

Supplementary information for:

A molecular engineering of the hole-transporting material spiro-OMeTAD via manipulation of alkyl groups

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General methods and materials

All chemicals were purchased from Aldrich Chemical Co and TCI Europe and used as received without further purification. The ¹H and ¹³C NMR spectra were taken on Varian Unity Inova (300 MHz) and Bruker Avance III (400 MHz) spectrometer at room temperature. The chemical shifts are given in ppm, downfield from tetramethylsilane (TMS, 0 ppm), used as internal standard. Used deuterated solvents are indicated for each compound. The course of the reactions products was monitored by TLC on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis (C, H and N) was performed with an Exeter Analytical CE-440 elemental analyser. Infrared (IR) spectra were measured on Perkin Elmer Spectrum GX FT-IR system spectrometer using KBr pellets. Mass spectra were recorded on a Waters Micromass ZQ 2000 (APCI⁺, 20V or 25V) instrument.

The UV/Vis spectra were recorded on a SHIMADZU UV-2600 spectrometer in 10⁻⁴ M solutions of investigated TM in THF; a microcell with an internal width of 1 mm was used.

Differential scanning calorimetry (DSC) was accomplished on a Q10 calorimeter (TA instruments) under nitrogen atmosphere. A scan rate for all DSC cycles was 10°C/min. The glass transition

temperatures of the investigated transporting materials were determined during the second heating. Melting points were determined using an electrothermal MEL-TEMP capillary melting point apparatus. Thermogravimetry measurements were performed on a Q50 thermogravimetric analyser (TA instruments) and Perkin Elmer (TGA 4000) in nitrogen atmosphere at a scan rate of 10°C/min; thermal decomposition temperature was registered at 5% weight loss.

Hole-Drift Mobility Measurement

Samples were prepared by casting the solutions of investigated compounds in THF. The substrate was polyester film with an Al layer. After coating, the samples were heated at 80 °C for 1 h. The hole drift mobility was measured by XTOF technique.^{S1} Positive corona charging created electric field inside the TM layer. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5 % of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the speed of the surface potential decrease dU/dt . The transit time t_t was determined by the kink on the curve of the dU/dt transient in linear or double logarithmic scale. The drift mobility was calculated by the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness, U_0 – the surface potential at the moment of illumination.

Ionization Potential Measurement

The solid-state ionisation potential (I_p) was measured by the electron photoemission in air method.^{S2} Samples were prepared by dissolving compounds in CHCl_3 and coating on Al plates precoated with $\sim 0.5 \mu\text{m}$ thick methylmethacrylate and methacrylic acid copolymer sublayer. The thickness of the TM layers was 0.5–1 μm . The ionization potential I_p was measured by the electron photoemission in air method. Usually the photoemission experiments are carried out in high vacuum, this is one of the main requirements for these measurements. If vacuum is not high enough the sample surface oxidation and gas adsorption are possible and influencing the measurement results. In our case, however, the organic materials investigated are stable enough to oxygen and the measurements may be carried out in the air. The measurement error is evaluated as 0.03 eV. The samples were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was

$(2-5) \cdot 10^{-8}$ W. The negative voltage of -300 V was supplied to the sample substrate. The counter-electrode with the 4.5×15 mm² slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. The $10^{-15} - 10^{-12}$ A strong photocurrent was flowing in the circuit under illumination. The photocurrent I is strongly dependent on the incident light photon energy $h\nu$. $I^{0.5} = f(h\nu)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by linear relationship between $I^{0.5}$ and $h\nu$ near the threshold^{S1}. The linear part of this dependence was extrapolated to the $h\nu$ axis and I_p value was determined as the photon energy at the interception point.

Fabrication and Characterization of Solar-Cells

Solid-state dye-sensitized solar-cells were fabricated and characterized at the Chemical Company BASF SE, Ludwigshafen, Germany. A TiO₂ blocking layer was prepared on a fluorine-doped tin oxide (FTO)-covered glass substrate using spray pyrolysis.^{S3} Next, a TiO₂ paste (Dyesol), diluted with terpineol, was applied by screen printing, resulting in a film thickness of 1.7 μ m. All films were then sintered for 45 min at 450 °C, followed by treatment in a 40 mM aqueous solution of TiCl₄ at 60 °C for 30 min, followed by another sintering step. The prepared samples with TiO₂ layers were pretreated with 5 mM solutions of 2-(*p*-butoxyphenyl)acetohydroxamic acid sodium salt or 2-(*p*-butoxyphenyl)acetohydroxamic acid tetrabutylammonium salt in ethanol. The electrodes were then dyed in 0.5 mM perylene monoimide dye ID504 solution in CH₂Cl₂. Respective hole-transporting material was applied by spin-coating from a solution in DCM (200 mg/mL) also containing 20 mM Li(CF₃SO₂)₂N. Fabrication of the device was completed by evaporation of 200 nm of silver as the counter electrode. The active area of the ssDSSC was defined by the size of these contacts (0.13 cm²), and the cells were masked by an aperture of the same area for measurements. The Current-voltage characteristics for all cells were measured with a Keithley 2400 under 1000 W/m², AM 1.5G conditions (LOT ORIEL 450 W). Device lifetime tests were conducted on ssDSSC devices that were sealed after fabrication and constantly kept at 60°C and 30% humidity for the duration of the experiment.

The detailed synthetic procedures

General procedure A: Mixture of dioxane (1 ml) and water (4 %) was purged with argon for 20 minutes. Pd(OAc)₂ (0.5 %) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) or 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (1.5 %) were added and mixture was heated to 80°C for 1.5 min. Respective aryl halide (1 mmol), amine (1.2 mmol) and NaO*t*-Bu (1.4 mmol) were added and the mixture was refluxed for indicated period of time. After termination of the reaction (TLC control) the mixture was diluted with ethyl acetate and washed with water. Organic layer was dried over anhydrous Na₂SO₄, filtered and solvent removed. The residue was purified by column chromatography.

General procedure B: Mixture of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (1 mmol) and respective amine (4.8–6 mmol) in dry toluene (10 ml) was purged with argon for 30 min. Pd(OAc)₂ (2 %) and tri-*tert*-butylphosphonium tetrafluoroborate (2.7 %) and NaO*t*-Bu (6 mmol) were added. Mixture was heated to reflux. After termination of the reaction (TLC control) mixture was diluted with toluene, filtered through Celite and washed with water. Organic layer was dried over anhydrous Na₂SO₄, filtered and solvent removed. The residue was purified by column chromatography.

3,4'-Dimethoxydiphenylamine (1).

Following general procedure A, a mixture of *m*-anisidine (1.47 g, 11.94 mmol), 1-iodo-4-methoxybenzene (2.34 g, 10 mmol), Pd(OAc)₂ (0.011 g, 0.049 mmol), SPhos (0.062 g, 0.15 mmol), NaO*t*-Bu (1.35 g, 14.05 mmol), water (0.004 g, 0.22 mmol) and dioxane (10 ml) was refluxed for 20 minutes. Product was purified by column chromatography using acetone: *n*-hexane (0.5:24.5, v/v) as an eluent. The product was obtained as whitish crystals (1.89 g, 96 %). mp 66-67.5°C.

MS (APCI⁺, 25V) *m/z*: 230 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ, ppm: 7.12 (m, 1H), 7.08 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.51–6.44 (m, 2H), 6.41–6.35 (m, 1H), 5.50 (broad s, 1H), 3.79 (s, 3H), 3.74 (s, 3H).

¹³C NMR (75 MHz, CDCl₃), δ, ppm: 160.87, 155.55, 146.81, 135.50, 130.18, 122.82, 114.76, 108.41, 104.79, 101.39, 55.67, 55.26.

IR (KBr), ν (cm⁻¹): 3400 (NH), 3062, 3033, 3009 (aromatic C-H), 2956, 2934, 2834 (aliphatic C-H), 1511 (C-C), 1261, 1233 (C-O-C), 827 (CH=CH of 1,4-disubstituted benzene), 767, 686 (CH=CH of 1,3-disubstituted benzene).

Anal. calcd for C₁₄H₁₅NO₂ (%): C, 73.34; H, 6.59, N, 6.11; found: C, 73.42; H, 6.63; N, 6.14.

3,5,4'-Trimethoxydiphenylamine (2).

Following general procedure A, a mixture of 3,5-dimethoxyaniline (0.55 g, 3.59 mmol), 1-iodo-4-methoxybenzene (0.70 g, 2.99 mmol), Pd(OAc)₂ (0.003 g, 0.013 mmol), SPhos (0.019 g, 0.046 mmol), NaOt-Bu (0.4 g, 4.16 mmol), water (0.001 g, 0.056 mmol) and dioxane (3 ml) was refluxed for 30 minutes. Product was purified by column chromatography using acetone: *n*-hexane (1:24 and 3:22, v/v) as an eluent. The product was obtained as pale yellow oil (0.7 g, 90 %).

MS (APCI⁺, 25V) *m/z*: 260 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ , ppm: 7.07 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.06 (d, *J* = 3.0 Hz, 2H), 5.97 (t, *J* = 3.0 Hz, 1H), 5.53 (broad s, 1H), 3.80 (s, 3H), 3.74 (s, 6H).

¹³C NMR (75 MHz, CDCl₃), δ , ppm: 161.78, 155.66, 147.49, 135.24, 123.24, 114.71, 94.00, 91.74, 55.64, 55.32.

IR (KBr), ν (cm⁻¹): 3383 (NH), 3000 (aromatic C-H), 2956, 2936, 2907, 2837 (aliphatic C-H), 1506, 1481 (C-C), 1243 (C-O-C), 819 (CH=CH of 1,4-disubstituted benzene), 772, 682 (CH=CH of 1,3-disubstituted benzene).

Anal. calcd for C₁₅H₁₇NO₃ (%): C, 69.48; H, 6.61, N, 5.40; found: C, 69.61; H, 6.49; N, 5.52.

4,4'-Dimethoxy-3-methyldiphenylamine (3).

Following general procedure A, a mixture of 4-methoxyaniline (1.79 g, 14.5 mmol), 5-bromo-2-methoxytoluene (2.44 g, 12.1 mmol), Pd(OAc)₂ (0.014 g, 0.06 mmol), XPhos (0.086 g, 0.18 mmol), NaOt-Bu (1.64 g, 17.1 mmol), water (0.004 g, 0.22 mmol) and dioxane (12 ml) was refluxed for 15 minutes. Product was purified by column chromatography using acetone: *n*-hexane (0.5:24.5, v/v) as an eluent. The product was obtained as whitish crystals (2.7 g, 92 %). mp 55-56.5°C.

MS (APCI⁺, 25V) *m/z*: 244 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ , ppm: 6.94 (d, *J* = 9.0 Hz, 2H), 6.85–6.77 (m, 4H), 6.73 (d, *J* = 9.0 Hz, 1H), 5.24 (broad s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.18 (s, 3H).

¹³C NMR (75 MHz, CDCl₃), δ , ppm: 154.22, 152.67, 138.22, 137.58, 127.74, 121.59, 119.58, 116.40, 114.80, 111.19, 55.92, 55.76, 16.46.

IR (KBr), ν (cm⁻¹): 3412 (NH), 3066, 3023 (aromatic C-H), 2961, 2935, 2837 (aliphatic C-H), 1505 (C-C), 1241, 1225 (C-O-C), 825, 805 (CH=CH of 1,4-disubstituted benzene).

Anal. calcd for C₁₅H₁₇NO₂ (%): C, 74.05; H, 7.04, N, 5.76; found: C, 74.36; H, 7.22; N, 5.61.

4,4'-Dimethoxy-3,3'-dimethyldiphenylamine (4).

Following general procedure A, a mixture of 3-methyl-4-methoxyaniline (1.0 g, 7.29 mmol), 5-bromo-2-methoxytoluene (1.22 g, 6.06 mmol), Pd(OAc)₂ (0.007 g, 0.031 mmol), XPhos (0.043 g, 0.09 mmol), NaO*t*-Bu (0.82 g, 8.53 mmol), water (0.002 g, 0.11 mmol) and dioxane (6 ml) was refluxed for 20 minutes. Product was purified by column chromatography using acetone: *n*-hexane (0.2:24.8, v/v) as an eluent. The product was obtained as whitish crystals (1.33 g, 85 %). mp 75-77°C.

MS (APCI⁺, 25V) *m/z*: 258 [M+H]⁺.

¹H NMR (400 MHz, CDCl₃), δ, ppm: 6.95–6.65 (m, 6H), 5.20 (broad s, 1H), 3.81 (s, 6H), 2.20 (s, 6H).

¹³C NMR (100 MHz, CDCl₃), δ, ppm: 152.63, 137.80, 127.69, 121.64, 116.33, 111.22, 55.96, 16.48.

IR (KBr), ν (cm⁻¹): 3341 (NH), 3024 (aromatic C-H), 2956, 2918, 2834 (aliphatic C-H), 1501 (C-C), 1234 (C-O-C), 866, 802, 761 (CH=CH of 1,3-disubstituted benzenes).

Anal. calcd for C₁₆H₁₉NO₂ (%): C, 74.68; H, 7.44, N, 5.44; found: C, 74.81; H, 7.62; N, 5.22.

4,4'-Dimethoxy-3,5-dimethylamine (5).

Following general procedure A, a mixture of 4-methoxyaniline (0.96 g, 7.80 mmol), 4-iodo-1,3-dimethyl-2-methoxybenzene (1.7 g, 6.49 mmol), Pd(OAc)₂ (0.007 g, 0.031 mmol), SPhos (0.04 g, 0.097 mmol), NaO*t*-Bu (0.88 g, 9.12 mmol), water (0.002 g, 0.11 mmol) and dioxane (6.5 ml) was refluxed for 15 minutes. Product was purified by column chromatography using acetone: *n*-hexane (0.9:24.1, v/v) as an eluent. The product was obtained as pale brown crystals (1.60 g, 96 %). mp 84-85°C.

MS (APCI⁺, 25V) *m/z*: 258 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ, ppm: 7.02 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.60 (s, 2H), 5.30 (broad s, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 2.24 (s, 6H).

¹³C NMR (75 MHz, CDCl₃), δ, ppm: 154.85, 150.76, 140.72, 136.89, 131.67, 121.30, 116.75, 114.78, 60.07, 55.72, 16.35.

Anal. calcd for C₁₆H₁₉NO₂ (%): C, 74.68; H, 7.44, N, 5.44; found: C, 74.61; H, 7.49; N, 5.48.

4-Ethoxy-4'-methoxy-3,5-dimethyldiphenylamine (6).

Following general procedure A, a mixture of 4-methoxyaniline (0.91 g, 7.39 mmol), 2-ethoxy-4-iodo-1,3-dimethylbenzene (1.7 g, 6.16 mmol), Pd(OAc)₂ (0.007 g, 0.031 mmol), SPhos (0.038 g, 0.093

mmol), NaOt-Bu (0.83 g, 8.63 mmol), water (0.002 g, 0.11 mmol) and dioxane (6.5 ml) was refluxed for 30 minutes. Product was purified by column chromatography using acetone: *n*-hexane (0.5:24.5, v/v) as an eluent. The product was obtained as whitish crystals (1.22 g, 85 %). mp 99-100.5°C.

MS (APCI⁺, 25V) *m/z*: 272 [M+H]⁺.

¹H NMR (400 MHz, CDCl₃), δ , ppm: 7.00 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.59 (s, 2H), 5.26 (broad s, 1H), 3.85–3.75 (m, 5H), 2.21 (s, 6H), 1.40 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃), δ , ppm: 154.79, 149.91, 140.51, 136.93, 132.00, 121.23, 116.71, 114.76, 68.19, 55.73, 16.63, 15.89.

IR (KBr), ν (cm⁻¹): 3363 (NH), 3038, 3001 (aromatic C-H), 2969, 2923, 2835 (aliphatic C-H), 1509, 1489 (C-C), 1233, 1213 (C-O-C), 824 (CH=CH of 1,4-disubstituted benzene).

Anal. calcd for C₁₇H₂₁NO₂ (%): C, 75.25; H, 7.80, N, 5.16; found: C, 75.49; H, 7.62; N, 5.28.

4'-Ethoxy-4-methoxy-3,5-dimethyldiphenylamine (7).

Following general procedure A, a mixture of 4-ethoxyaniline (1.07 g, 7.80 mmol), 4-iodo-2-methoxy-1,3-dimethylbenzene (1.7 g, 6.49 mmol), Pd(OAc)₂ (0.007 g, 0.031 mmol), SPhos (0.04 g, 0.093 mmol), NaOt-Bu (0.87 g, 9.05 mmol), water (0.002 g, 0.11 mmol) and dioxane (6.5 ml) were refluxed for 15 minutes. Product was purified by column chromatography using acetone: *n*-hexane (0.5:24.5, v/v) as an eluent. The product was obtained as whitish crystals (1.6 g, 91 %). mp 78.5-80°C.

MS (APCI⁺, 25V) *m/z*: 272 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ , ppm: 7.00 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.60 (s, 2H), 5.29 (broad s, 1H), 4.02 (q, *J* = 6.9 Hz, 2H), 3.69 (s, 3H), 2.23 (s, 6H), 1.42 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃), δ , ppm: 154.20, 150.71, 140.71, 136.76, 131.65, 121.32, 116.70, 115.45, 63.94, 60.08, 16.36, 15.09.

IR (KBr), ν (cm⁻¹): 3357 (NH), 3033 (aromatic C-H), 2984, 2972, 2923, 2877 (aliphatic C-H), 1508, 1488 (C-C), 1220 (C-O-C), 832 (CH=CH of 1,4-disubstituted benzene).

Anal. calcd for C₁₇H₂₁NO₂ (%): C, 75.25; H, 7.80, N, 5.16; found: C, 75.45; H, 7.64; N, 5.26.

2,2',7,7'-Tetrakis(3,4'-dimethoxydiphenylamino)-9,9'-spirobifluorene (HTM1).

Following general procedure B, a mixture of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.4 g, 0.63 mmol), 3,4'-dimethoxydiphenylamine (**1**) (0.88 g, 3.84 mmol), Pd(OAc)₂ (0.003 g, 0.013 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.005 g, 0.017 mmol) and NaOt-Bu (0.36 g, 3.75 mmol) in

toluene (6 ml) was refluxed for 3 hours. Product was purified by column chromatography using acetone: *n*-hexane (7:18, v/v) as an eluent and then precipitated from 20% solution in acetone into 10-fold excess of methanol. The precipitate was filtered off and washed with methanol to give product as yellow solid. The yield was 0.60 g (77 %).

MS (APCI⁺, 25V) *m/z*: 1225.5 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ , ppm: 7.45 (d, *J* = 7.8 Hz, 4H), 7.07 (t, *J* = 9.0 Hz, 4H), 6.99 (d, *J* = 9.0 Hz, 8H), 6.90 (d, *J* = 7.8 Hz, 4H), 6.82 (d, *J* = 9.0 Hz, 8H), 6.67 (d, *J* = 1.8 Hz, 4H), 6.50-6.39 (m, 12H), 3.79 (s, 12H), 3.65 (s, 12H).

¹³C NMR (75 MHz, CDCl₃), δ , ppm: 160.40, 156.10, 150.01, 149.63, 146.82, 140.67, 136.37, 129.60, 126.94, 124.13, 120.23, 119.36, 114.73, 114.28, 108.08, 107.66, 106.72, 67.79, 55.55, 55.26.

Anal. calcd for C₈₅H₇₆N₄O₁₂ (%): C, 75.87; H, 5.69, N, 4.16; found: C, 75.95; H, 5.81; N, 4.02.

2,2',7,7'-Tetrakis(3,5,4'-trimethoxydiphenylamino)-9,9'-spirobifluorene (HTM2).

Following general procedure B, a mixture of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.20 g, 0.316 mmol), 3,5,4'-trimethoxydiphenylamine (**5b**) (0.50 g, 1.93 mmol), Pd(OAc)₂ (0.002 g, 0.009 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.003 g, 0.01 mmol) and NaO*t*-Bu (0.19 g, 1.98 mmol) in toluene (5 ml) was refluxed for 2.5 hours. Product was purified by column chromatography using acetone: *n*-hexane (3:22 and 4:21, v/v) as an eluent and then precipitated from 20% solution in THF into 10-fold excess of *n*-hexane. The precipitate was filtered off and washed with *n*-hexane to give product as pale green solid. The yield was 0.30 g (64 %).

MS (APCI⁺, 25V) *m/z*: 1345.5 [M+H]⁺.

¹H NMR (400 MHz, CDCl₃), δ , ppm: 7.43 (d, *J* = 8.4 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 8H), 6.87 (d, *J* = 8.4 Hz, 4H), 6.79 (d, *J* = 8.8 Hz, 8H), 6.65 (s, 4H), 6.10–5.95 (m, 12H), 3.78 (s, 12H), 3.57 (s, 24H).

¹³C NMR (100 MHz, CDCl₃), δ , ppm: 161.19, 156.33, 149.97, 149.92, 146.64, 140.43, 136.19, 127.43, 123.76, 120.22, 118.89, 114.78, 100.16, 93.96, 65.91, 55.56, 55.39.

Anal. calcd for C₈₁H₆₈N₄O₈ (%): C, 79.39; H, 5.59, N, 4.57; found: C, 79.48; H, 5.65; N, 4.63.

2,2',7,7'-Tetrakis(4,4'-dimethoxy-3-methyldiphenylamino)-9,9'-spirobifluorene (HTM3).

Following general procedure B, a mixture of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.28 g, 0.44 mmol), 4,4'-dimethoxy-3-methyldiphenylamine (**3**) (0.75 g, 3.08 mmol), Pd(OAc)₂ (0.002 g, 0.009 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.004 g, 0.013 mmol) and NaO*t*-Bu (0.25 g, 2.60

mmol) in toluene (5 ml) was refluxed for 4 hours. Product was purified by column chromatography using acetone: *n*-hexane (1:24 and 2:23, v/v) as an eluent and then precipitated from 20% solution in acetone into 10-fold excess of methanol. The precipitate was filtered off and washed with methanol to give product as pale yellow solid. The yield was 0.45 g (80 %).

MS (APCI⁺, 25V) *m/z*: 1281.6 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ , ppm: 7.33 (d, *J* = 7.8 Hz, 4H), 7.17–6.21 (m, 36H), 3.75 (s, 24H), 2.10 (s, 12H). ¹³C NMR (75 MHz, CDCl₃), δ , ppm: 155.21, 153.70, 150.12, 147.35, 146.05, 140.41, 135.08, 127.49, 127.42, 125.20, 122.37, 121.98, 119.80, 117.74, 114.44, 110.66, 67.81, 55.67, 55.57, 16.40.

IR (KBr), ν (cm⁻¹): 3035 (aromatic C-H), 2995, 2947 2832 (aliphatic C-H), 1507 (C-C), 1286, 1237 (C-O-C), 811 (CH=CH of 1,4-disubstituted benzene).

Anal. calcd for C₈₅H₇₆N₄O₈ (%): C, 79.66; H, 5.98, N, 4.37; found: C, 79.59; H, 5.87; N, 4.48.

2,2',7,7'-Tetrakis(4,4'-dimethoxy-3,3'-dimethyldiphenylamino)-9,9'-spirobifluorene (HTM4).

Following general procedure B, a mixture of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.4 g, 0.63 mmol), 4,4'-dimethoxy-3,3'-dimethyldiphenylamine (**4**) (0.81 g, 3.15 mmol), Pd(OAc)₂ (0.003 g, 0.013 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.005 g, 0.017 mmol) and NaO*t*-Bu (0.36 g, 3.75 mmol) in toluene (8 ml) was refluxed for 3.5 hours. Product was purified by column chromatography using acetone: *n*-hexane (2:23 and 3:22, v/v) as an eluent and then precipitated from 20% solution in THF into 10-fold excess of methanol. The precipitate was filtered off and washed with methanol to give product as yellow solid. The yield was 0.74 g (87 %).

MS (APCI⁺, 25V) *m/z*: 1337.6 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ , ppm: 8.05–5.90 (m, 36H), 3.82 (s, 24H), 2.10 (s, 24H).

Anal. calcd for C₈₉H₈₄N₄O₈ (%): C, 79.91; H, 6.33, N, 4.19; found: C, 79.99; H, 6.41; N, 4.09.

2,2',7,7'-Tetrakis(4,4'-dimethoxy-3,5-dimethyldiphenylamino)-9,9'-spirobifluorene (HTM5).

Following general procedure B, a mixture of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.30 g, 0.47 mmol), 4,4'-dimethoxy-3,5-dimethyldiphenylamine (**5**) (0.71 g, 2.83 mmol), Pd(OAc)₂ (0.002 g, 0.009 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.004 g, 0.012 mmol) and NaO*t*-Bu (0.27 g, 2.81 mmol) in toluene (6 ml) was refluxed for 3 hours. Product was purified by column chromatography using acetone: *n*-hexane (2:23 and 3:22, v/v) as an eluent and then precipitated from 20% solution in

THF into 10-fold excess of methanol. The precipitate was filtered off and washed with methanol to give product as pale yellow solid. The yield was 0.59 g (70 %).

MS (APCI⁺, 25V) *m/z*: 1337.6 [M+H]⁺.

¹H NMR (300 MHz, CDCl₃), δ , ppm: 7.37 (d, *J* = 8.1 Hz, 4H), 6.96 (d, *J* = 8.7 Hz, 8H), 6.85–6.72 (m, 12H), 6.68–6.55 (m, 12H), 3.79 (s, 12H), 3.69 (s, 12H), 2.13 (s, 24H).

¹³C NMR (75 MHz, CDCl₃), δ , ppm: 155.65, 152.05, 149.97, 147.04, 143.58, 141.26, 135.42, 131.34, 126.45, 123.28, 122.28, 119.76, 117.79, 114.62, 65.89, 59.96, 55.55, 16.27.

Anal. calcd for C₈₉H₈₄N₄O₈ (%): C, 79.91; H, 6.33, N, 4.19; found: C, 79.99; H, 6.42; N, 4.11.

2,2',7,7'-Tetrakis(4-ethoxy-4'-methoxy-3,5-dimethyldiphenylamino)-9,9'-spirobifluorene (HTM6).

Following general procedure B, a mixture of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.39 g, 0.62 mmol), 4-ethoxy-4'-methoxy-3,5-dimethyldiphenylamine (**6**) (1.0 g, 3.69 mmol), Pd(OAc)₂ (0.003 g, 0.013 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.005 g, 0.017 mmol) and NaO*t*-Bu (0.35 g, 3.64 mmol) in toluene (7.5 ml) was refluxed for 4 hours. Product was purified by column chromatography using acetone: *n*-hexane (2:23 and 3:22, v/v) as an eluent and then precipitated from 20% solution in THF into 10-fold excess of methanol. The precipitate was filtered off and washed with methanol to give product as pale yellow solid. The yield was 0.65 g (76 %).

MS (APCI⁺, 25V) *m/z*: 1393.7 [M+H]⁺.

¹H NMR (400 MHz, CDCl₃), δ , ppm: 7.48–7.26 (m, 4H), 7.18–6.30 (m, 32H), 3.90–3.70 (m, 20H); 2.13 (s, 24H); 1.40 (t, *J* = 6.9 Hz, 12H).

Anal. calcd for C₉₃H₉₂N₄O₈ (%): C, 80.14; H, 6.65, N, 4.02; found: C, 80.03; H, 6.50; N, 4.11.

2,2',7,7'-Tetrakis(4'-ethoxy-4-methoxy-3,5-dimethyldiphenylamino)-9,9'-spirobifluorene (HTM7).

Following general procedure B, a mixture of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.30 g, 0.47 mmol), 4'-ethoxy-4-methoxy-3,5-dimethyldiphenylamine (**7**) (0.77 g, 2.84 mmol), Pd(OAc)₂ (0.002 g, 0.009 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.004 g, 0.012 mmol) and NaO*t*-Bu (0.27 g, 2.81 mmol) in toluene (6 ml) was refluxed for 3 hours. Product was purified by column chromatography using acetone: *n*-hexane (2:23 and 3:22, v/v) as an eluent and then precipitated from 20% solution in THF into 10-fold excess of methanol. The precipitate was filtered off and washed with methanol to give product as yellow solid. The yield was 0.46 g (70 %).

MS (APCI⁺, 25V) *m/z*: 1393.7 [M+H]⁺.

^1H NMR (400 MHz, CDCl_3), δ , ppm: 7.78–7.42 (m, 4H), 7.20–5.90 (m, 32H); 4.10–3.95 (m, 8H); 3.67 (s, 12H); 2.10 (s, 24H); 1.40 (t, $J = 6.8$ Hz, 12H).

Anal. calcd for $\text{C}_{93}\text{H}_{92}\text{N}_4\text{O}_8$ (%): C, 80.14; H, 6.65, N, 4.02; found: C, 80.01; H, 6.47; N, 4.13.

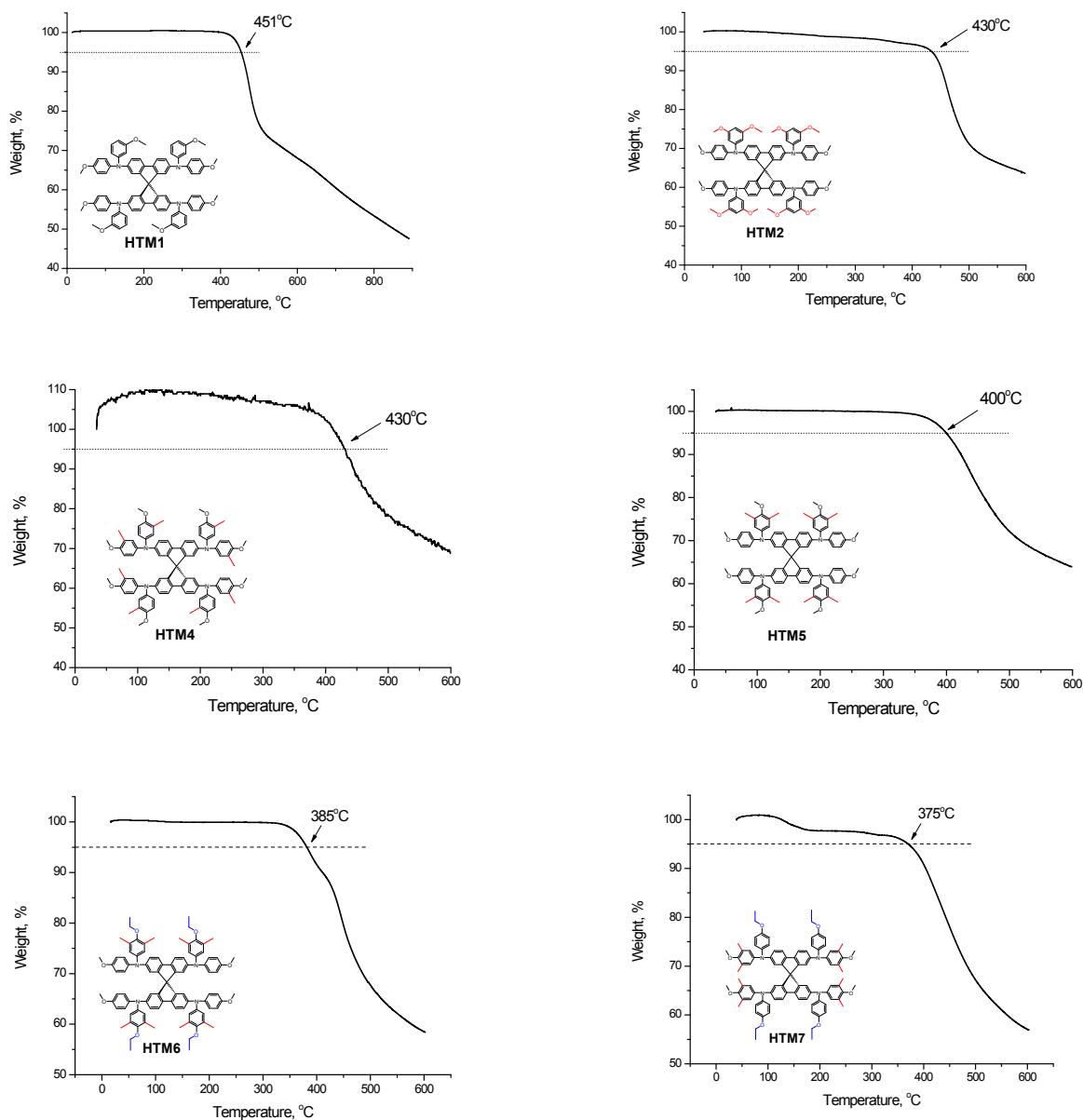


Figure S1. Thermogravimetric heating curves of: **HTM1, HTM2, HTM4-7** (heating rate $10\text{ }^\circ\text{K min}^{-1}$).

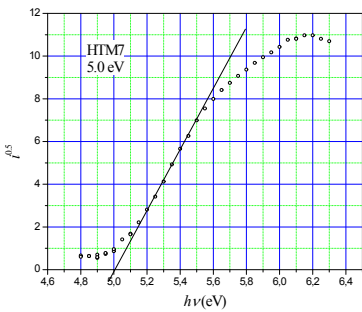
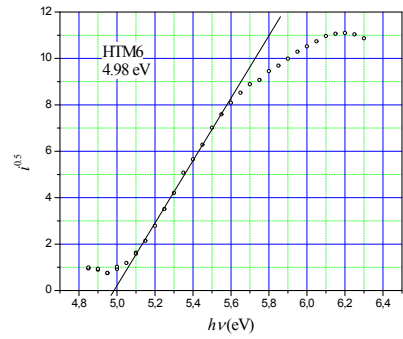
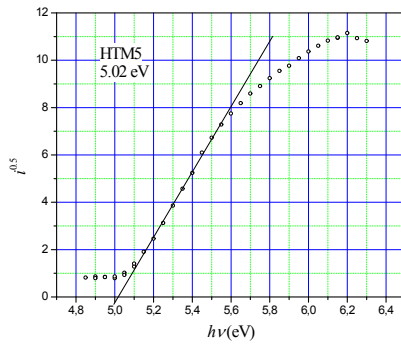
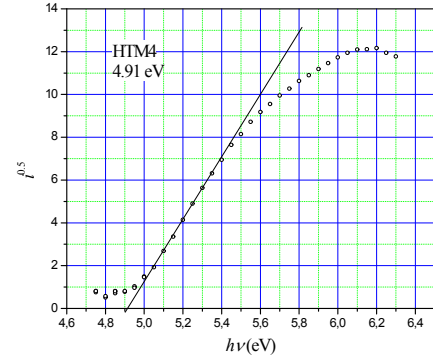
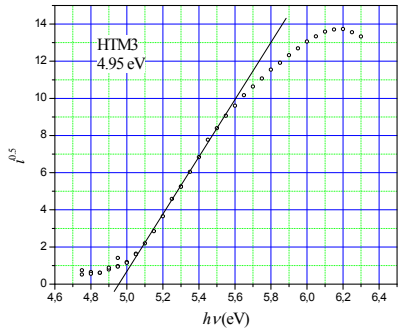
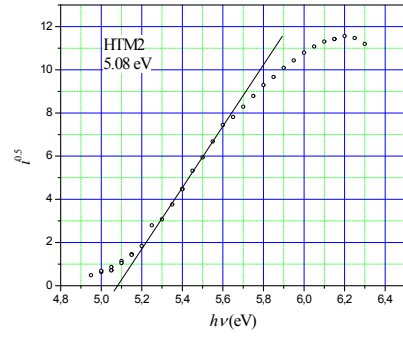
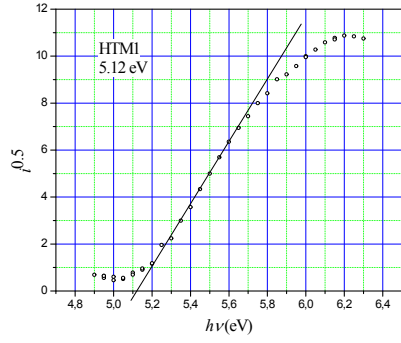


Figure S2. Photoemission in air spectra of: **HTM1-HTM7**

- S1 E. Montrimas, V. Gaidelis, and A. Pazera, *Lithuanian J. Phys.* 1966, 6, 659;
- S2 E. Miyamoto, Y. Yamaguchi and M. Yokohama, *Electrophotography* 1989, 28, 364;
- S3 B. Peng, G. Jungmann, C. Jäger, D. Haarer, H. W. Schmidt and M. Thelakkat, *Chem. Rev.* 2004, 248, 1479.