.28 Hz, 4H), 6.69 (dt, *J* = 9.36, 2.16 Hz, 2H), 3.75 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 157.79, 154.25, 139.04, 138.34, 128.22, 125.65, 115.80, 115.31, 55.60 ppm. HRMS (ESI+): m/z calculated for $[C_{20}H_{18}N_2O_4]H^+$ = 351.1267; found = 351.1356.

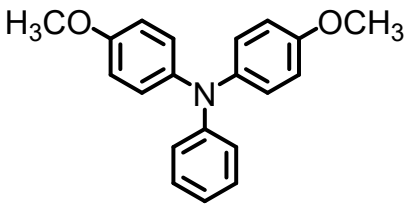
**4-Amino-4',4''-dimethoxytriphenylamine** (**4**)[1]




4,4'-Dimethoxy-4''-nitrotriphenylamine (404 mg, 1.15 mmol) and 10% palladium on carbon (41.3 mg) was suspended in dry THF (10 mL). The mixture was vigorously stirred while degassing with nitrogen, during which time hydrazine hydrate (0.39 ml, 8.07 mmol) was added dropwise. The mixture was then heated under reflux (66 °C) for 16 hours. The mixture was cooled to room temperature after which it was filtered through a short pad of celite to remove the palladium catalyst. Ethyl acetate was used to collect washings from the flask. The product was then recrystallised from $H_2O$ and collected as grey crystals (350 mg, 95% crude yield). The entire yield was used immediately for the final condensation step, due to its instability in air which was observed during NMR sample preparation. The colourless solution gradually turned dark grey when exposed to the air for a short period of time. $R_f$ = 0.1 (30% diethyl ether/petroleum ether). $^1$H-NMR ($CDCl_3$, 400MHz) δ = 6.95 (dt, *J* = 9.04, 2.24 Hz, 4H), 6.87 (dt, *J* = 8.68, 2.12 Hz, 2H),

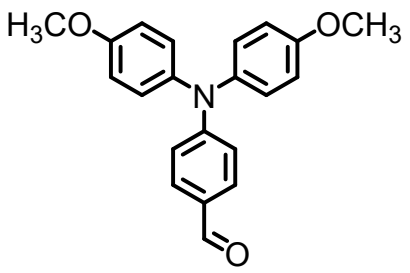
6.76 (dt, *J* = 9.04, 2.32 Hz, 4H), 6.60 (dt, *J* = 8.68, 2.12 Hz, 2H), 3.77 (s, 6H), 3.51 (s, 2H) ppm. Product rapidly decomposes in air and thus $^{13}C$ NMR and mass spectra could not be recorded.

**4-Methoxy-N-(4-methoxyphenyl)-N-phenylaniline** (**6**)[4]




Methanol (50 mL) was cooled down to 0 °C in an ice bath. Sodium (3420 mg, 148.8 mmol) was added in small portions to the solvent, causing effervescence as the metal dissolved in the solvent. The mixture was left to stir at 0 °C until no traces of sodium metal were left in the reaction flask. After complete dissolution of the sodium was observed, 4-bromo-N-(4-bromophenyl)-N-phenylaniline (3000 mg, 7.48 mmol), copper (I) iodide (5810 mg, 30.5 mmol) and DMF (20 mL) were added, causing a colour change to an opaque green. The mixture was degassed with nitrogen, heated to 100 °C, and stirred vigorously for 12 hours, during which time a colour change to a red-brown mixture was observed. The reaction mixture was then allowed to cool to room temperature and washed three times with brine and once with distilled water. The organic layer was then collected and dried over anhydrous $MgSO_4$. The dried mixture was then filtered, and the solvent was removed under vacuum. The solid obtained was further purified by column chromatography (10% ethyl acetate/petroleum ether) to yield the pure product as an off-white solid. Recrystallisation from 2-propanol yielded white crystals of the product (1746 mg, 77%). $R_f$ = 0.67 (10% ethyl acetate/petroleum ether). Mpt .109 – 111°C. $^1$H-NMR ($CDCl_3$, 400 MHz) δ = 7.20 – 7.13 (2H, m), 7.02 – 6.95 (4H, m), 6.94 – 6.85 (4H, m), 6.85 – 6.80 (1H, m), 6.80 – 6.69 (2H, m), 3.73 (6H, s) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d_6$) δ = 155.54, 148.41, 140.32, 129.04, 126.38, 120.23, 119.79, 114.88, 55.19 ppm. HRMS (ESI+): m/z calculated for $[C_{20}H_{19}NO_2]H^+$ = 306.1416; found = 306.1491.

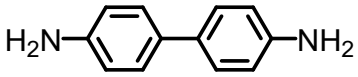
**4-(Bis(4-methoxyphenyl)amino)benzaldehyde** (**7**)[5]




4-Methoxy-N-(4-methoxyphenyl)-N-phenylaniline (629 mg, 2.05 mmol) was dissolved in DMF (10 mL) and the mixture was cooled to 0 °C by stirring over an ice bath. Phosphorus (V) oxychloride (0.38 mL, 4.10 mmol) was added dropwise to the solution under a nitrogen atmosphere, causing

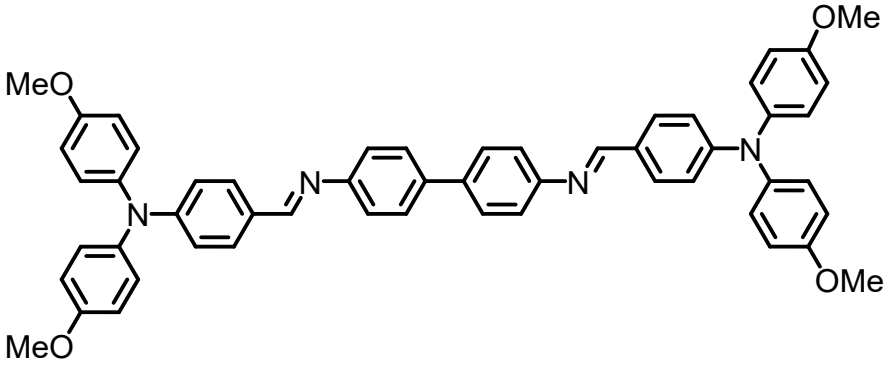
the reaction mixture to turn from pale yellow to bright yellow. The mixture was heated to 90 °C with vigorous stirring for 12 hours, during which time the solution took on a dark red colour. The reaction was cooled to room temperature and washed with a saturated solution of sodium acetate and then distilled water. The organic layer was then collected, dried over anhydrous $MgSO_4$, filtered and the solvent was removed under vacuum. The crude product was further purified by column chromatography (50% ethyl acetate/petroleum ether) and collected as a bright yellow solid (380 mg, 55%). $R_f$ = 0.72 (50% ethyl acetate/petroleum ether). Mpt. 124 – 126°C. $^1$H-NMR ($CDCl_3$, 400MHz) δ = 9.75 (1H, s), 7.65 – 7.59 (2H, dt), 7.17 – 7.06 (4H, dt), 6.92 – 6.87 (4H, dt), 6.86 – 6.82 (2H, dt), 3.82 (6H, s) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 190.43, 157.45, 154.21, 138.96, 131.56, 128.20, 127.91, 116.89, 115.35, 55.63 ppm. HRMS (ESI+): m/z calculated for $[C_{21}H_{19}NO_3]H^+$ = 334.1365; found = 334.1450.

**4,4'-Diaminobiphenyl** (**Benzidine**, **9**)[6]



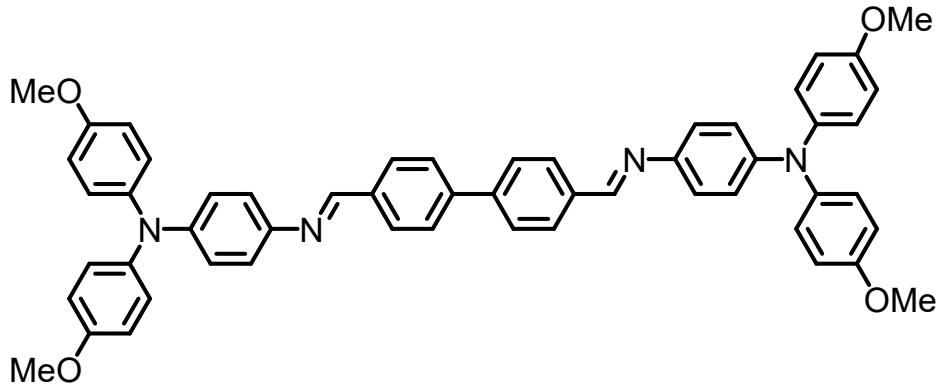

4,4'-Dinitro-1,1'-biphenyl (776 mg, 3.18 mmol) and 10% palladium on carbon (111.5 mg) was suspended in dry THF (20 mL), which was then degassed thoroughly with $N_2$ with vigorous stirring. Hydrazine hydrate (1.0 mL, 21.5 mmol) was added dropwise, after which the reaction mixture was heated under reflux (66°C) for 16 hours. After reaction completion, the mixture was cooled to room temperature and filtered through a short pad of celite to remove the palladium catalyst. Ethyl acetate was used to collect washings from the flask. The product was then recrystallised from isopropanol and collected as off-white crystals (380 mg, 67%). $R_f$ = 0.11 (50% ethyl acetate/petroleum ether). Mpt. 124 – 126°C.$^1$H-NMR ($CDCl_3$, 400MHz) δ = 7.42 – 7.28 (4H, dt), 6.77 – 6.68 (4H, dt), 3.65 (4H, s) ppm. Product rapidly decomposes in air and thus $^{13}$C NMR and mass spectra could not be recorded.

**($N^4$E,$N^{4'}$E)-$N^4$,$N^{4'}$-Bis(4-(bis(4-methoxyphenyl)amino)benzylidene)-[1,1'-biphenyl]-4,4'-diamine** (**BiPh-inv-OMeTPA**, **10**)[7]



4-[Bis(4-methoxyphenyl)amino]benzaldehyde (350 mg, 1.05 mmol) and 4,4'-diaminobiphenyl (100 g, 0.52 mmol) were added to ethanol (30 mL) along with anhydrous magnesium sulfate (~500 mg). The reaction was heated to reflux (80 °C) and a catalytic amount of *para*-toluenesulfonic acid (~1 mg) was added. The reaction mixture immediately turned red followed by the gradual precipitation of the yellow product. The reaction was stirred under reflux for 16 hours and then gradually cooled to room temperature. Distilled water was added to quench the reaction and fully precipitate any dissolved product (500 mL). The product was filtered and was washed with a 10% NaOH solution (100 mL) followed by distilled water (100 mL). The crude product was allowed to dry under vacuum and then further purified by column chromatography using base-treated silica (20% ethyl acetate/petroleum ether with ~1% $Et_3N$). The product was then precipitated from dichloromethane/petroleum ether to yield a yellow solid (370 mg, 43%). Mpt. 85°C. $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 2H), 7.76 – 7.67 (m, 4H), 7.63 (d, J = 8.5 Hz, 4H), 7.30 – 7.23 (m, 4H), 7.18 – 7.07 (m, 8H), 6.93 (d, J = 8.8 Hz, 4H), 6.91 – 6.80 (m, 8H), 3.82 (s, 12H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 159.46, 156.67, 151.62, 139.85, 137.82, 129.97, 127.83, 127.49, 127.47, 121.41, 118.58, 114.90, 77.22, 55.51 ppm. FTIR: ν(cm$^{-1}$): 2990 (weak), 2929 (weak), 2832 (weak), 1607 (weak), 1581 (medium), 1558 (weak), 1499 (strong), 1462 (medium), 1430 (medium), 1319 (medium), 1281 (medium), 1236 (strong), 1159 (strong), 1103 (medium), 1030 (strong), 976 (medium), 883 (weak), 823 (strong), 721 (medium), 671 (weak). HRMS (ESI+): m/z calculated for $[C_{54}H_{46}N_4O_4]H^+$ = 815.3592; found = 815.3588.

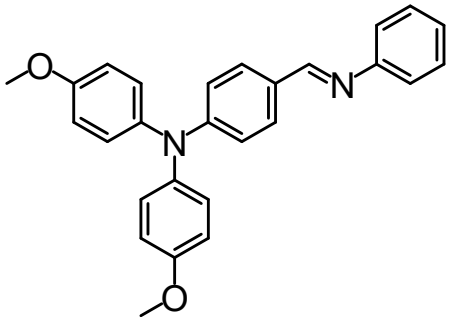
**(N$^1$,N$^1$''E,N$^1$,N$^1$''E)-N$^1$,N$^1$''-([1,1'-Biphenyl]-4,4'-diylbis(methanylylidene))bis(N$^4$,N$^4$-bis(4-methoxyphenyl)benzene-1,4-diamine)** (**BiPh-OMeTPA**, **12**)[7]




[1,1'-Biphenyl]-4,4'-dicarbaldehyde (201.9 mg, 0.96 mmol) and 4-amino-4',4''-dimethoxytriphenylamine (685.6 mg, 2.14 mmol) were dissolved in ethanol (20 mL) and then, anhydrous magnesium sulfate (~500 mg) was added. The mixture was degassed with $N_2$, after which a catalytic amount of *para*-toluenesulfonic acid (~1 mg) was added. The reaction mixture immediately turned red, and the gradual precipitation of an orange product was observed. The reaction mixture was stirred at 25 °C for 16 hours, after which distilled water (500 mL) was added to precipitate the product. The crude product was collected by filtration as an orange solid. The solid product was collected and dissolved in dichloromethane (30 mL) and washed with brine (2×100 mL) and distilled water (100 mL). The organic layer was collected and dried over

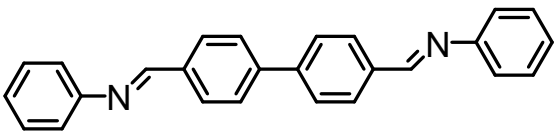
anhydrous magnesium sulfate, which was then removed by filtration. The crude product was further purified by column chromatography using base-treated silica (40% ethyl acetate/petroleum ether and ~1% $Et_3N$). The pure product was collected as an orange solid (408 mg, 49%). $R_f$ = 0.89 (40% ethyl acetate/petroleum ether and ~1% $Et_3N$). Mpt. 166 – 169 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.55 (2H, s), 8.00 – 7.94 (4H, d), 7.78 – 7.71 (4H, d), 7.20 – 7.13 (4H, dt), 7.10 – 7.04 (8H, dt), 7.01 – 6.94 (4H, dt), 6.87 – 6.80 (8H, dt), 3.80 (12H, s) ppm. $^{13}$C NMR (100 MHz, toluene-$d_8$) δ = 156.46, 148.02, 145.37, 142.78, 141.61, 137.46, 136.85, 129.47, 127.49, 126.70, 122.65, 122.07, 54.90 ppm. FTIR: v(cm$^{-1}$): 2990 (weak), 2929 (weak), 2833 (weak), 1622 (medium), 1603 (medium) 1580 (weak), 1500 (strong), 1316 (medium), 1235 (strong), 1170 (medium), 1103 (medium), 1031 (strong), 880 (weak), 822 (strong), 719 (weak), 574 (medium). HRMS (ESI+): m/z calculated for $[C_{54}H_{46}N_4O_4]H^+$ = 815.3599, found = 815.3519.

**(E)-4-Methoxy-N-(4-methoxyphenyl)-N-(4-((phenylimino)methyl)phenyl)aniline** (**Ph-OMeTPA**, **14**)



4-(Bis(4-methoxyphenyl)amino)benzaldehyde (500 mg, 1.50 mmol) and aniline (0.15 mL, 1.65 mmol) were dissolved in ethanol (20 mL). A spatula of anhydrous magnesium sulfate (~100 mg) was added. The mixture was degassed with $N_2$, after which a catalytic amount of *para*-toluenesulfonic acid (~1 mg) was added causing an immediate colour change to a red solution. The reaction mixture was allowed to stir at 25 °C for 16 hours. The reaction was then diluted with petroleum ether (100 mL) in order to precipitate the product as pale brown crystals (235.7 mg, 38.5%). $R_f$ = 0.77 (30% ethyl acetate/petroleum ether). Mpt. 121 – 123°C. $^1$H NMR (400 MHz, acetone-$d_6$) δ = 8.44 (s, 1H), 7.79 – 7.74 (d, 2H), 7.44 – 7.35 (m, 2H), 7.25 – 7.13 (m, 7H), 7.04 – 6.94 (m, 4H), 6.91 – 6.84 (m, 2H), 3.85 (s, 6H) ppm. $^{13}$C NMR (100 MHz, acetone-$d_6$) δ = 160.3, 158.2, 153.8, 152.8, 140.7, 130.9, 130.1, 128.8, 126.1, 121.8, 118.7, 116.0, 55.95 ppm. HRMS (ESI+): m/z calculated for $[C_{27}H_{24}N_2O_2]H^+$ = 409.1918, found = 409.1925.

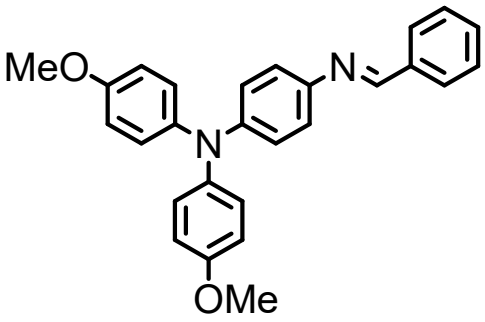
**(N,N'E,N,N'E)-N,N'-([1,1'-Biphenyl]-4,4'-diylbis(methanylylidene))dianiline** (**Ph-BiPh**, **15**)[9]



[1,1'-Biphenyl]-4,4'-dicarbaldehyde (508 mg, 2.42 mmol) and aniline (0.45 mL, 5.0 mmol) were dissolved in ethanol (20 mL). A spatula of anhydrous magnesium sulfate (~100 mg) was added.

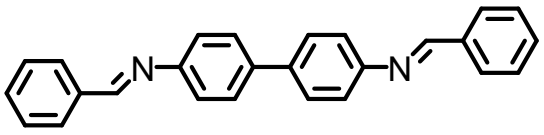
The mixture was degassed with $N_2$, after which a catalytic amount of *para*-toluenesulfonic acid (~1 mg) was added causing an immediate precipitation of a white solid. The reaction mixture was allowed to continue stirring for 16 hours at 25 °C. The reaction mixture was then diluted with petroleum ether (50 mL) to precipitate the product, which was then collected by filtration and recrystallised from toluene to form pale yellow crystals (688.7 mg, 80%). Mpt. 290 – 292°C. $^1$H NMR (400 MHz, toluene-$d_8$) δ = 8.18 (2H, s), 7.87 – 7.84 (4H, d), 7.45 – 7.41 (4H, d), 7.25 – 7.15 (8H, m), 7.07 – 7.03 (2H, m) ppm. The $^{13}$C NMR spectrum, recorded in toluene, is dominated by solvent peaks due to insufficient solubility in deuterated solvents combined with the low natural abundance of the $^{13}$C nuclei. HRMS (ESI+): m/z calculated for $[C_{26}H_{20}N_2]H^+$ = 361.1706, found = 361.1704.

**(E)-N$^1$-Benzylidene-N$^4$,N$^4$-bis(4-methoxyphenyl)benzene-1,4-diamine** (**Ph-inv-OMeTPA, 17**)




4-Amino-4',4''-dimethoxytriphenylamine (685.6 mg, 2.14 mmol) and benzaldehyde (0.24 mL, 2.35 mmol) were dissolved in ethanol (20 mL). A spatula of anhydrous magnesium sulfate (~100 mg) was added. The mixture was degassed with $N_2$, after which a catalytic amount of *para*-toluenesulfonic acid (~1 mg) was added causing an immediate colour change to a dark red solution. The reaction mixture was allowed to stir at 25 °C for 16 hours. The crude product was concentrated under vacuum, and then further purified by column chromatography (1% triethylamine in petroleum ether) to collect the pure product as a waxy, brown solid (235.7 mg, 38.5%). $R_f$ = 0.77 (30% ethyl acetate/petroleum ether). $^1$H NMR (400 MHz, acetone-$d_6$) δ = 8.64 (s, 1H), 7.98 – 7.91 (m, 2H), 7.54 – 7.47 (m, 3H), 7.23 (dt, 2H), 7.07 (dt, 4H), 6.92 (dt, 6H), 3.81 (s, 6H) ppm. $^{13}$C NMR (100 MHz, acetone-$d_6$) δ = 158.22, 157.26, 148.59, 145.49, 141.95, 138.10, 131.80, 129.69, 129.42, 127.49, 123.06, 121.97, 115.80, 55.89 ppm. HRMS (ESI+): m/z calculated for $[C_{27}H_{24}N_2O_2]H^+$ = 409.1918, found = 409.1902

**(N$^4$E,N$^{4'}$E)-N$^4$,N$^{4'}$-Dibenzylidene-[1,1'-biphenyl]-4,4'-diamine** (**Ph-inv-BiPh**, **18**)[8]




Benzidine (217.4 mg, 1.18 mmol) and benzaldehyde (0.23 mL, 2.28 mmol) were dissolved in ethanol (20 mL). A spatula of anhydrous magnesium sulfate (~100 mg) was added. The mixture

was degassed with $N_2$, after which a catalytic amount of *para*-toluenesulfonic acid (~1 mg) was added. The solution immediately turned cloudy as the product precipitated out of solution as a yellow solid. The reaction mixture was allowed to continue stirring at room temperature for 16 hours, after which it was diluted with petroleum ether (50 mL) in order to fully precipitate the product. The crude product was collected by filtration and recrystallised from toluene to form yellow crystals (256.3 mg, 65%). Mpt. 268 – 271 °C. $^1$H NMR (400 MHz, toluene-$d_8$) δ = 8.22 (s, 2H), 7.84 – 7.81 (d, 4H), 7.53 – 7.49 (d, 4H), 7.27 – 7.21 (d, 4H), 7.17 – 7.12 (m, 6H) ppm. Only solvent peaks are visible in the $^{13}$C NMR, due to insufficient solubility in deuterated solvents combined with the low natural abundance of the $^{13}$C nuclei. HRMS (ESI+): m/z calculated for $[C_{26}H_{20}N_2]H^+$ = 361.1706, found = 361.1697.

## 1.2 Conductivity measurements

Indium-tin oxide (**ITO**) glass substrates were cleaned by scrubbing both sides with a 2% solution of HELLMANEX III detergent in deionised water. More deionised water was then used to wash off the detergent, after which successive washings with acetone, ethanol, and deionised water were applied to remove traces of organic contaminants on the substrates. A compressed air gun was used to remove residual water. All cleaned substrates were patterned using a Rofin EasyMark IV F20 laser etcher, using an interdigitated pattern which created a channel ~60 μm wide and 37.2 cm long across which the conductivity of a thin film could be measured.

Patterned ITO substrates were then cleaned again using the procedure described above, then transferred to a nitrogen-filled glove box for deposition after UV/Ozone treatment for 15 minutes.

All HTM solutions were prepared in chlorobenzene solvent. Doping was performed by direct addition of the oxidant solution in acetonitrile into the HTM solution. HTM films were spin coated on the substrates using a static deposition method. Spinning was then accelerated to 3000 rpm and spun at this speed for 5 seconds. After spin coating, the films were left in the glove box for 12 hours before measurement, in order to remove traces of residual solvent. The current-voltage characteristics of all HTMs were then measured by means of a Keithley 2611b source meter, measuring the resulting current. A randomly pulsed voltage setup was used in order to eliminate any ionic conductivity, allowing selective measurement of electron/hole conductivity. Film thicknesses used for the estimation of conductivity were measured using a DekTak XT contact profiler equipped with a 2 μm stylus tip.

## 1.3 Solar cell measurements

To prepare the perovskite, lead (II) iodide (**$PbI_2$**) (99.999%) was procured from TCI, formamidinium iodide (**FAI**), methylammonium iodide (**MAI**), methylammonium chloride (**MACl**), and $TiO_2$ nanoparticle suspension were acquired from Greatcell Solar Materials Ltd. Tin (IV) oxide

(**$SnO_2$**) was obtained from Fisher Scientific. All chemicals and solvents were utilised without additional purification unless specified.

Solar cells were then prepared as follows: Fluorine-doped tin oxide (**FTO**)-coated glass substrates (TEC-15) were washed with Hellmanex III, deionised water, acetone, and isopropanol, and then dried using compressed air. Substrates were then treated with UV ozone for 30 minutes. Spray pyrolysis at 500 ºC using a titanium (IV) diisopropoxide bis(acetylacetonate) precursor solution (75% in isopropanol) diluted in ethanol at a 1/19 ratio resulted in a compact $TiO_2$ blocking layer on the FTO substrates. The substrates were spin coated with a colloidal $SnO_2$ solution at 5000 rpm for 30 seconds, then annealed at 150°C for 20 minutes in air. The substrate was moved to an argon-filled glovebox and annealed at 150ºC for 20 minutes. The perovskite, ($Cs_{0.05}FA_{0.9}MA_{0.05}PbI_3$) solution was spin-coated on top of the $SnO_2$ layer using an antisolvent-assisted two-step technique. The process involved spinning at 1000 rpm for 10 seconds, then 6000 rpm for 30 seconds, followed by an annealing at 100 ºC for 1 hour and 150 ºC for 10 minutes.

HTM solution was prepared at a concentration of 25 mM in chlorobenzene, with the regular additives *i.e.* 17.5 µL of LiTFSI stock solution (260 mg in 1 mL of acetonitrile), 21.9 µL of FK209 stock solution (200 mg in 1 mL of acetonitrile) and 28.8 µL of 4-*tert*-butylpyridine (***t*BP**). The HTM was then spin coated onto the perovskite layer by depositing 30 – 40 µL of HTM solution at 1000 rpm for 30 seconds then 2000 rpm for 5 seconds. The solar cell was completed with a gold electrode (~70 nm thick) deposited by thermal evaporation under high vacuum.

Current-density (*J*–*V*) curves were then recorded with a Keithley 2400 source meter and a Newport ORIEL AAA solar simulator under 100 mW cm² (AM1.5) irradiation. Calibration was conducted using an NREL-certified monocrystalline silicon solar cell. The photocurrent was measured at a scan rate of 100 mV $s^{-1}$ and a 0.09 cm² black metal mask was used while the external quantum efficiency (EQE) spectrum of compound **12** was obtained utilizing a 150W xenon light and a Bentham PVE300 system.

# 2 NMR Spectra

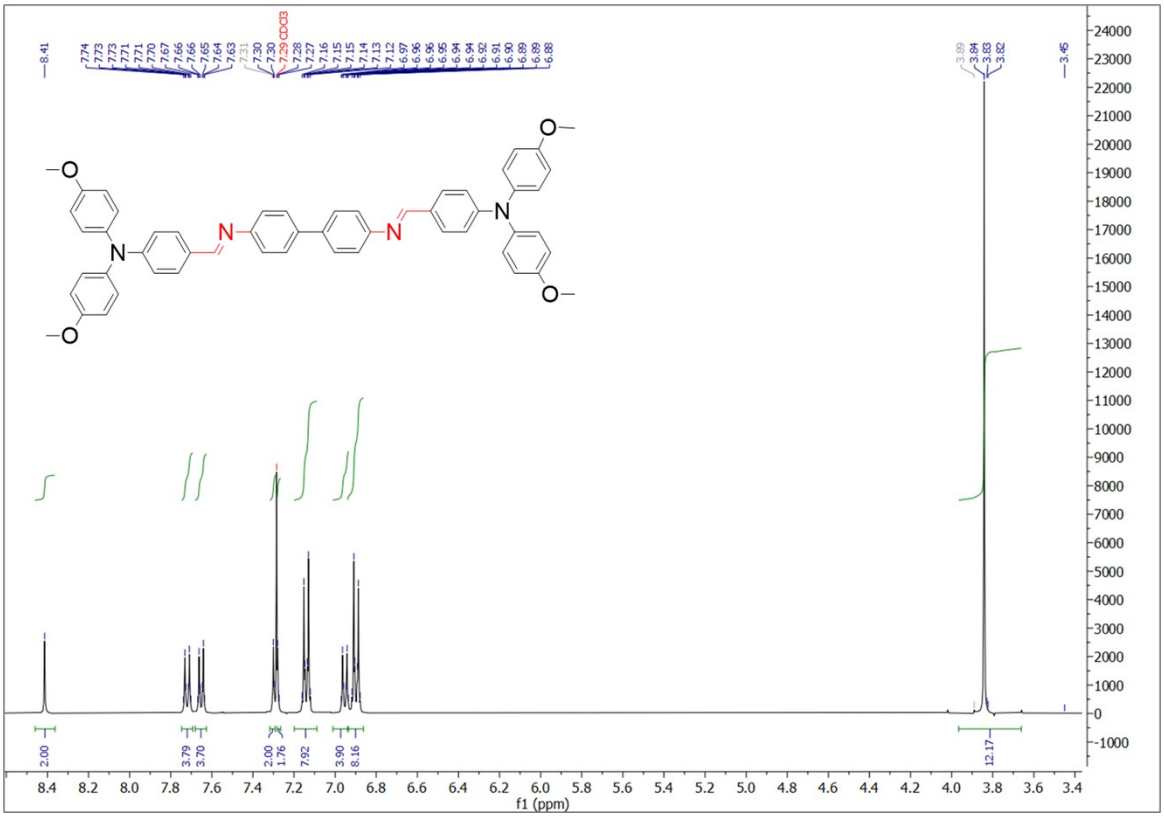



Figure S1: $^{1}$H-NMR spectrum of compound **10**, recorded in $CDCl_3$.

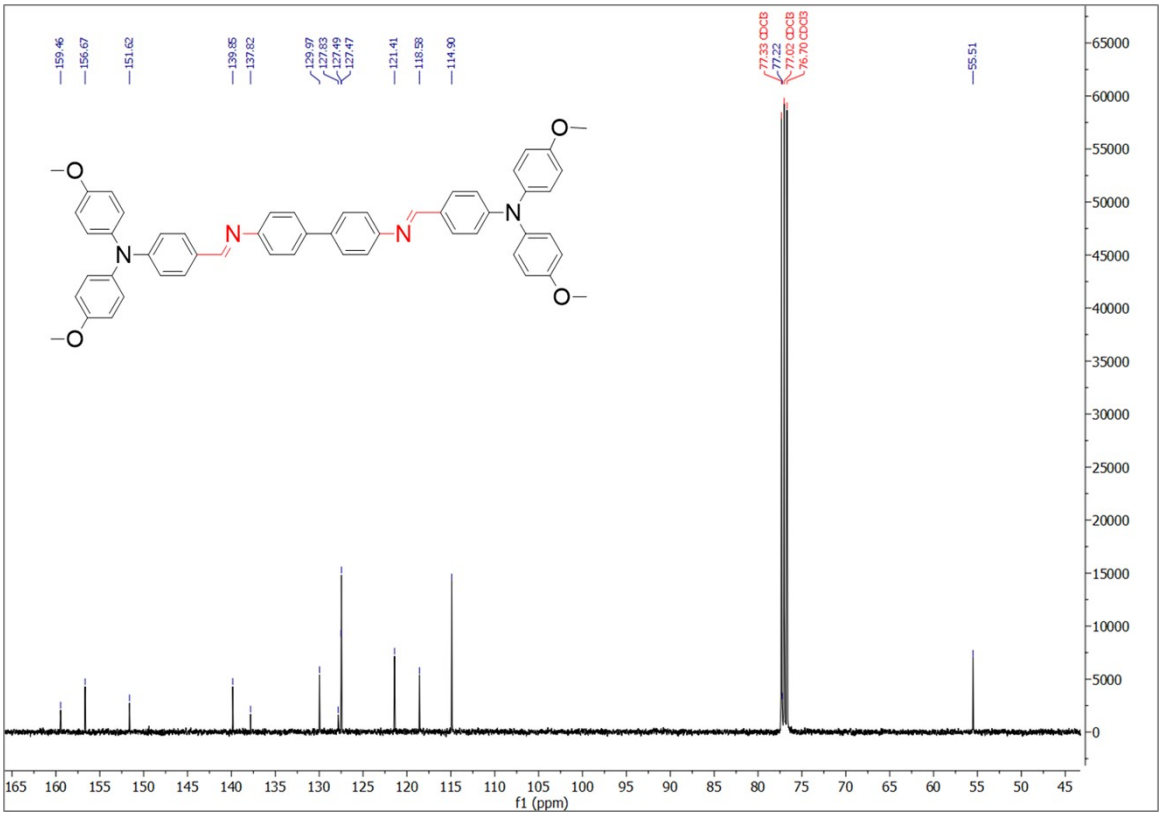


Figure S2: $^{13}$C-NMR spectrum of compound **10**, recorded in $CDCl_3$.

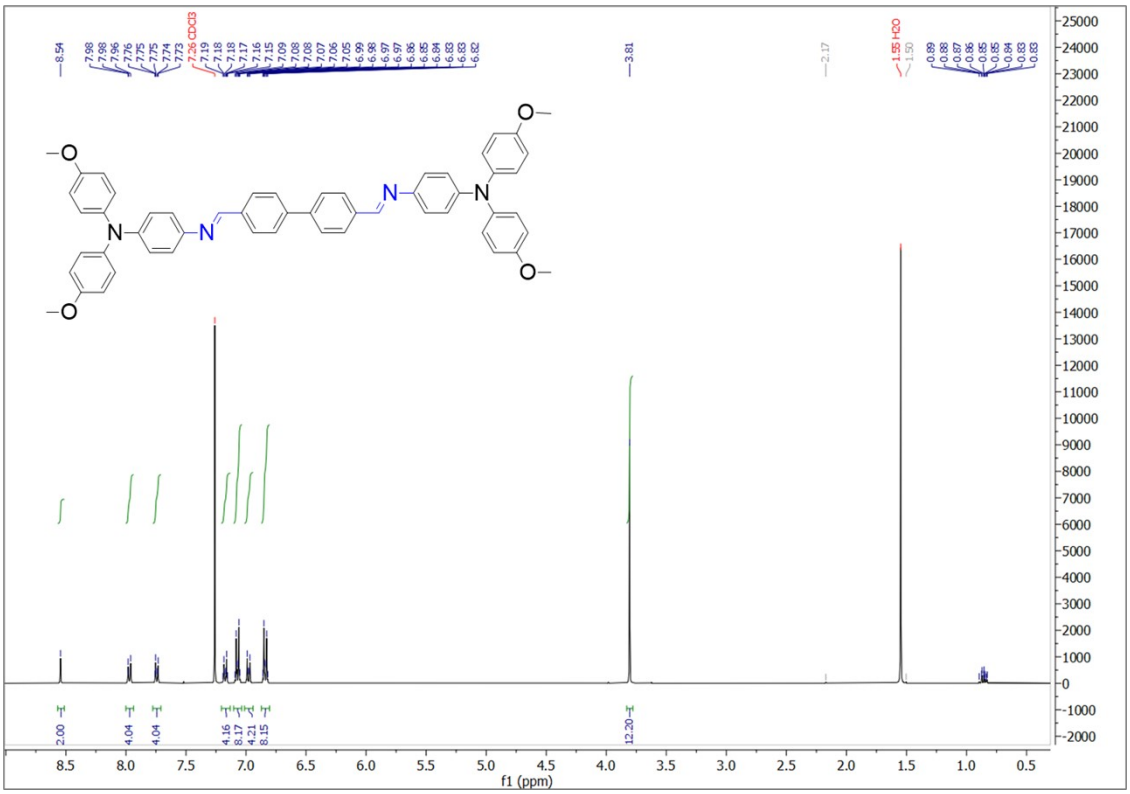



Figure S3: $^{1}$H-NMR spectrum of compound **12**, recorded in $CDCl_3$.

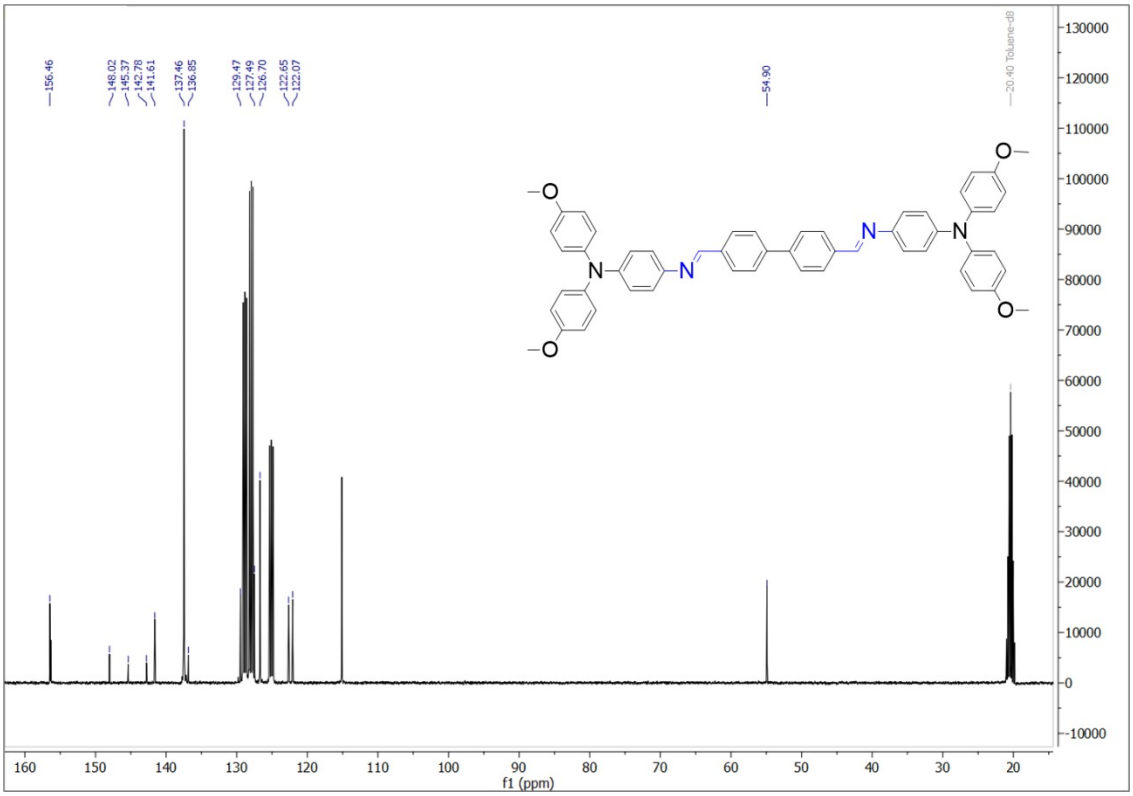



Figure S4: $^{13}$C-NMR spectrum of compound **12**, recorded in toluene-$d_8$.

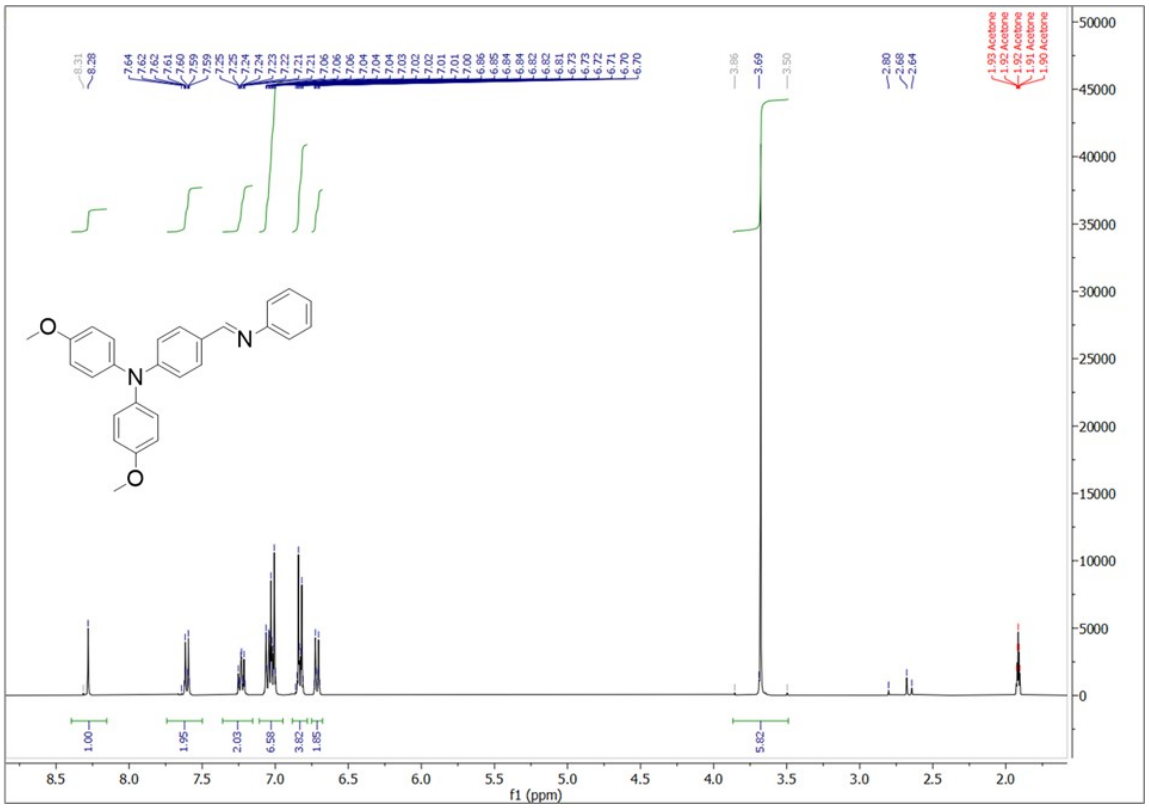



Figure S5: $^{1}$H-NMR spectrum of compound **14**, recorded in acetone-$d_6$.

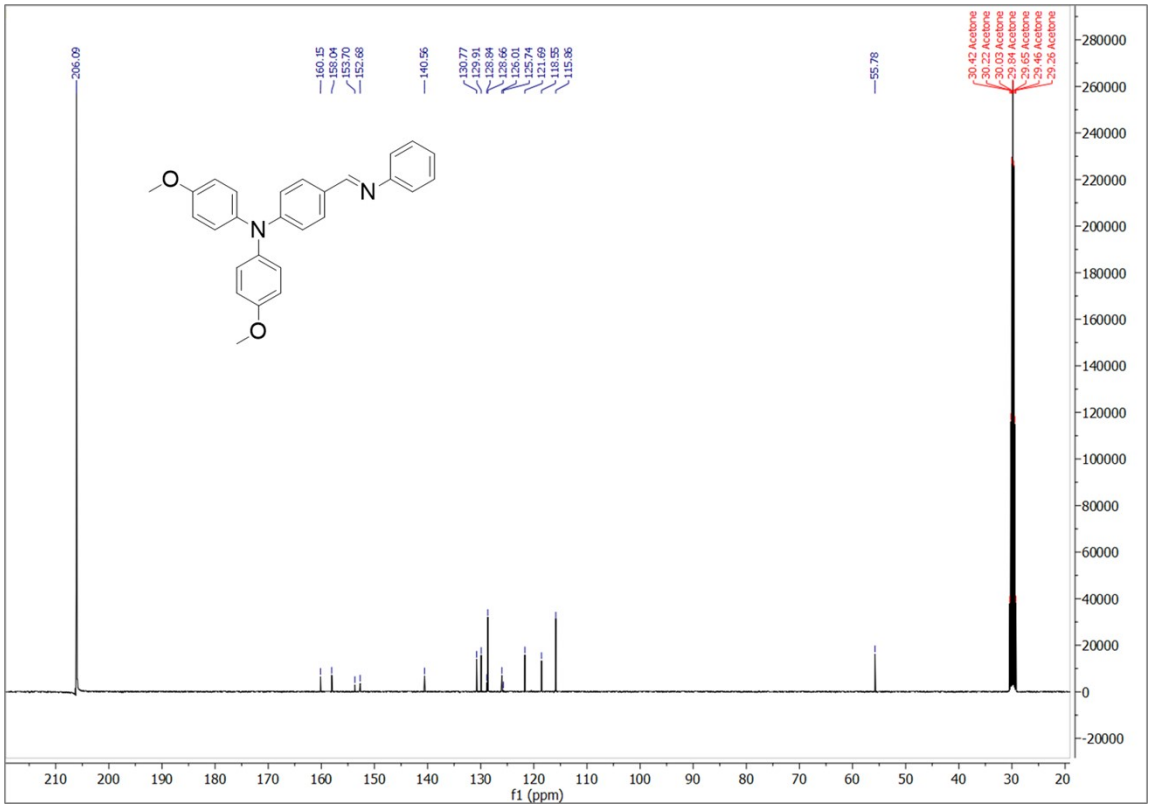



Figure S6: $^{13}$C-NMR of compound **14**, recorded in acetone-$d_6$.

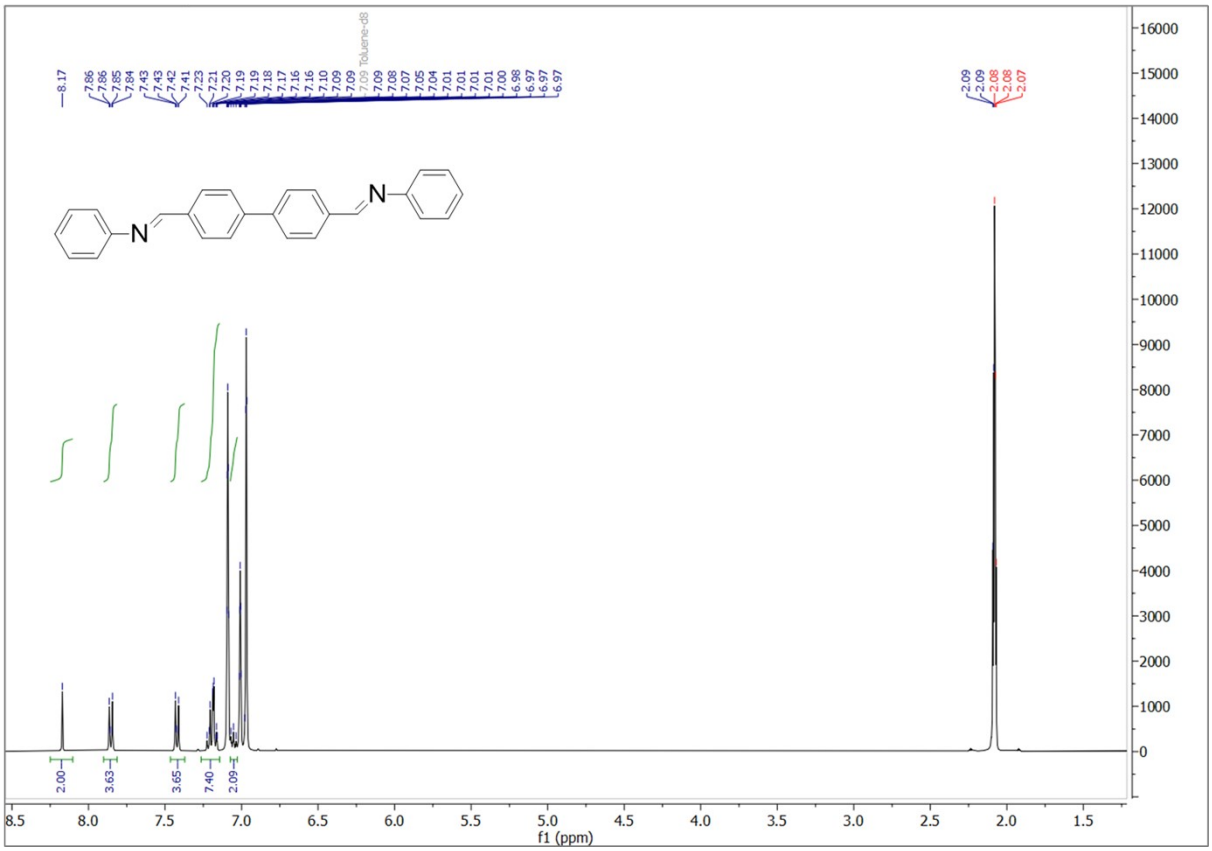



Figure S7: $^{1}$H-NMR of compound **15**, recorded in toluene-$d_8$.

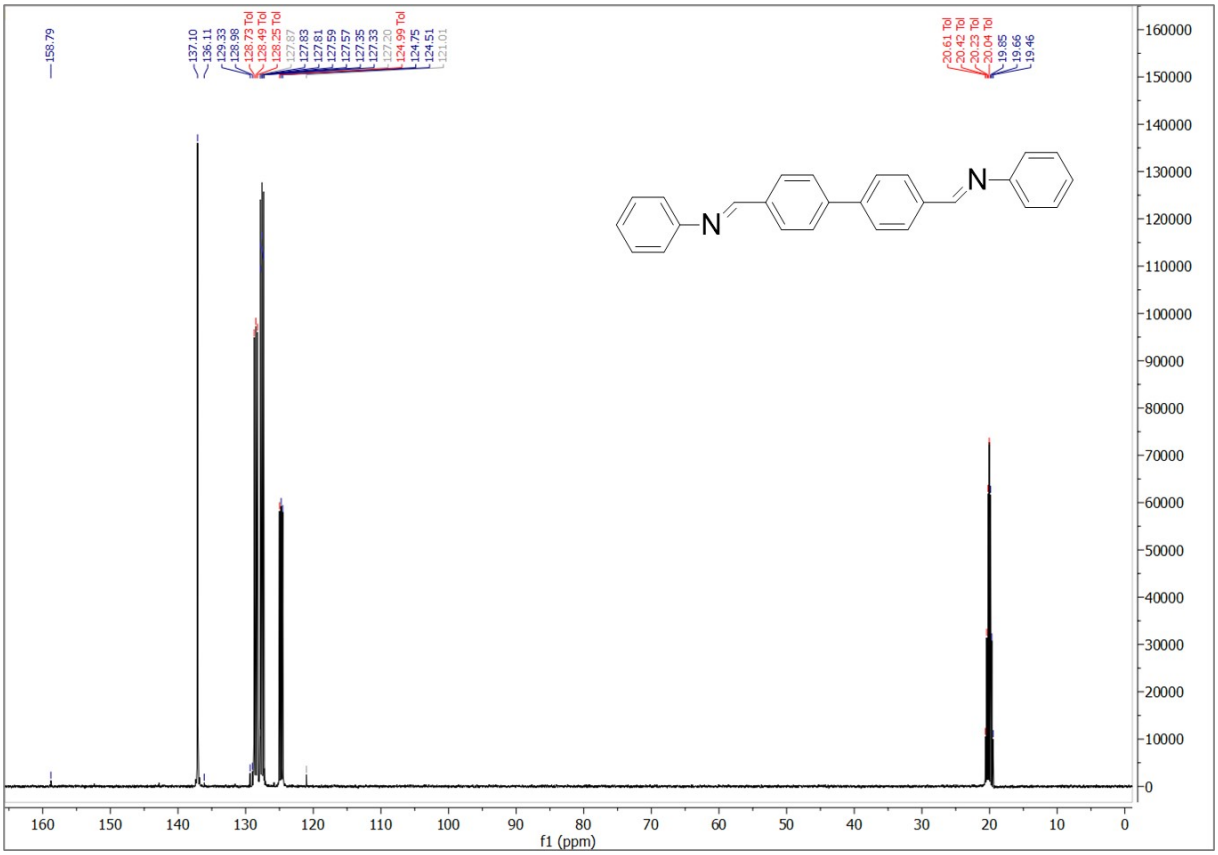



Figure S8: $^{13}$C-NMR spectrum of compound **15**, recorded in toluene-d8.

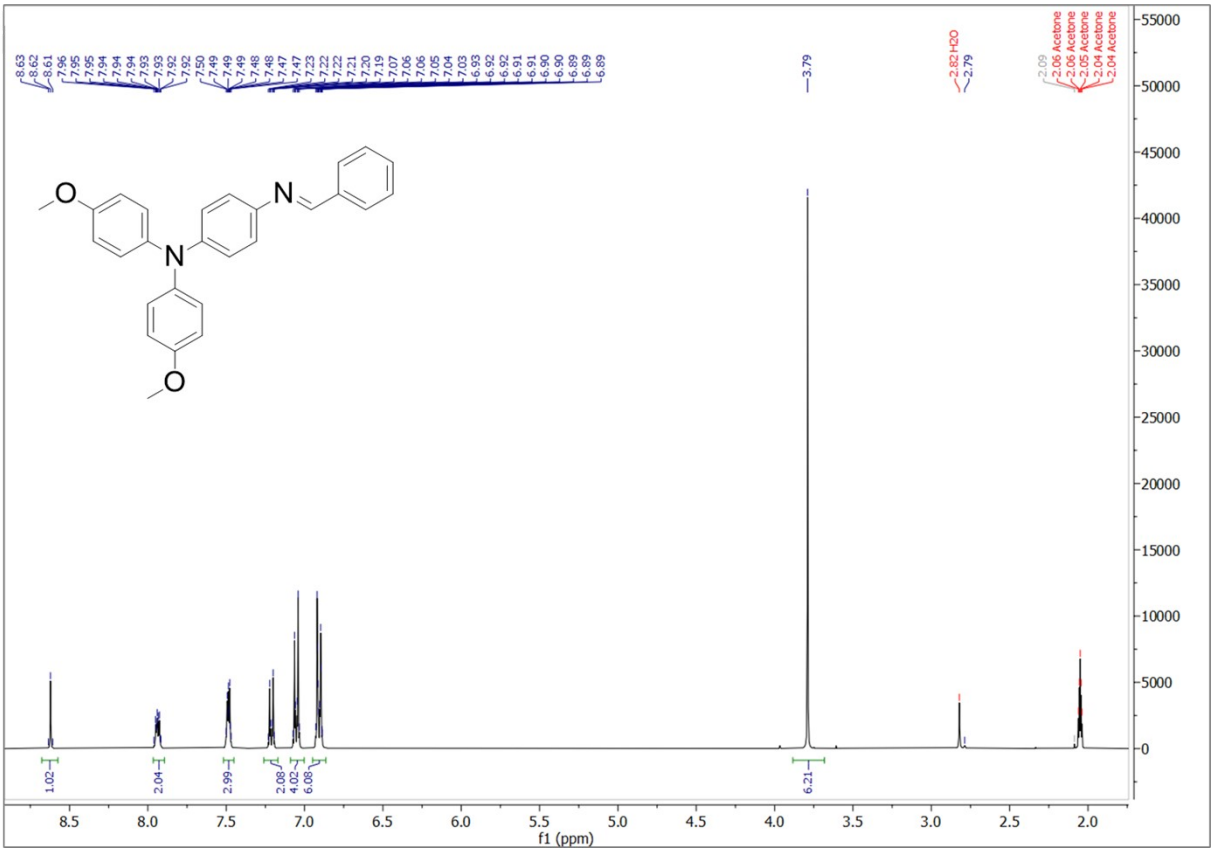



Figure S9: $^{1}$H-NMR spectrum of compound **17**, recorded in acetone-$d_6$.

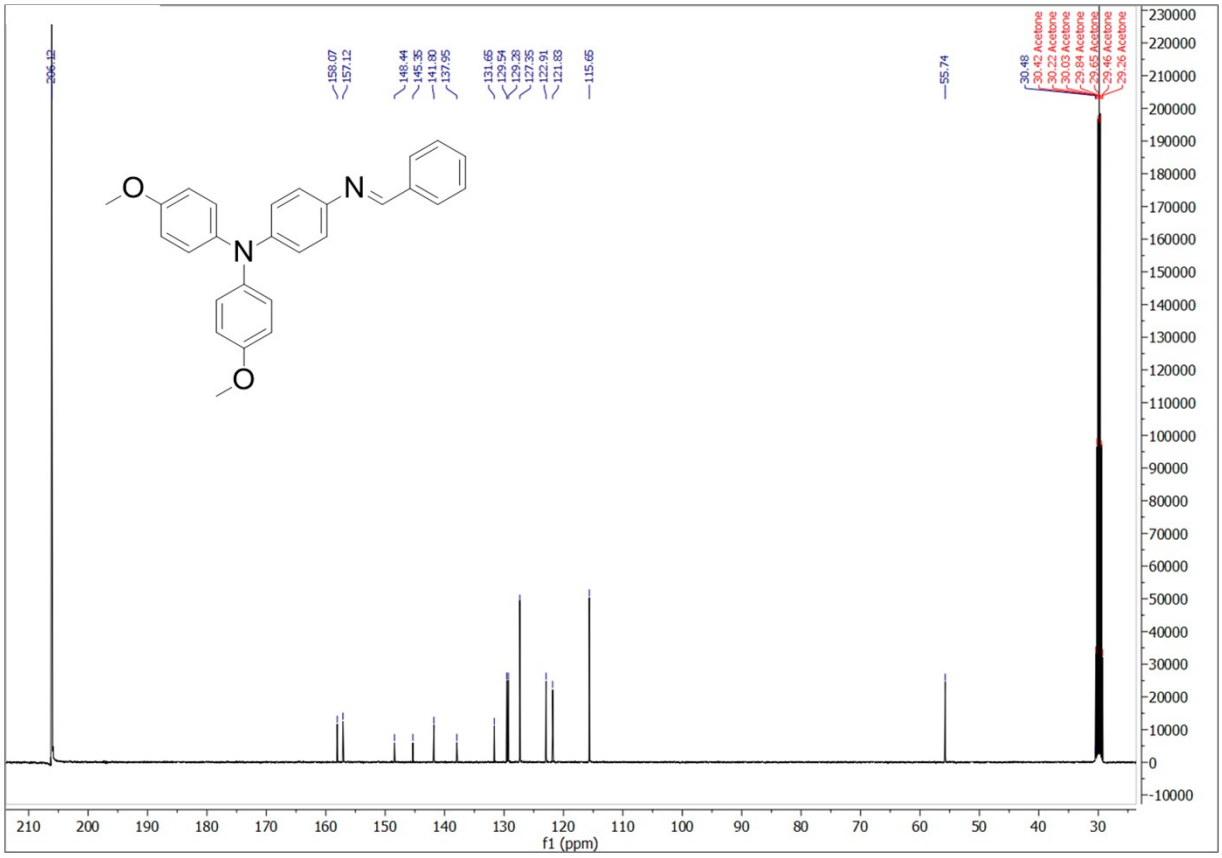



Figure S10: $^{13}$C-NMR spectrum of compound **17**, recorded in acetone-$d_6$.

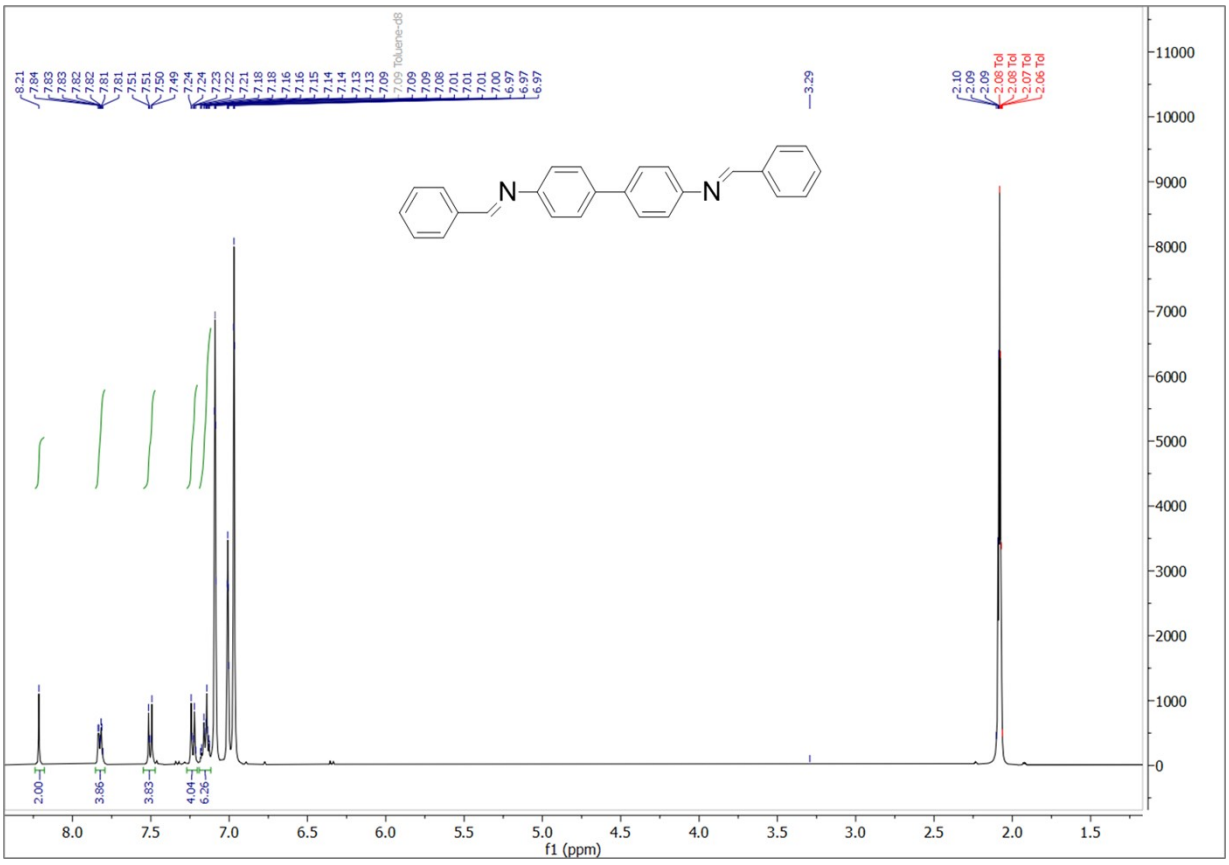



Figure S11: $^{13}$C-NMR spectrum of compound **18**, recorded in toluene-$d_8$.

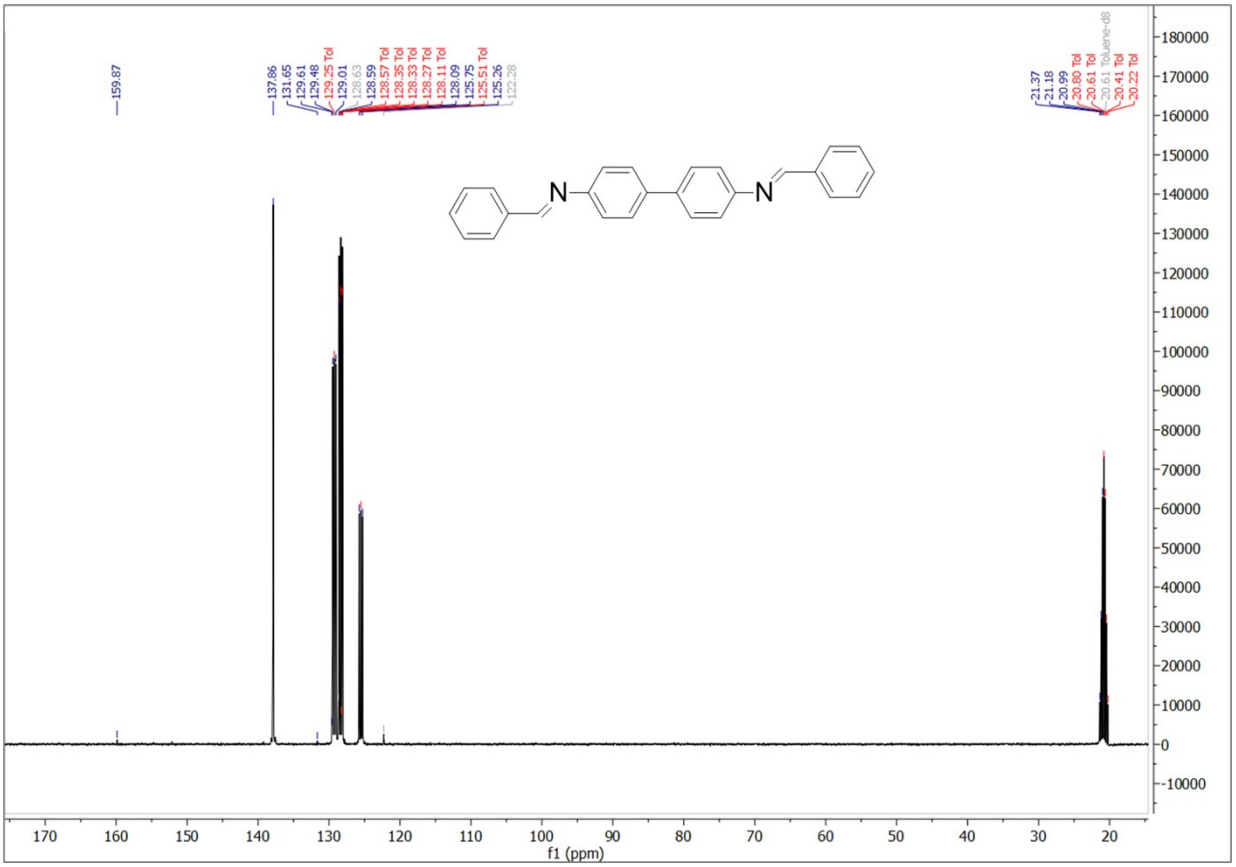



Figure S12: $^{13}$C-NMR spectrum of compound **18**, recorded in toluene-$d_8$.

# 3 Appendix: Additional Figures

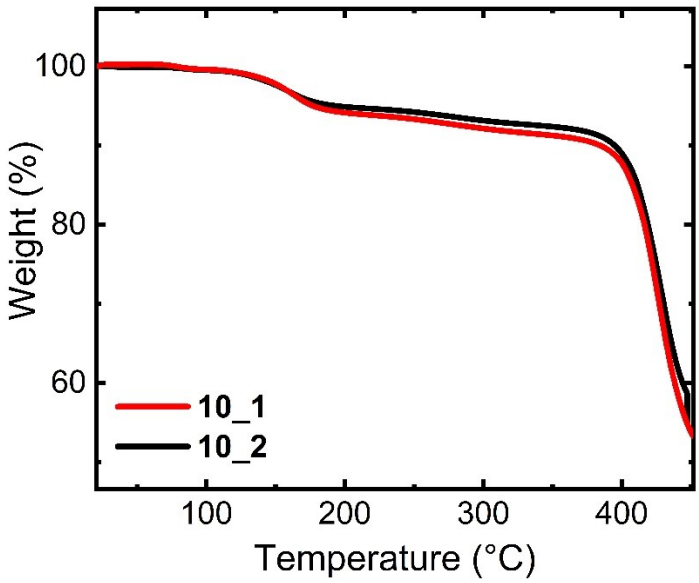



Figure S13: Stacked TGA traces recorded for HTM **10** samples after drying the solid under vacuum for 12 hours (**10_1**) and again for an additional 12 hours (**10_2**).

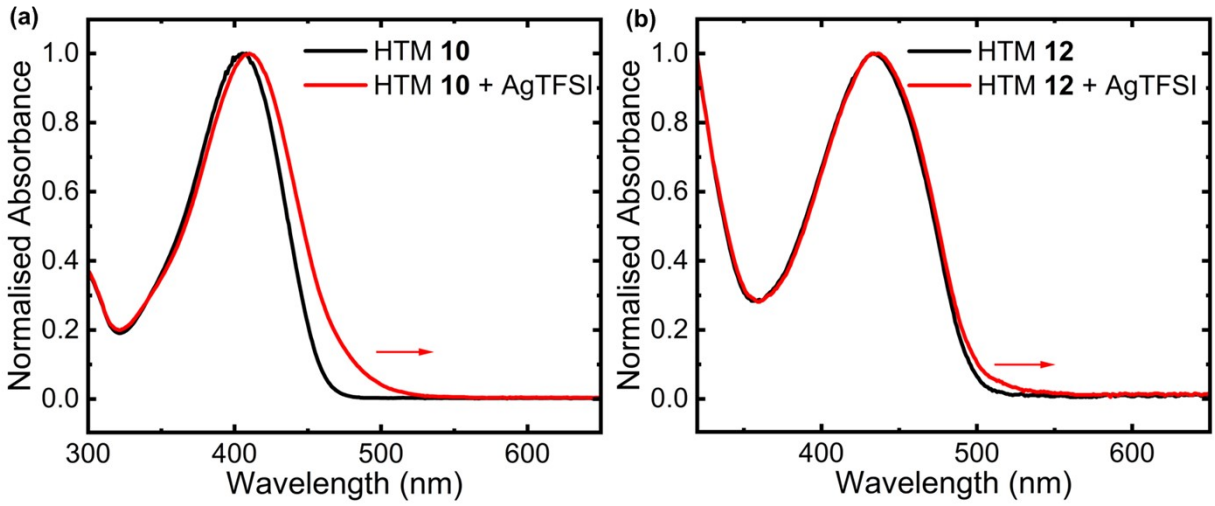



Figure S14: Film UV-Visible absorption spectra of HTMs 10 and 12, before and after the addition of one equivalent of AgTFSI.

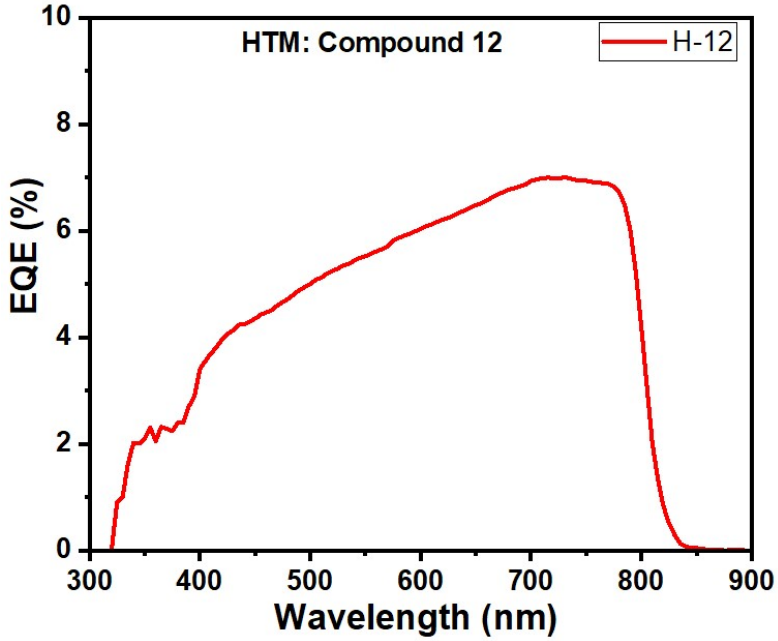



Figure S15: Measured external quantum efficiency (EQE) spectrum for the champion device containing compound **12** as HTM.

# 4 References

1 M. L. Petrus, K. Schutt, M. T. Sirtl, E. M. Hutter, A. C. Closs, J. M. Ball, J. C. Bijleveld, A. Petrozza, T. Bein, T. J. Dingemans, T. J. Savenije, H. Snaith and P. Docampo, *Adv. Energy Mater.*, 2018, **8**, 1801605.

2 G. S. Liou and C. W. Chang, *Macromolecules*, 2008, **41**, 1667–1674.

3 M. L. Petrus, T. Bein, T. J. Dingemans and P. Docampo, *J. Mater. Chem. A*, 2015, **3**, 12159–12162.

4 R. Matsubara, T. Shimada, Y. Kobori, T. Yabuta, T. Osakai and M. Hayashi, *Chem. Asian J.*, 2016, **11**, 2006–2010.

5 X. R. Jia, H. J. Yu, J. Chen, W. J. Gao, J. K. Fang, Y. S. Qin, X. K. Hu and G. Shao, *Chem. - A Eur. J.*, 2018, **24**, 19053–19059.

6 J. P. Jeon, Y. J. Kim, S. H. Joo, H. J. Noh, S. K. Kwak and J. B. Baek, *Angew. Chem. Int.*, 2023, **62**, e202217416.

7 M. L. Petrus, A. Music, A. C. Closs, J. C. Bijleveld, M. T. Sirtl, Y. Hu, T. J. Dingemans, T. Bein and P. Docampo, *J. Mater. Chem. A*, 2017, **5**, 25200–25210.

8 B. Jarząbek, B. Kaczmarczyk and D. Sęk, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 2009, **74**, 949–954.

9 S. Sellarajah, T. Lekishvili, C. Bowring, A. R. Thompsett, H. Rudyk, C. R. Birkett, D. R. Brown and I. H. Gilbert, *J. Med. Chem.*, 2004, **47**, 5515–5534.