Supporting Information

Hole Transporting Materials for Perovskite Solar Cells and A Simple Approach for Determining the Performance Limiting Factors

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1. Experimental section

**General Methods.** Chemicals and reagents were purchased from commercial suppliers and used as received. All solvents were dried according to standard procedures. Air-sensitive reactions were carried out under nitrogen atmosphere. The device preparation was done in a glovebox under nitrogen atmosphere. Flash chromatography was performed using silica gel (Fluorochem, Silicagel 60A, 40-63 micron). Analytical thin layer chromatography (TLC) was performed using aluminum-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Advance 300 (\(^1\)H: 400 MHz; \(^{13}\)C: 101 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (\(J\)) are denoted in Hz and chemical shifts (\(\delta\)) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. UV-vis spectra were recorded in a Varian Cary 50 spectrophotometer. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. Mass spectra Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a MAT 95 thermo spectrometer and a Bruker REFLEX spectrometer respectively. Differential scanning calorimetry (DSC) was run on a Discovery DSC from TA instruments. Three cycles were recorded under nitrogen, heating (until 400 °C) and cooling (50 °C) at 20 °C/min of scanning rate. Cyclic voltammetry (CV) experiments were performed in deaerated 0.1 M Bu4NPF6 DCM solutions at a scan rate of 100 mV s\(^{-1}\). Glassy carbon was used as a working electrode and platinum wires as counter and reference electrodes. Before each measurement, solutions were deoxygenated with N\(_2\). Ferrocene was added as an internal standard; its oxidation potential in DCM was set at 0.7 V vs. NHE, and materials oxidation potentials were recalculated referenced to NHE.

2. Synthetic details and characterization

**4,4’-(3,6-Dibromo-9H-fluorene-9,9-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (3).**

[Structure image]

Into a 100 mL 2-neck round bottom flask fitted with a condenser, 3,6-dibromo-9H-fluoren-9-one (42 (750 mg, 2.24 mmol), 62 (1.71 g, 5.59 mmol) were dissolved in dry toluene (20 mL), under nitrogen atmosphere. The resulting mixture was heated up to 110 °C, then Eaton’s reagent (0.67 mL, 8.87 mmol) was added dropwise and the reaction stirred for 18 h. After cooling to room temperature, the mixture was quenched with saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (3 x 15 mL). Combined organic extracts were dried over anhydrous Na2SO4, filtered
and solvent removed under reduced pressure. Reaction crude was purified by flash chromatography (silica gel, hexane/dichloromethane 1:7) yielding a white solid (1.25 g, 60%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.82 (d, $J = 1.7$ Hz, 2H), 7.40 (dd, $J = 8.2, 1.8$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H), 7.02 (d, $J = 7.7$ Hz, 8H), 6.93 (d, $J = 8.5$ Hz, 4H), 6.80 (d, $J = 8.9$ Hz, 8H), 6.75 (d, $J = 8.1$ Hz, 4H), 3.78 (s, 12H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 156.0, 151.3, 147.7, 140.9, 136.1, 131.2, 128.5, 127.9, 126.8, 123.6, 121.5, 119.9, 114.8, 64.1, 55.6 ppm. HRMS (MALDI-TOF) $m/z$: calculated for C$_{53}$H$_{42}$Br$_2$N$_2$O$_4$: 930.1455, found: 928.1487. FTIR (neat): 3734, 3618, 3035, 2937, 2831, 1740, 1600, 1495, 1461, 1318.61, 1273, 1233, 1169, 1102, 1028, 873, 815, 758, 718, 665, 571 cm$^{-1}$. M.p.: 279.0–281.0 °C.

**HTM1**

Into a 100 mL 2-neck round bottom flask fitted with a condenser, 3 (1.03 g, 1.10 mmol), 4 (558 mg, 2.43 mmol), Pd$_2$(dba)$_3$ (25.0 mg, 0.03 mmol), XPhos (52.0 mg, 0.11 mmol) were dissolved in dry toluene (20 mL) under nitrogen atmosphere. The mixture was degassed for 30 min. Then NaO'Bu (317 mg, 3.30 mmol) was added in one portion and the resulting mixture was stirred at 110 °C for 18 h. Upon cooling to room temperature, the mixture was quenched with H$_2$O (15 mL) and extracted with Et$_2$O (3 × 10 mL). Combined organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered and evaporated under reduced pressure. Reaction crude was purified by flash chromatography (silica gel, dichloromethane/ethyl acetate 20:1) yielding a white powder (742 mg, 55%). $^1$H NMR (400 MHz, THF-d$_8$) δ: 7.21 (d, $J = 2.1$ Hz, 2H), 7.17 (d, $J = 8.3$ Hz, 2H), 7.01–6.93 (m, 20H), 6.81–6.74 (m, 18H), 6.70 (d, $J = 8.7$ Hz, 4H), 3.72 (s, 12H), 3.71 (s, 12H) ppm. $^{13}$C NMR (101 MHz, THF-d$_8$) δ: 157.3, 156.9, 149.4, 148.2, 146.5, 142.6, 142.1, 142.0, 139.5, 129.6, 127.6, 127.4, 126.7, 122.8, 120.5, 115.53, 115.5, 114.4, 64.1, 55.7, 55.6 ppm. HRMS (MALDI-TOF) $m/z$: calculated for C$_{81}$H$_{70}$N$_4$O$_8$: 1226.5166, found: 1226.5188. FTIR (neat): 3034, 2998, 2948, 2834, 1743, 1607, 1502, 1453, 1239, 1175, 1106, 1035, 824, 731, 580 cm$^{-1}$. M.p.: 165.1–167.1 °C.
Into a 100 mL 2-neck round bottom flask fitted with a condenser, 3 (173 mg, 0.12 mmol), 5 (176 mg, 0.41 mmol) and Pd(PPh₃)₄ (22.0 mg, 0.02 mmol) were dissolved in dry DMF (20 mL) under nitrogen atmosphere, the mixture was then degassed for 30 min. Thereafter, K₃PO₄ (631 mg, 2.97 mmol) was added in one portion and the mixture was stirred at 90 °C for 18 h. Upon cooling to room temperature, the mixture was quenched with H₂O (30 mL). The resulting precipitate was filtered off and washed with water. After vacuum drying the remaining moisture, the crude was purified by flash chromatography (silica gel dichloromethane/ethyl acetate 17:1) yielding a white powder (180 mg, 70%).

**1H NMR (400 MHz, THF-d₈) δ:** 7.50 (d, J = 8.4 Hz, 4H), 7.47–7.39 (m, 4H), 7.10–7.01 (m, 12H), 6.96 (d, J = 8.5 Hz, 14H), 6.84 (d, J = 8.6 Hz, 8H), 6.77 (d, J = 8.7 Hz, 8H), 6.72 (d, J = 8.4 Hz, 4H), 3.75 (s, 12H), 3.71 (s, 12H) ppm.

**13C NMR (101 MHz, THF-d₈) δ:** 157.5, 157.4, 157.2, 151.7, 149.4, 148.4, 142.1, 142.0, 141.8, 141.4, 139.0, 134.4, 129.7, 128.0, 127.6, 126.9, 121.6, 120.8, 119.1, 115.6, 115.5, 65.0, 55.8, 55.7 ppm.

**HRMS (MALDI-TOF) m/z:** calculated for C₉₃H₇₈N₄O₈: 1378.5814, found: 1378.5831.

**FTIR (neat):** 3037, 2925, 2837, 1740, 1606, 1503, 1318, 1274, 1174, 1106, 1035, 822, 728, 605, 576 cm⁻¹.

**M.p.:** 215.3–217.3 °C.

**2,6-Dibromo-4-(dibromomethylene)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene (7)**

2,6-dibromo-4H-cyclopenta[2,1-b:3,4-b’]dithiophen-4-one (200 mg, 0.60 mmol), PPh₃ (640 mg, 2.44 mmol) and CBr₄ (400 mg, 1.22 mmol) were dissolved in dry CH₂Cl₂ (15 mL). The reaction mixture was stirred for 30 minutes at room temperature, thereafter, distilled water (15 mL) was added to quench the reaction. The organic layer was separated, washed with water, dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The reaction crude was purified by flash chromatography (silica gel, hexane/dichloromethane 1:1) yielding a pink solid (160 mg, 55%).

**1H NMR (400 MHz, CDCl₃) δ:** 7.63 (s, 2H) ppm.

**13C NMR (101 MHz, CDCl₃) δ:** 141.2, 136.5, 129.9, 126.7, 111.1, 96.5 ppm.

**HRMS (MALDI-TOF) m/z:** calculated for C₉₃H₇₈N₄O₈: 1378.5814, found: 1378.5831.

**FTIR (neat):** 3101, 2921, 2850, 1614, 1575, 1459, 1366, 1302, 1270, 1182, 1046, 942, 901, 829, 756, 694, 626 cm⁻¹. **M.p.:** decomp >300 °C.
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HTM3

Into a 100 mL 2-neck round bottom flask, 7 (60 mg, 0.14 mmol), 5 (300 mg, 0.69 mmol), Pd(PPh₃)₄ (30 mg, 0.03 mmol), and Na₂CO₃ (230 mg 2.24 mmol) were added to a 5:1 THF/H₂O mixture (25 mL) under nitrogen atmosphere. The mixture was degassed for 40 min and then stirred at 90 °C for 4 h. Upon completion, THF was removed under reduced pressure, and CHCl₃ (50 mL) added. The organic layer was washed with H₂O (3 × 50 mL), dried over anhydrous Na₂SO₄ and filtered. After removing the solvent under reduced pressure, the reaction crude was purified by flash chromatography (silica gel, hexane/ethyl acetate 4:1) yielding a dark brown solid (100 mg 50%). 

¹H NMR (400 MHz, THF-d₈) δ: 7.25 (t, J = 8.2 Hz, 8H), 7.08 (dd, J = 18.2, 8.7 Hz, 16H), 6.92 (dd, J = 8.6, 2.3 Hz, 8H), 6.84 (dd, J = 17.4, 8.8 Hz, 16H), 6.58 (s, 2H), 3.76 (s, 12H), 3.71 (s, 12H) ppm. 

¹³C NMR (101 MHz, THF-d₈) δ: 157.8, 157.5, 151.0, 149.1, 146.6, 143.2, 141.8, 141.5, 133.95, 133.6, 128.8, 127.9, 127.5, 126.5, 121.7, 120.1, 119.1, 115.8, 115.7, 55.8, 55.76 ppm. HRMS (MALDI-TOF) m/z: calculated for C₉₀H₇₄N₄O₈S₂: 1402.4944, found 1402.4943. FTIR (neat): 2998, 2935, 2830 1740, 1595, 1497, 1317, 1273, 1231, 1167, 1103, 1029, 819, 757, 629, 575 cm⁻¹.
3. NMR, FTIR & MS spectra

Figure S1. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of compound 3.

Figure S2. $^{13}$C NMR (101 MHz, CDCl$_3$, 298 K) of compound 3.
Figure S3. FTIR of compound 3.

Figure S4. MALDI-TOF mass spectrum of 3.
Figure S5. $^1$H NMR (400 MHz, THF-$d_8$, 298 K) of compound HTM1.

Figure S6. $^{13}$C NMR (101 MHz, THF-$d_8$, 298 K) of compound HTM1.
Figure S7. FTIR of compound HTM1.

Figure S8. MALDI-TOF mass spectrum of HTM1.
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Figure S9. $^1$H NMR (400 MHz, THF-d$_8$, 298 K) of compound HTM2.

Figure S10. $^{13}$C NMR (101 MHz, THF-d$_8$, 298 K) of compound HTM2.
Figure S11. FTIR of compound HTM2.

Figure S12. MALDI-TOF mass spectrum of HTM2.
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**Figure S13.** $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of compound 7.

**Figure S14.** $^{13}$C NMR (101 MHz, CDCl$_3$, 298 K) of compound 7.
**Supporting Information**

*Figure S15.* MALDI-TOF mass spectrum of 7.

*Figure S16.* FTIR of compound 7.
Figure S17. $^1$H NMR (400 MHz, THF-$d_8$, 298 K) of compound HTM3.

Figure S18. $^{13}$C NMR (101 MHz, THF-$d_8$, 298 K) of compound HTM3.
Figure S19. FTIR of compound HTM3.

Figure S20. MALDI-TOF mass spectrum of HTM3.
4. Optical properties

![Figure S21](image.png)

**Figure S21.** UV-Vis spectra of HTM1, HTM2 and HTM3 in DCM solution (10⁻⁵M).

**Table S1.** Optical properties of HTM1, HTM2 and HTM3.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \lambda_{\text{max}} ) [nm]ᵃ</th>
<th>( \lambda_{\text{onset}} ) [nm]ᵃ</th>
<th>( E_{\text{gap}}^{\text{opt}} ) [eV]ᵇ</th>
<th>( \varepsilon \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTM1</td>
<td>308</td>
<td>365</td>
<td>3.39</td>
<td>11.1</td>
</tr>
<tr>
<td>HTM2</td>
<td>306</td>
<td>390</td>
<td>3.17</td>
<td>7.90</td>
</tr>
<tr>
<td>HTM3</td>
<td>404</td>
<td>640</td>
<td>1.93</td>
<td>6.66</td>
</tr>
</tbody>
</table>

[a] Measured in DCM solution, \( E_{\text{gap}}^{\text{opt}} = 1240/\lambda_{\text{onset}} \) [eV]; [b] Molar absorption of the lower energy band in DCM solution.
5. Electrochemistry

![Figure S22. Cyclic voltammograms of the novel HTMs, HTM1, HTM2 and HTM3.](image)

Table S2. Electrochemical properties of HTM1, HTM2 and HTM3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^{\text{ox}}$ [V]$^a$</th>
<th>$E_{\text{HOMO}}$ [eV]$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTM1</td>
<td>0.88</td>
<td>−5.28</td>
</tr>
<tr>
<td>HTM2</td>
<td>0.89</td>
<td>−5.29</td>
</tr>
<tr>
<td>HTM3</td>
<td>0.57</td>
<td>−4.96</td>
</tr>
</tbody>
</table>

[a] Determined from CV measurements vs. normal hydrogen electrode (NHE). [b] $E_{\text{HOMO}}$ was estimated in eV as $E_{\text{HOMO}} = −4.44 \text{ eV} − E_{1/2}^{\text{ox}}$. 
6. Differential Ideality Factor

Figure S23. Differential Ideality Factor calculated by equation (4) in the main text.
7. TPC Fit

Figure S24. TPC fits of Spiro-OMeTAD (SP): Orange solid, green dash, red dash-dot and purple dot lines represent the fits by single, double, triple and stretched exponential decay functions, respectively. The legend indicates the BGL light intensity (sun).

Figure S25. TPC fits of HTM1: Orange solid, green dash, red dash-dot and purple dot lines represent the fits by single, double, triple and stretched exponential decay functions, respectively. The legend indicates the BGL light intensity (sun).
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Figure S26. TPC fits of HTM2: Orange solid, green dash, red dash-dot and purple dot lines represent the fits by single, double, triple and stretched exponential decay functions, respectively. The legend indicates the BGL light intensity (sun).

Figure S27. TPC fits of HTM3: Orange solid, green dash, red dash-dot and purple dot lines represent the fits by single, double, triple and stretched exponential decay functions, respectively. The legend indicates the BGL light intensity (sun).
8. TPV Fit

**Figure S28.** TPV fits of SP: Orange solid, green dash, red dash-dot and purple dot lines represent the fits by single, double, triple and stretched exponential decay functions, respectively. The legend indicates the BGL light intensity (sun).

**Figure S29.** TPV fits of HTM1: Orange solid, green dash, red dash-dot and purple dot lines represent the fits by single, double, triple and stretched exponential decay functions, respectively. The legend indicates the BGL light intensity (sun).
Figure S30. TPV fits of HTM2: Orange solid, green dash, red dash-dot and purple dot lines represent the fits by single, double, triple and stretched exponential decay functions, respectively. The legend indicates the BGL light intensity (sun).

Figure S31. TPV fits of HTM3: Orange solid, green dash, red dash-dot and purple dot lines represent the fits by single, double, triple and stretched exponential decay functions, respectively. The legend indicates the BGL light intensity (sun).
9. TPC amplitudes as a function of BGL

Figure S32. TPC amplitudes of the different HTMs as function of BGL.
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10. Variation of $Q$ (TPC integral) with BGL and integration time

Figure S33. Integrated TPC ($Q$) vs. integration time for all HTMs.
11. **I-V Curves / EQE**

**Figure S34.** I-V curves of the devices with Spiro-OMeTAD and HTM3 as HTM, and Cu as hole collection electrode instead of Au.

**Figure S35.** EQE data (solid lines) and integrated current densities (dashed lines) of the novel HTMs.
12. Simulation

12.1. Main Simulation Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ETM</th>
<th>Perovskite</th>
<th>HTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trap density ($m^3 eV^{-1}$)</td>
<td>5e22</td>
<td>5e22</td>
<td>5e22</td>
</tr>
<tr>
<td>Mobility ($m^2 V^{-1} s^{-1}$)</td>
<td>1e-3</td>
<td>2e-3</td>
<td>1e-6</td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>9</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Density of states ($m^{-3}$)</td>
<td>5e25</td>
<td>5e25</td>
<td>5e25</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>3.3</td>
<td>1.6</td>
<td>3.02</td>
</tr>
<tr>
<td>Free carrier recombination rate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>constant ($m^3 s^{-1}$)</td>
<td>1e-16</td>
<td>1e-16</td>
<td>1e-16</td>
</tr>
</tbody>
</table>

12.2. Carrier Generation Rate

12.3. J-V curves for HTMs with different HOMO energy levels
12.4. **HTM trap-density/mobility/HOMO and device shunt resistance on $V_{oc}$**

![Graphs showing Voc vs Light intensity (sun) for HTM hole mobility, HTM HOMO, HTM trap density, and device shunt resistance.](image-url)
12.5. Impact of HTM trap-density/mobility/HOMO and series resistance on TPC at 0.1 sun

12.6. BGL intensity dependence of TPC under low/moderate/high HTM trap-density/mobility and series resistance
12.7. Impact of HTM trap-density/mobility/HOMO and shunt resistance on TPV at 0.1 sun

12.8. BGL intensity dependence of TPV under low/moderate/high HTM trap-density/mobility and shunt resistance
12.9. Impact of shunts on the BGL intensity dependence of TPV under moderate HTM trap-density

![Graphs showing the impact of shunts on TPV intensity dependence under moderate HTM trap-density.](image-url)