Supporting Information

Efficient and Stable Perovskite Solar Cells based on Perfluorinated Polymers

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1. Synthesis of intermediate 4

1-(2-ethylhexyloxy)-4-iodobenzene (S2)

Potassium carbonate (3.86 g, 27.9 mmol) was added to a solution of 4-iodophenol (S1, 4.00 g, 18.2 mmol) and 2-ethylhexyl bromide (3.90 mL, 21.8 mmol) in 20 mL of dimethylformamide. The reaction mixture was stirred for 6 h at 130 °C. After cooling down, the suspension was filtrated and the solvent removed under vacuum. The resulting residue was diluted with DCM (40 mL) and washed with water (3 x 40 mL) and brine (1 x 40 mL). The organic phase was dried over anhydrous Na₂SO₄, concentrated under reduced pressure and purified by flash column chromatography using hexane as eluent yielding the target product as colourless oil (5.00 g, 83%). ¹H NMR (300 MHz, CD₂Cl₂), δ (ppm): 7.57-7.52 (m, 2H, Hₐ), 6.71-6.66 (m, 2H, H₇), 3.81 (d, J = 5.7 Hz, 2H, H₈), 1.76-1.64 (m, 1H, H₉), 1.56-1.26 (8H, H₁₀-g + H₁₁), 0.94-0.88 (6H, H₁₂ + H₁₃).

4-bromo-N,N-bis(4-(2-ethylhexyloxy)phenyl)aniline (S3)
A procedure reported in the literature was adapted with some modifications. 1-(2-ethylhexyloxy)-4-iodobenzene ($S_2$, 1.00 g, 3.01 mmol) was put in a Schlenk flask and three cycles of argon-vacuum were applied. Next, 4-bromoaniline (0.17 g, 1.00 mmol), potassium hydroxide (0.65 g, 11.6 mmol) and anhydrous toluene (10 mL) were added and the flask was purged with argon for 30 min. Upon addition of copper (I) iodide (12.5 mg, 0.07 mmol) and phenantroline (12.0 mg, 0.07 mmol) the mixture was refluxed for 20 h. Afterwards, the reaction was allowed to cool and the crude product was dissolved in 20 mL of DCM and washed with 20 mL of HCl 1 M. The aqueous phase was extracted with DCM (2 x 20 mL) and the combined organic phases were washed with brine (1 x 40 mL). The organic phase was dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure and purified by flash column chromatography using PE:DCM (20:1→10:1) as eluent to give the title product as an orangish solid (0.46 g, 80%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$), $\delta$ (ppm): 7.26-7.19 (m, 2H, $H_a$), 7.01 (d, $J = 8.7$ Hz, 4H, $H_d$), 6.87-6.80 (m, 4H, $H_c$), 6.75 (d, $J = 8.7$ Hz, 4H, $H_b$), 3.82 (d, $J = 5.7$ Hz, 4H, $H_e$), 1.77-1.64 (m, 2H, $H_f$), 1.55-1.27 (16H, $H_g$-i + $H_k$), 1.00-0.81 (12H, $H_j$ + $H_l$).

$N^1,N^4$-bis(4-((2-ethylhexyl)oxy)phenyl)-$N^2,N^7$-diphenylbenzene-1,4-diamine ($S_4$)$^3$

Compound $S_3$ (2.20 g, 3.79 mmol) was put in a Schlenk flask and three cycles of argon-vacuum were then applied. Next tri-tert-butyl phosphine (1 M in toluene, 0.40 mL, 0.40 mmol) and sodium tert-butoxide (1.09 g, 11.4 mmol) were dissolved in dry toluene (18 mL) degassed
with argon for 30 min. Upon addition of Pd$_2$dba$_3$ (0.04 g, 0.04 mmol), diphenylamine (0.64 g, 3.79 mmol) was added and the mixture was refluxed over-night. Afterwards, the reaction was allowed to cool down and 20 mL of water and 20 mL of DCM were added to the crude product. The aqueous phase was extracted with DCM (2 x 20 mL) and the combined organic phases were washed with brine (1 x 40 mL). The organic phase was dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure and purified by column chromatography using PE:DCM (10:1) as eluent to give the title product as an orange-yellowish solid (2.17 g, 86%). MS (MALDI-TOF, LDI): calculated for C$_{46}$H$_{56}$N$_2$O$_2$ [M$^+$]: 668.434, found: 668.403. $^1$H NMR (300 MHz, (CD$_3$)$_2$CO), δ (ppm): 7.29-7.21 (4H, H$_b$), 7.08-6.83 (18H, H$_a$ + H$_c$ + H$_{d-g}$), 3.89 (d, J = 5.6 Hz, 4H, H$_h$), 1.80-1.68 (m, 2H, H$_i$), 1.61-1.32 (16H, H$_{j-l}$ + H$_n$), 1.02-0.88 (12H, H$_m$ + H$_o$).$^{13}$C NMR (75 MHz, (CD$_3$)$_2$CO), δ (ppm): 156.54 (q), 148.99 (q), 145.90 (q), 141.82 (q), 141.47 (q), 130.03 (CH), 127.10 (CH), 127.02 (CH), 123.86 (CH), 122.92 (CH), 122.66 (CH), 116.18 (CH), 71.25 (CH$_2$), 40.34 (CH), 31.32 (CH$_2$), 29.82 (CH$_2$, overlapping with the solvent signal), 24.60 (CH$_2$), 23.73 (CH$_2$), 14.37 (CH$_3$), 11.46 (CH$_3$).

$N^1$,N$^4$-bis(4-bromophenyl)-$N^4$,N$^1$-bis(4-((2-ethylhexyl)oxy)phenyl)benzene-1,4-diamine (S5)$^3$

![Chemical structure of S5](image.png)

Compound S4 (0.73 g, 1.08 mmol) was dissolved in 15 mL of dimethylformamide and the solution was degassed for 30 min with an argon stream. After cooling down the solution to 0 °C, NBS (0.41 g, 2.27 mmol) was added in small portions under exclusion of light. Next, the reaction mixture was allowed to stir for 24 h at room temperature. Afterwards, the solvent was removed under reduced pressure and 20 mL of DCM and 20 mL of water were added. The phases were separated and the aqueous phase was extracted with DCM (2 x 20 mL). The combined organic phases were washed with water (2 x 50 mL) and brine (1 x 50 mL), dried over Na$_2$SO$_4$, filtered and the solvent removed under reduced pressure. The residue was purified by flash column chromatography using PE:DCM (30:1→10:2) as eluent to give the title compound.
as black oil (0.54, 60%). MS (MALDI-TOF, LDI): calculated for C_{46}H_{54}Br_{2}N_{2}O_{2} [M^+]: 824.255, found: 824.557. ¹H NMR (300 MHz, (CD$_3$)$_2$CO, δ (ppm): 7.43-7.33 (m, 4H, H$_a$), 7.08-6.81 (16H, H$_a$ + H$_c$-f), 3.87 (d, J = 5.6 Hz, 4H, H$_g$), 1.77-1.65 (m, 2H, H$_h$), 1.59-1.27 (16H, H$_{ik}$ + H$_m$), 0.98-0.85 (12H, H$_n$ + H$_o$). ¹³C NMR (75 MHz, (CD$_3$)$_2$CO, δ (ppm): 157.23 (q), 148.27 (q), 147.33 (q), 141.90 (q), 140.28 (q), 133.47 (CH), 128.10 (CH), 127.84 (CH), 125.76 (CH), 122.50 (CH), 116.67 (CH), 115.40 (q), 71.46 (CH$_2$), 40.53 (CH), 31.52 (CH$_2$), 30.05 (CH$_2$, overlapping with the solvent signal), 24.81 (CH$_2$), 23.94 (CH$_2$), 14.58 (CH$_3$), 11.68 (CH$_3$).

**Intermediate 4**

![Diagram of Intermediate 4]

Compound S5 (0.67 g, 0.81 mmol), bis(pinacolato) diboron (0.62 g, 2.43 mmol) and potassium acetate (0.64 g, 6.47 mmol) were dissolved in 15 mL of anhydrous 1,4-dioxane. The solution was degassed for 15 min with an argon stream and PdCl$_2$(ddpf) (0.02 g, 0.02 mmol) was added. The reaction mixture was allowed to stir for 3 d at 80 ºC. After cooling to room temperature, 40 mL of water and 40 mL of DCM were added and the phases were separated. The aqueous phase was extracted with DCM (3 x 40 mL) and the combined organic layers were washed with water (2 x 100 mL), brine (1 x 100 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane:AcOEt (15:1) with 0.5% NEt$_3$ as eluent to give the title product as a white solid (0.29 g, 39%). MS (MALDI-TOF, LDI): calculated for C$_{58}$H$_{78}$B$_2$N$_2$O$_6$ [M^+]: 920.600, found 920.595. ¹H NMR (500 MHz, (CD$_3$)$_2$CO), δ (ppm): 7.66-7.65 (4H, H$_a$), 7.14-6.89 (16H, H$_b$-g), 3.90 (d, J = 5.0 Hz, 4H, H$_g$), 1.79-1.68 (m, 2H, H$_h$), 1.63-1.26 (40H, H$_{ik}$ + H$_m$ + H$_n$), 1.01-0.88 (12H, H$_i$ + H$_o$). ¹³C NMR (125 MHz, (CD$_3$)$_2$CO) δ (ppm): 136.83 (q), 128.18 (CH), 125.76 (CH), 122.50 (CH), 116.67 (CH), 115.40 (q), 71.46 (CH$_2$), 40.53 (CH), 31.52 (CH$_2$), 30.05 (CH$_2$, overlapping with the solvent signal), 24.81 (CH$_2$), 23.94 (CH$_2$), 14.58 (CH$_3$), 11.68 (CH$_3$).
30.14 (CH$_2$), 29.99 (CH$_2$), 29.84 (CH$_2$), 29.68 (CH$_2$), 29.53 (CH$_2$), 25.35 (CH$_3$), 24.74 (CH$_3$), 23.87 (CH$_2$), 14.59 (CH$_3$), 11.59 (CH$_3$).

2. Synthesis of additives D1, D2 and D3

Additive D1

![Chemical structure of additive D1]

Compound 2 (0.22 g, 0.52 mmol), 1,4-dibromo-2,5-bis(perfluorohexyl) benzene (1) (0.21 g, 0.24 mmol), aq. NaHCO$_3$ 0.2 M (4.70 mL, 0.94 mmol) were dissolved in 3 mL of anhydrous toluene. The resulting suspension was degassed with an argon stream before and after Pd(PPh$_3$)$_4$ (37.0 mg, 0.03 mmol) was added and the mixture was stirred and refluxed for 4 d under argon atmosphere. After cooling to room temperature, 20 mL of water and 20 mL of DCM were added and the phases separated. The aqueous phase was extracted with DCM (3 x 20 mL) and the combined organic phases were washed with water (20 mL) and brine (20 mL). The organic phase was dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using toluene (0.5% NEt$_3$) as eluent to give the title product as a yellowish solid (128 mg, 41%). MS (ESI-TOF): calcd for C$_{58}$H$_{38}$F$_{26}$N$_2$O$_4$ [M$^+$] 1320.24, found 1320.51. $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.58 (s, 2H, H$_e$), 7.14-7.03 (12H, H$_b$ + H$_d$), 6.94-6.89 (m, 4H, H$_c$), 6.89-6.82 (m, 8H, H$_a$). $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ (ppm): -126.33 (4F), -122.99 (4F), -121.92 (4F), -119.61 (4F), -103.25 (4F), -81.13 (6F). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ (ppm): 156.81 (q), 149.17 (q), 142.56 (q), 141.16 (q), 133.78 (CH), 130.66 (q), 130.38 (CH), 130.17-129.42 (C-F) 127.44 (CH), 119.13 (CH), 115.24 (CH), 55.98 (CH$_3$). IR-ATRν (cm$^{-1}$): 3000-2830, 1605, 1505, 1465, 1282, 1239, 1213, 1198, 1137, 1086, 1035, 828, 729, 718, 674, 643, 613, 575, 531, 492, 420.

Additive D2
Monomer 3 (100 mg, 160 µmol) was put in a Schlenk flask under argon. Next, anhydrous toluene (4 mL), water (1 mL) and NaHCO$_3$ (540 mg, 6.40 mmol) were injected together with 1,4-dibromo-2,5-bis(perfluorohexyl) benzene (1) (140 mg, 160 mmol) under argon atmosphere. The reaction mixture was purged with argon for 30 min before and after Pd(PPh$_3$)$_4$ (11.0 mg, 9.60 µmol) was added. The mixture was stirred vigorously and refluxed for 5 d and after cooling, 20 mL of DCM and 20 mL of water were added. The phases were separated and the aqueous phase was extracted with DCM (1 x 20 mL) and the combined organic phases were washed with 50 mL of brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was dissolved in DCM and dripped into 150 mL of cold MeOH. The obtained precipitate was collected by filtration and washed consecutively with MeOH (3 d) and acetonitrile (3 d) using a Soxhlet extractor. Each washing lasted until no residue could be found in the chosen solvent (80 mg, 46%). SEC: $M_n = 10231$, $M_w = 16144$, PDI = 1.6. MS (MALDI-TOF, DITHRANOL): calculated for C$_{44}$H$_{31}$F$_{26}$NO $[M^+]$: 1083.198, found: building blocks.\textsuperscript{1}H NMR (400 MHz, CD$_2$Cl$_2$), $\delta$ (ppm): 7.65 (s, 2H, H$_a$), 7.20-7.04 (8H, H$_b$-$d$), 6.94-6.85 (2H, H$_e$), 3.89-3.80 (2H, H$_f$), 1.79-1.67 (1H, H$_g$), 1.59-1.29 (8H, H$_h$-$j$ + H$_l$), 1.01-0.85 (6H, H$_k$ + H$_m$).\textsuperscript{19}F NMR (376 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): -126.50 (4F), -123.09 (4F), -122.01 (4F), -119.61 (4F), -103.28 (4F), -81.31 (6F).

Additive D3
Monomer 4 (143 mg, 155 µmol) was put in a Schlenk flask under argon. Next, anhydrous toluene (3.8 mL) and aq. NaHCO$_3$ 0.2 M (1.41 mL, 282 µmol) were injected together with 1,4-dibromo-2,5-bis(perfluorohexyl) benzene (1) (135 mg, 155 µmol) under argon atmosphere. The reaction mixture was purged with argon for 30 min before and after Pd(PPh$_3$)$_4$ (11.0 mg, 9.30 µmol) was added. The mixture was stirred vigorously and refluxed for 5 d and after cooling, 20 mL of DCM and 20 mL of water were added. The phases were separated and the aqueous phase was extracted with DCM (1 x 20 mL) and the combined organic phases were washed with 50 mL of brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was dissolved in DCM and dripped into 150 mL of cold MeOH. The obtained precipitate was collected by filtration and washed consecutively with MeOH (3 d) and acetonitrile (3 d) using a Soxhlet extractor. Each washing lasted until no residue could be found in the chosen solvent (156 mg, 73%). SEC: Mn = 10750, Mw = 17600, PDI = 1.6. MS (MALDI-TOF, DITHRANOL): calculated for C$_{64}$H$_{56}$F$_{26}$N$_2$O$_2$ [M + ]: 1378.392, found: building blocks.$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.63 (s, 2H, H$_a$), 7.21-6.77 (20H, H$_{b-g}$), 3.81 (d, J= 5.4 Hz, 4H, H$_h$), 1.74-1.66 (2H, H$_i$), 1.50-1.27 (16H, H$_{j-l}$ + H$_n$), 0.96-0.84 (12H, H$_m$ + H$_o$).$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ (ppm): -126.46 (4F), -123.05 (4F), -121.96 (4F), -119.57 (4F), -103.21 (4F), -81.30 (6F).

3. $^1$H NMR and $^{13}$C NMR spectra of compound D1
**Figure S1.** $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of D1.
D1 ($^{13}$C NMR, 400 MHz, CD$_2$Cl$_2$, 298K)

Figure S2. $^{13}$C NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of D1.

4. $^1$H NMR spectra of polymers D2 and D3
**D2** ($^1$H NMR, 400 MHz, CD$_2$Cl$_2$, 298K)

![Chemical Structure of D2](figure)

**Figure S3.** $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of D2.
D3 (\textsuperscript{1}H NMR, 400 MHz, CDCl\textsubscript{3}, 298K)

\begin{center}
\begin{figure}
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\includegraphics[width=\textwidth]{figs.png}
\caption{\textsuperscript{1}H NMR spectrum (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K) of P3.}
\end{figure}
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5. IR-ATR spectrum of molecule D1
Figure S5. IR-ATR spectrum of molecule D1.

6. Mass spectrometry of molecule D1 and polymer D3

Figure S6. ESI-TOF for D1.
Figure S7. MALDI-TOF for D3.

7. Water contact angle measurements

Figure S8. Water contact angles of a) molecule D1, b) polymer D2 and c) polymer D3.
Figure S9. Water contact angle measurements after dropping water onto a) FTO/SnO$_2$/perovskite film, b) FTO/SnO$_2$/perovskite+D1 film and c) FTO/SnO$_2$/perovskite + D2 film and c) FTO/SnO$_2$/perovskite + D3 film.

8. Statistics

Figure S10. Comparison of the devices parameters for reference and stabilized perovskite solar cells. Whiskers show minimum and maximum value, box represents the values between 25% and 75%, circle show mean value.

9. Hysteresis

In case of devices prepared in this chapter, frequently, all the devices from certain batch showed no hysteresis (Table 11). In order to quantify the hysteresis magnitude the hysteresis index (HI) is used as reported in literature.$^4$ The HI for the cases when PCE (reverse) > PCE (forward) is calculated using the equation 1, while for cases when PCE (reverse) < PCE (forward), equation 2 is used:
HI = \left[ \frac{P_{\text{max},r}}{P_{\text{max},f}} \right]^{-1} \quad (1)

HI = \left[ \frac{P_{\text{max},f}}{P_{\text{max},r}} \right]^{-1} \quad (2)

where $P_{\text{max},r}$ and $P_{\text{max},f}$ are the maximum power points on the forward and the reserve scan, respectively.

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<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R</td>
<td>1.06</td>
<td>18.07</td>
<td>73.61</td>
<td>14.07</td>
<td>2.25</td>
<td></td>
</tr>
</tbody>
</table>

Table S1. Examples of hysteresis index form one batch. F= forward scan; R= reverse scan.
**Figure S11.** $I$-$V$ curves of a reference-based PSC by forward (solid line) and reverse (dash line) scan. Device A in Table S1.

**Figure S12.** $I$-$V$ curves of a D1-based PSC by forward (solid line) and reverse (dash line) scan. Device A in Table S1.
**Figure S13.** $I-V$ curves of a D2-based PSC by forward (solid line) and reverse (dash line) scan. Device A in Table S1.

**Figure S14.** $I-V$ curves of a D3-based PSC by forward (solid line) and reverse (dash line) scan. Device B in Table S1.

10. Additional stability measurements
Figure S15. Normalized power measured as a function of time for reference and doped cells kept at MPP in air.

Figure S16. Normalized power measured as a function of time for reference and D1-doped cells kept at MPP in air.
Figure S17. Normalized power measured as a function of time for reference and D2-doped cells kept at MPP in air.

11. Temperature and humidity measurements
Figure S18. Temperature and humidity tracking in the cavity of the solar simulator where the MPP measurements took place (short-term stability measurement).
**Figure S19.** Temperature and humidity tracking in the place where the cells were kept until they were measured (long-term stability measurement).

## 12. References


