Supplementary Information

Electric field dependent photocurrent generation in a thin-film organic photovoltaic device with a [70]fullerene-benzodifuranone dyad†

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1. **Synthetic procedures**

![Chemical structure](image)

3-(4-(2-Hydroxyethoxy)phenyl)-7-phenylbenzo[1,2-b:4,5-b’]difuran-2,6-dione (2)

[1]: Compound S1 (267 mg, 1.26 mmol) and 5-hydroxy-3-phenylbenzofuran-2(3H)-one [2] (420 mg, 1.86 mmol, 1.48 equiv) were mixed together and heated to 195 °C over the course of 45 min while stirring. The viscous red oil was stirred for another 1.5 h at 195 °C. Column chromatography (EtOAc/CH₂Cl₂ 1:9) afforded a red band that was concentrated in vacuo. The intermediate product was dissolved in THF (10 mL) and chloranil (227 mg, 0.923 mmol, 0.73 equiv) was added, followed by stirring at 65 °C for 2 h, resulting in a darkened red solution. Column chromatography (EtOAc/CH₂Cl₂ 1:10 to 1:3) afforded 2 as a dark red powder (186 mg, 0.465 mmol, 37% yield). ^1H NMR (500 MHz, CDCl₃) δ 3.6 (br s, 1H, OH), 4.03 (t, J = 4.0 Hz, 2H, CH₂OH), 4.18 (t, J = 4.0 Hz, 2H, CH₂OAr), 6.90 (s, 1H, benzodifuranone), 6.92 (s, 1H, benzodifuranone), 7.08 (d, J = 8.6 Hz, 2H, Ar), 7.47-7.55 (m, 3H, Ar), 7.79-7.84 (m, 4H, Ar); ^13C NMR spectra could not be obtained because of low solubility; UV/Vis (CH₂Cl₂): λ_max [nm] (ε [L mol⁻¹ cm⁻¹]) = 326 (6’000), 497 (41’000); APCI-HRMS (−): calcld for C₂₄H₁₆O₆ [M]⁺ 400.0947, found 400.0955.

(±)-2-Hydroxy-2-(4-(2-hydroxyethoxy)phenyl)acetic acid (S1) [3]: (±)-4-

Hydroxymandelic acid (1.50 g, 8.92 mmol) was dissolved in water, followed by the addition
of 2-chloroethanol (2.3 mL, 34 mmol, 3.8 equiv). The mixture was heated to 90 ºC. Aqueous NaOH (1.9 M, 15 mL, 29 mmol, 3.3 equiv) was added dropwise into the reaction mixture over 50 min and the solution was then kept stirring at 90 ºC for 15 h. The flask was put into an ice bath and aqueous hydrochloric acid (37%, 1.5 mL) was added slowly, which resulted in the formation of a white precipitate. Filtration and recrystallization from water (ca. 20 mL) afforded S1 as a white powder (991 mg, 4.67 mmol, 52% yield).

\[ \text{S1} \]

\[ \delta 3.69 (q, J = 4.6 \text{ Hz}, 2H, CH_2OH), 3.95 (t, J = 4.6 \text{ Hz}, 2H, CH_2OAr), 4.85 (t, J = 5.0 \text{ Hz}, 1H, CH_2OH), 4.94 (s, 1H, CHOAr), 6.89 (d, J = 9.2 \text{ Hz}, 2H, Ar), 7.29 (d, J = 9.2 \text{ Hz}, 2H, Ar), 12.5 (br s, 1H, CO_2H) \]

\[ 13C\left\{^1H\right\} \text{NMR (125 MHz, } d_6-\text{DMSO}) \delta 59.52 (1C, CH_2OH), 69.45 (1C, CH_2OAr), 71.86 (1C, CH), 114.04 (2C, Ar), 127.83 (2C, Ar), 132.22 (1C, Ar), 158.17 (1C, Ar), 174.29 (1C, CO_2H); APCI-HRMS (−): calcd for C_{10}H_{11}O_3 [(M − H) − ] 211.0607, found 211.0591. \]

(±)-2-Hydroxy-2-(4-(2-(nonyloxy)ethoxy)phenyl)acetic acid (S2): Compound S1 (300 mg, 1.41 mmol) was dissolved in DMSO. 1-Bromononane (400 µL, 2.09 mmol, 1.5 equiv) and N\((n\)-butyl)_4HSO_4 (24 mg, 0.071 mmol, 0.05 equiv) were added and the reaction mixture was stirred vigorously at 24 ºC. NaOH (284 mg, 7.1 mmol, 5 equiv) was dissolved in water (300 µL) and was added dropwise to the reaction mixture over 20 min. The reaction mixture was then heated to 45 ºC and stirred for 18 h, resulting in a slightly yellow suspension. Addition of aqueous hydrochloric acid (ca. 0.5 M, 20 mL), followed by stirring for 2 h resulted in the formation of a precipitate that was filtered and washed with water (5 mL) and hexane (10 mL). Recrystallization from EtOH afforded S2 (106 mg, 0.313 mmol, 22% yield) as a white powder. \[ 1H \text{ NMR (500 MHz, CDCl}_3\right) \delta 0.88 (t, J = 6.9 \text{ Hz}, 3H, CH}_3, \]
1.23-1.30 (m, 12H, CH2), 1.58-1.62 (m, 2H, OCH2CH2), 3.53 (t, J = 6.9 Hz, 2H, OCH2), 3.79 (t, J = 4.6 Hz, 2H, ArOCH2CH2O), 4.11 (t, J = 4.6 Hz, 2H, ArOCCH2), 5.18 (s, 1H, CHO), 6.89 (d, J = 8.6 Hz, 2H, Ar), 7.33 (d, J = 9.2 Hz, 2H, Ar); 13C{1H} NMR (125 MHz, d6-DMSO) δ 13.91 (1C, CH3), 22.04 (1C, CH2), 25.57 (1C, CH2), 28.60 (1C, CH2), 28.80 (1C, CH2), 28.94 (1C, CH2), 29.11 (1C, CH2), 31.23 (1C, CH2), 67.12 (1C, CH2O), 68.49 (1C, CH2O), 70.35 (1C, CH2O), 71.82 (1C, CH), 114.04 (2C, Ar), 127.83 (2C, Ar), 132.31 (1C, Ar), 157.99 (1C, Ar), 174.28 (1C, CO2H); APCI-HRMS (−): calcd for C19H29O5 [(M – H)] 337.2015, found 337.2008.

3-(4-(2-(Nonyloxy)ethoxy)phenyl)-7-phenylbenzo[1,2-b:4,5-b']difuran-2,6-dione (S3): Compound S2 (89 mg, 0.26 mmol) and 5-hydroxy-3-phenylbenzofuran-2(3H)-one [2] (85 mg, 0.38 mmol, 1.5 equiv) were mixed together and heated to 195 ºC over the course of 45 min while stirring. The viscous red oil was stirred for another 2.5 h at 195 ºC. Column chromatography (CH2Cl2) afforded a red band that was concentrated in vacuo. The intermediate product was dissolved in THF (5 mL) and chloranil (19 mg, 0.077 mmol, 0.30 equiv) was added, followed by stirring at 65 ºC for 1 h, resulting in a darkened red solution. Column chromatography (CH2Cl2) afforded S3 as a dark red powder (39.4 mg, 0.0673 mmol, 26% yield, ca. 90% purity). Further column chromatography (Hexane/CH2Cl2 1:4) afforded analytically pure material (17.5 mg, 0.0332 mmol, 13% yield). 1H NMR (500 MHz, CDCl3) δ 0.88 (t, J = 6.9 Hz, 3H, CH3), 1.26-1.34 (m, 12H, CH2), 1.59-1.65 (m, 2H, OCH2CH2), 3.55 (t, J = 6.9 Hz, 2H, OCH2), 3.82 (t, J = 5.2 Hz, 2H, ArOCH2CH2O), 4.21 (t, J = 4.6 Hz, 2H,
ArOCH₂), 6.89 (s, 1H, benzodifuranone), 6.92 (s, 1H, benzodifuranone), 7.08 (d,  J = 8.6 Hz, 2H, Ar), 7.47-7.55 (m, 3H, Ar), 7.79-7.83 (m, 4H, Ar); \(^{13}\)C\{\(^{1}\)H\} NMR (125 MHz, CDCl₃) \(\delta\)
14.09 (1C, CH₂), 22.66 (1C, CH₂), 26.07 (1C, CH₂), 29.26 (1C, CH₂), 29.46 (1C, CH₂), 29.56 (1C, CH₂), 29.62 (1C, CH₂), 31.87 (1C, CH₂), 67.74 (1C, OCH₂), 68.92 (1C, OCH₂), 71.81 (1C, OCH₂), 97.87, 98.49, 115.57, 122.35, 124.94, 125.73, 129.12, 129.19, 129.58, 130.33, 130.92, 136.27, 153.88, 154.53, 161.04, 167.80 (1C, C=O), 167.88 (1C, C=O); UV/Vis (CH₂Cl₂): \(\lambda_{\text{max}}\) [nm] (\(\varepsilon\) [L mol\(^{-1}\) cm\(^{-1}\)]) = 331 (6’700), 501 (45’000); \(\Phi_{\text{Fl}}\) (25 °C, CH₂Cl₂, standard: fluorescein in 0.1 M aq. NaOH, \(\Phi_{\text{Fl}}=0.93\) [4], corrected for refractive index) = 0.09; APCI-HRMS (–): calcd for C\(_{33}\)H\(_{34}\)O\(_6\) [M ] 526.2356, found 526.2334.

2. Dynamic Scanning Calorimetry (DSC) trace for compound 3 (bottom: 1st heating, top: 1st cooling).

![DSC Trace](image)

3. Cyclic voltammogram of compound S3 in THF.

![Cyclic Voltammogram](image)

\(E_{1/2}^{\text{red1}} = -0.95, E_{1/2}^{\text{red2}} = -1.43\) V vs. Fe/Fc\(^+\).
4. UV/Vis and photoluminescence spectrum of compound S3 (in CH$_2$Cl$_2$, black: absorption, grey: photoluminescence, $\lambda_{ex} = 500$ nm).

![Graph of UV/Vis and photoluminescence spectrum of compound S3](image)

5. Simulation of IPCE spectra

IPCE spectra are explained based on the estimation of the number of photons absorbed in both donor and acceptor layer.[5] For simplicity, we assume an effective active thickness of the donor and acceptor layer (expressed as $d_D^*$ and $d_A^*$), where all the absorbed photons are converted to electric current with internal quantum efficiencies of 75% and 99% for the donor and acceptor layer, respectively ($\Phi_D$ and $\Phi_A$). These internal quantum efficiencies are roughly estimated from experimental results. The total number of electrons generated in the donor and acceptor are expressed by equation (1) and (2), respectively.

\[
\text{IPCE}_D(\lambda) = \Phi_D \left( 1 - e^{-\alpha_D(\lambda)d_D^*} \right) \left\{ e^{-\alpha_D(\lambda)d_D^*} + R_{Al} \cdot e^{-\alpha_D(\lambda)d_D^* - \alpha_Ad_A^*} \right\} 
\]

\[
\text{IPCE}_A(\lambda) = \Phi_A \left( 1 - e^{-\alpha_A(\lambda)d_A^*} \right) \cdot e^{-\alpha_A(\lambda)d_D^*} \cdot \left( 1 + R_{Al} \cdot e^{-\alpha_A(\lambda)d_A^*} \right) 
\]

We assume reflectivity of the top aluminum electrode ($R_{Al} \approx 80\%$), transmittance of ITO, PEDOT:PSS, and the cathode buffer layer ($T \approx 100\%$). The absorption coefficients of the donor and acceptor ($\alpha_D$ and $\alpha_A$) obtained from experimental results are used in this simulation. Total thickness of the donor and acceptor layer is $d_D$ and $d_A$. In the Figure below (section 6), the calculated IPCE$_D$ and IPCE$_A$ spectra, assuming $d_D^*$ and $d_A^*$ to be 7 nm, are shown. Even
though we used quite rough assumptions for the calculation, the total IPCE spectra reproduce the features of the observed IPCE spectra well.

6. **Calculated IPCE spectra of the pn heterojunction devices**

![Graph of calculated IPCE spectra]

7. **References**


