

Supporting Information for

3,6-Carbazole vs 2,7-carbazole: A comparative study of hole-transporting polymeric materials for inorganic–organic hybrid perovskite solar cells

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Synthesis of carbazole derivatives, ¹H NMR and IR spectra of the polymers, and OFET performances

Synthesis

Synthesis of 3,6-dibromo-9-(2-ethylhexyl)carbazole

Analogously to the description in [S1], a solution of 3,6-dibromocarbazole (1.00 g, 3.10 mmol) and NaH (0.20 g, 4.5 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min. 2-Ethylhexyl bromide (0.90 g, 4.5 mmol) was added by a syringe. The mixture was stirred at room temperature for 24 h. Water was added, and the organic layer was extracted with CH₂Cl₂ (30 mL × 3). After the combined organic layers were dried over MgSO₄, the solvent was removed under reduced pressure. Column chromatography (SiO₂, hexane) gave the desired product as colorless liquid (1.00 g, 75%). ¹H NMR (300 MHz, CDCl₃): δ 8.08 (d, *J* = 1.7 Hz, 2H), 7.53 (dd, *J* = 1.8, 8.7 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 4.02 (d, *J* = 7.5 Hz, 2H), 2.15–1.83 (m, 1H), 1.41–1.08 (m, 8H), 1.00–0.69 ppm (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 140.49, 129.72, 124.12, 123.93, 112.64, 111.38, 48.23, 39.93, 31.54, 29.35, 24.93, 23.61, 14.61, 11.46 ppm. IR (neat): *v* = 2958, 2928, 2869, 1847, 1719, 1622, 1588, 1548, 1470, 1437, 1380, 1363, 1343, 1285, 1147, 1057, 1018, 965, 911, 867, 834, 795, 742, 713, 665, 644, 614 cm⁻¹.

Synthesis of 2,7-dibromo-9-(2-ethylhexyl)carbazole

Analogously to the description in [S2], a solution of 2,7-dibromocarbazole (1.00 g, 3.10 mmol) and NaH (0.2 g, 4.5 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min. 2-Ethylhexyl bromide (0.90 g, 4.5 mmol) was added by a syringe. The mixture was stirred at room temperature for 24 h. Water was added, and the organic layer was extracted with CH₂Cl₂ (30 mL × 3). After the combined organic layers were dried over MgSO₄, the solvent was removed under reduced pressure. Column chromatography (SiO₂, hexane) gave the desired product as colorless liquid (1.1 g, 82%). ¹H NMR (300 MHz, CDCl₃): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 1.1 Hz, 2H),

7.33 (dd, $J = 1.4, 8.3$ Hz, 2H), 4.00 (dd, $J = 2.7, 7.5$ Hz, 2H), 2.33–1.70 (m, 1H), 1.45–1.15 (m, 8H), 1.02–0.82 ppm (m, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 142.70, 123.35, 122.26, 122.07, 120.49, 113.12, 48.39, 39.84, 31.46, 29.23, 25.00, 23.72, 14.70, 11.56 ppm. IR (neat): $\nu = 2958, 2925, 2859, 1859, 1682, 1620, 1584, 1482, 1451, 1327, 1310, 1225, 1247, 1131, 1054, 997, 967, 946, 910, 876, 843, 820, 796, 767, 743, 701, 685, 666, 651, 638$ cm^{-1}

^1H NMR and IR spectra

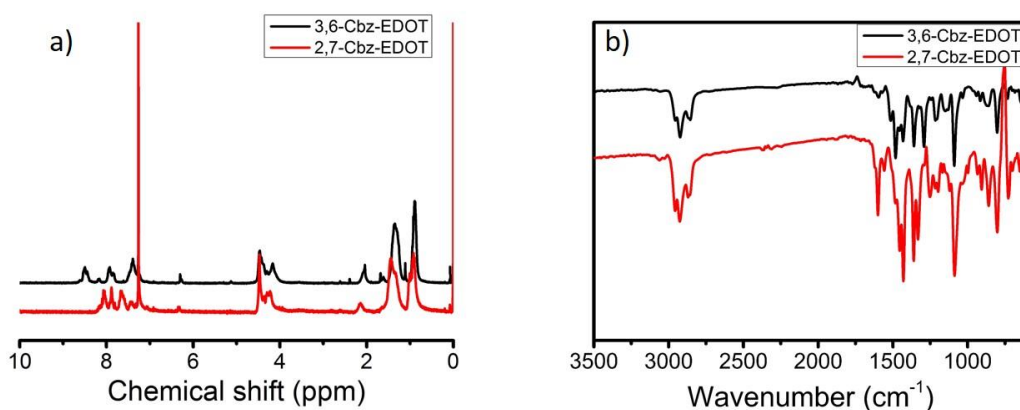


Figure S1: a) ^1H NMR spectra of 3,6-Cbz-EDOT and 2,7-Cbz-EDOT in CDCl_3 and b) IR spectra of 3,6-Cbz-EDOT and 2,7-Cbz-EDOT.

OFET performances

Top-contact/bottom-gate type organic field effect transistor (OFET) devices were fabricated using n^+ -Si/SiO₂ substrates where n^+ -Si and SiO₂ were used as the gate electrode and gate dielectric, respectively. After the substrates were washed by ultrasonication in acetone, 2-propanol, and deionized water, they were further cleaned by a UV-O₃ cleaner (Technovision, Model 208). The cleaned substrates were modified with hexamethyldisilazane (HMDS) to form a self-assembled monolayer (SAM). The polymer solutions in CH₂Cl₂ (7.0 g mL⁻¹) were spin-coated on the treated substrate to form the polymer thin films (40–60 nm thickness) in air. After that, 50 nm thick gold was deposited as the source and drain contacts using a shadow mask. The OFET devices had a channel length (L) of 100 μ m and a channel width (W) of 1 mm. The OFET performances were measured in air using a Keithley 4200 parameter analyzer on a probe stage. The hole mobilities, μ , were calculated from the data in the saturated regime using Equation S1:

$$I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2 \quad (S1)$$

where I_{SD} is the drain current in the saturated regime, W and L are the semiconductor channel width and length, respectively, C_i ($C_i = 13.7$ nF cm⁻²) is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage, respectively. $V_G - V_T$ of the devices was determined from the square root values of I_{SD} at the saturated regime.

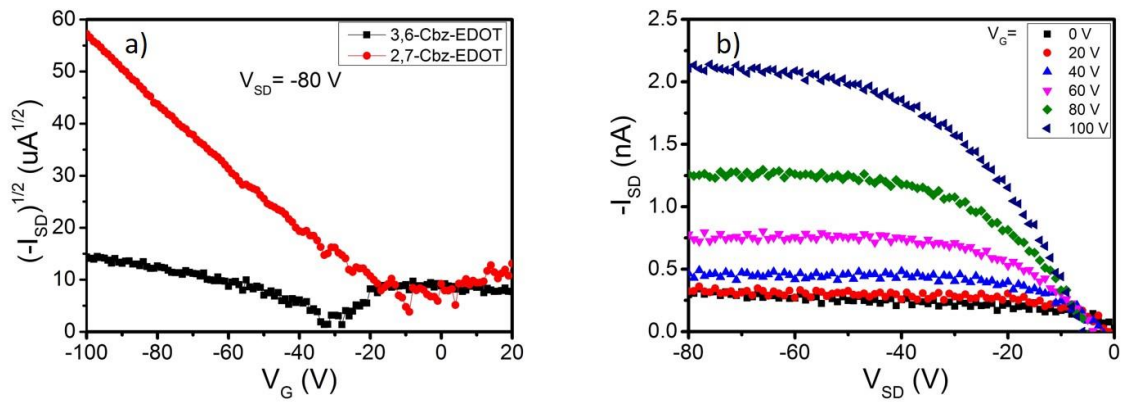


Figure S2: (a) Transfer characteristics of the OFETs based on 3,6-Cbz-EDOT and 2,7-Cbz-EDOT and (b) output characteristics of the OFET based on 2,7-Cbz-EDOT.

References

- S1. Fujita, H.; Michinobu, T. *Macromol. Chem. Phys.*, **2012**, 213, 447-457.
- S2. Michinobu, T.; Osako, H.; Shigehara, K. *Macromolecules*, **2009**, 42, 8172-8180.