Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPORTING INFORMATION

Molecular Engineering of Face-on Oriented Dopant-free Hole Transporting Material for 19% Perovskite Solar Cells

Kasparas Rakstys,‡[1] Sanghyun Paek,‡[1] Peng Gao,[1] Paul Gratia,[1] Tomasz Marszalek,[2] Giulia Grancini,[1] Kyung Taek Cho,[1] Kristijonas Genevicius,[3] Vygintas Jankauskas,[3] Wojciech Pisula,[2] Mohammad Khaja Nazeeruddin[1]*

[1]Group for Molecular Engineering of Functional Materials, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1951 Sion, Switzerland.

[2]Organisch-Chemisches Institut, Ruprecht-Karls-Universitt, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.

[3]Department of Solid State Electronics, Vilnius University, Sauletekio 3, Vilnius 10222, Lithuania.

Table of contents

Page 3 General information;

Page 4 Synthetic methods and procedures;

Page 14 ^{1}H and ^{13}C NMR spectra;

Page 17 MALDI-TOF-MS spectra;

Page 20 DFT calculations;

Page 22 CW photoluminescence spectra and Thermogravimetric analysis (TGA);

Page 23 2D GIWAXS measurements and Cross-sectional SEM micrograph;

Page 24 Electron photoemission in air spectra;

Page 25 Space-charge limited current (SCLC) hole mobility measurement;

Page 26 Solar cell fabrication and characterization;

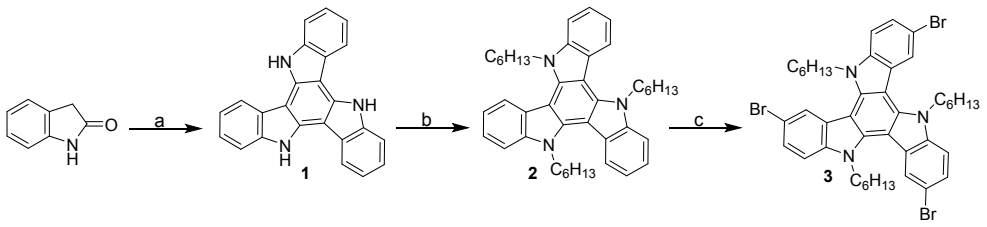
Page 27 Current (J)-voltage (V) curves with hysteresis loop;

Page 28 Statistical distribution of perovskite solar cells performance with KR321 and KR353.

General Information

All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N_2 ambience, unless otherwise noted. All dry reactions were performed with glassware that was flamed under high-vacuum and backfilled with N_2. All extracts were dried over powdered $MgSO_4$ and solvents removed by rotary evaporation under reduced pressure. Flash chromatography was performed using Silicycle UltraPure SilicaFlash P60, 40-63 μm (230-400 mesh). Thin-layer chromatography (TLC) was conducted with Merck KGaA pre-coated TLC Silica gel 60 F_{254} aluminum sheets and visualized with UV. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz), Bruker AvanceIII-400 (400 MHz), Bruker DPX-400 (400 MHz) or Bruker DRX-600 (600 MHz) spectrometer and are reported in ppm using solvent as an internal standard: Chloroform-d at 7.24 ppm and 77.23 ppm for ^{1}H and ^{13}C, respectively; Benzene-d_6 at 7.16 ppm and 128.39 ppm for ^{1}H and ^{13}C, respectively; Dimethyl Sulfoxide-d_6 at 2.50 ppm and 39.51 ppm for ^{1}H and ^{13}C, respectively. Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration. MS were recorded on 6530 Accurate-Mass Q-TOF LC/MS (Agilent Technologies) using electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) techniques or Axima-CFR plus (Shimadzu) using matrix-assisted laser desorption/ionization (MALDI) technique. UV-Vis spectra were measured with a Hewlett Packard 8453 UV-Vis spectrometer. Photoluminescence (PL) spectra were recorded with Fluorolog®-3 - Horiba fluorimeter. Cyclic voltammetry (CV) was measured with an Autolab Eco Chemie cyclic voltammeter. Thermogravimetric analysis (TGA) data were collected using TGA 4000 from PerkinElmer. A field-emission scanning electron microscope (FESEM, Merlin) was employed to analyze the morphology of the samples. An electron beam accelerated to 3 kV was used with an in-lens detector.

Synthetic methods and procedures



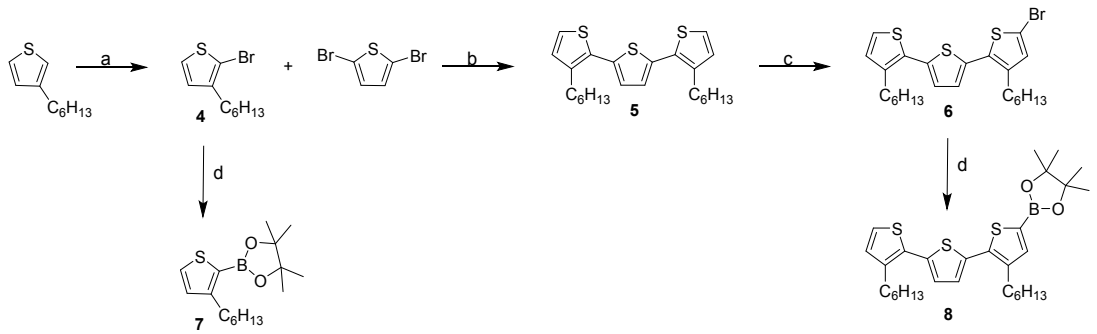
(a) $POCl_3$, 100 °C; (b) 1-iodohexane, NaH, DMF, 25–120 °C; (c) NBS in DMF, $CHCl_3$, 0–25 °C.

10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (1). Prepared with a slight modification to what was published in literature. A mixture of 2-indolinone (10 g, 75 mmol) and $POCl_3$ (50 mL) was heated at 100 °C for 8h. Then, the reaction mixture was poured into ice and neutralized carefully with NaOH. After neutralization, the precipitate was filtered to give the crude product as a brown solid. The crude solution in MeOH was absorbed on silica-gel, dried, loaded and eluated through a thick silica-gel pad with a DCM as a mobile phase. After evaporation of eluate at reduced pressure and recrystallization from acetone, pure pale yellow solid was obtained. (5.5 g, 63 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (s, 3H), 8.66 (d, J = 7.4 Hz, 3H), 7.71 (d, J = 7.9 Hz, 3H), 7.41 – 7.28 (m, 6H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 141.0, 136.4, 124.8, 124.5, 121.5, 121.4, 112.9, 103.3. $C_{24}H_{15}N_3[M^+]$ Exact Mass = 345.1266, MS (ESI-TOF) = 345.1034.

5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (2). To a solution of (1) (500 mg, 1.45 mmol, 1 eq.) in DMF (10 mL), NaH (0.1 g, 5.1 mmol, 3.5 eq.) was added at room temperature and stirred for half hour, then 1-iodohexane (1.23 g, 5.8 mmol, 4 eq.) was added via syringe and the mixture was then refluxed for 2h. The cooled mixture was poured into water and extracted with DCM. The organic phase was dried over $MgSO_4$. The product was isolated off on a silica gel column with 20 % DCM in hexane to give a product as a pale yellow solid (650 mg, 75%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.29 (d, J = 8.0 Hz, 3H), 7.64 (d, J = 8.0 Hz, 3H), 7.45 (t, J = 7.4 Hz, 3H), 7.34 (t, J = 7.6 Hz, 3H), 4.92 (m, 6H), 1.99 (p, J = 7.9 Hz, 6H), 1.38 – 1.16 (m, 18H), 0.81 (t, J = 7.1 Hz, 9H). ^{13}C NMR (100 MHz, Chloroform-d) δ 13.80, 21.56, 25.70, 29.17, 31.15, 44.76, 107.14, 110.30, 118.79, 119.80, 120.96, 127.47, 137.25, 138.29. $C_{42}H_{51}N_3[M^+]$ Exact Mass = 597.4083, MS (ESI-QTOF) = 597.4080.

3,8,13-tribromo-5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (3). To a solution of (2) (350 mg, 0.58 mmol, 1 eq.) in 30 mL $CHCl_3$, (320 mg, 1.8 mmol, 3.1 eq.) of NBS

in 5 mL DMF was added dropwise via syringe at 0 °C. After addition reaction mixture was stirred for 1h at room temperature. The mixture was extracted with DCM and organic phase was dried over $MgSO_4$. The product was isolated off on a silica gel column with 10 % DCM in hexane to give a product as a pale-yellow solid (400 mg, 82%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (d, J = 8.6 Hz, 3H), 7.71 (s, 3H), 7.42 (d, J = 8.6 Hz, 3H), 4.81 – 4.70 (m, 6H), 1.96 – 1.76 (m, 6H), 1.12 – 1.28 (m, 18H), 0.80 (t, J = 7.0 Hz, 9H). ^{13}C NMR (100 Hz, Chloroform-d) δ 125.9, 124.9, 124.2, 124.0, 123.1, 122.7, 113.4, 112.2, 53.7, 47.4, 31.8, 30.4, 26.5, 22.8, 14.2. $C_{42}H_{48}Br_3N_3[M^+]$ Exact Mass = 831.1398, MS (ESI-QTOF) = 831.1389.



(a) NBS, CH_3COOH, RT; (b) Mg, Ni(dppp)Cl_2, $(C_2H_5)O$, THF, RT–reflux; (c) NBS, DMF, -40 °C–RT; (d) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, -78 °C–RT.

2-bromo-3-hexylthiophene (4). To a solution of 3-hexylthiophene (7.66 g, 45.5 mmol, 1 eq.) in glacial acetic acid (25 mL) was added N-bromosuccinimide (8.02 g, 45.5 mmol, 1 eq.) in one portion under nitrogen at room temperature. The mixture was left to stir at RT for 24 h and was washed with water three times, extracted with hexane and the organic phase was dried over $MgSO_4$. After removal of the solvent, the residual was purified on a silica gel column using hexane as eluent. (10.7 g, 95% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.18 (d, J = 5.6 Hz, 1H), 6.79 (d, J = 5.6 Hz, 1H), 2.62-2.49 (m, 2H), 1.60-1.54 (m, 2H), 1.36-1.26 (m, 6H), 0.91-0.86 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 142.1, 128.4, 125.3, 108.9, 77.4, 77.2, 76.9, 31.8, 29.9, 29.5, 29.0, 22.8, 14.2. $C_{10}H_{15}BrS[M^+]$ Exact Mass = 246.0078, MS (ESI-QTOF) = 246.01.

3,3''-dihexyl-2,2':5',2''-terthiophene (5). Mg turnings (0.89 g, 36.6 mmol, 3.8 eq.) were suspended in 30 mL of diethyl ether. A solution of (4) (7 g, 28.3 mmol, 2.9 eq.) in 20 mL of diethyl ether was added dropwise to the reaction vessel and the mixture was refluxed for 1 h. The

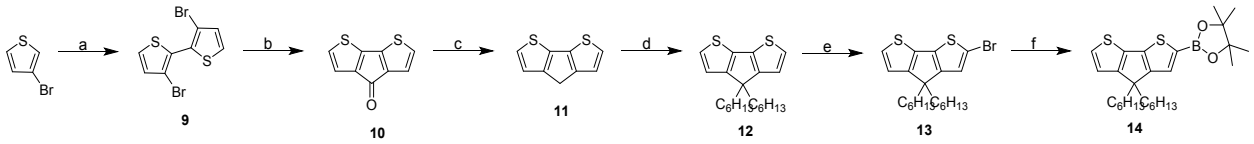
solution was cannulated into a second flask, which contained a solution of 2,5-dibromothiophene (2.35 g, 9.7 mmol, 1 eq.) and Ni(dppp)Cl_2 (65 mg, 0.12 mmol, 12%) in 30 mL of diethyl ether and was refluxed for 1.5 h. The organic layer was washed with water three times and extracted with DCM. The solvent was removed via rotary evaporation to yield a brown oil which was purified on a silica gel column using hexane as eluent to yield 3.5 g (86%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.21 (d, 2H), 7.09 (s, 2H), 6.98 (d, 2H), 2.82 (t, 4H), 1.71-0.91 (m, 22H). ^{13}C NMR (100 MHz, Chloroform-d) δ 139.72, 136.09, 130.07, 126.08, 123.76, 31.72, 30.76, 29.34, 29.28, 22.67, 14.12. $C_{24}H_{32}S_3[M^+]$ Exact Mass = 416.1666, MS (ESI-QTOF) = 416.1668.

5-bromo-3,3''-dihexyl-2,2':5',2''-terthiophene (6). Compound (5) (3 g, 7.2 mmol, 1 eq.) was dissolved in DMF (40 mL) and cooled to -40 °C. NBS (1.28 g, 7.2 mmol, 1 eq.) was added in small portions during the period of 4 h. After stirring the reaction mixture at RT overnight, water was added, and the solution was extracted with DCM. The crude product was purified by column chromatography on silica gel using hexane. Yield 2.4 g of yellow oil (67%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.06 (d, J = 5.2, 2H), 7.01 (d, J = 3.6, 2H), 6.89 (s, 1H) 2.74 (t, J = 8.0, 4H), 1.58 (m, 4H), 1.31 (m, 12H), 0.90 (t, J = 6.6, 6H). $C_{24}H_{31}BrS_3[M^+]$ Exact Mass = 494.0771, MS (ESI-QTOF) = 494.068.

2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7). Compound (4) (3.8 g, 15 mmol, 1 eq.) was dissolved in 50 mL THF. The solution was cooled to -78 °C. *n*-Butyllithium (2.5M in hexane, 7 mL, 16.5 mmol, 1.1 eq.) was added dropwise by syringe and the solution was stirred for 1 h at -78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.14 g, 16.5 mmol, 1.1 eq.) was added dropwise by syringe. The solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding 30 mL of water. The organic layer was extracted with DCM (2 x 40 mL), washed with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. After filtration, the organic layer was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 40% DCM in hexane. Yield 2.7 g of yellow oil (71%). ^{1}H NMR (400 MHz, Dichloromethane-d_2) δ 7.43 (s, 1H), 7.21 (d, J = 5.2 Hz, 1H), 7.14 (d, J = 3.7 Hz, 1H), 7.08 (d, J = 3.8 Hz, 1H), 6.97 (d, J = 5.2 Hz, 1H), 2.80 (t, J = 7.6 Hz, 4H), 1.78 – 1.55 (m, 4H), 1.34 (s, 24H), 0.88 (t, J = 6.1 Hz, 6H). $C_{30}H_{43}BO_2S_3[M^+]$ Exact Mass = 542.2518, MS (ESI-QTOF) = 542.252.

2-(3,3''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8). Compound (6) (2.2 g, 4.4 mmol, 1 eq.) was dissolved in 30 mL THF. The solution was cooled to

-78 °C. *n*-Butyllithium (2.5M in hexane, 2 mL, 4.9 mmol, 1.1 eq.) was added dropwise by syringe and the solution was stirred for 1 h at -78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.9 g, 4.9 mmol, 1.1 eq.) was added dropwise by syringe. The solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding 30 mL of water. The organic layer was extracted with DCM (2 x 40 mL), washed with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. After filtration, the organic layer was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 20-50% DCM in hexane. Yield 1.2 g (50%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 (d, J = 4.6 Hz, 1H), 7.01 (d, J = 4.7 Hz, 1H), 2.89 (t, J = 7.7 Hz, 2H), 1.65-1.57 (m, 2H), 1.33 (s, 12H), 1.29 (m, 6H), 0.91-0.89 (t, 3H). ^{13}C NMR (101 MHz, CDCI3) δ 154.83, 148.34, 131.39, 130.42, 83.65, 31.91, 31.81, 30.26, 29.11, 24.93, 22.76, 14.26. $C_{16}H_{27}BO_2S[M^+]$ Exact Mass = 294.1825, MS (ESI-QTOF) = 294.203.



(a) LDA, $CuCl_2$, THF, -78 °C–RT; (b) *n*-BuLi, dimethyl carbamoyl chloride, Et_2O, -78 °C–RT; (c) KOH, $NH_2NH_2{\cdot}H_2O$, ethylene glycol, 180 °C; (d) $C_6H_{13}Br$, KOH, KI, DMSO, -78 °C–RT; (e) NBS, DMF, -40 °C–RT; (f) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, -78 °C–RT.

3,3'-dibromo-2,2'-bithiophene (9). To a solution of 3-bromothiophene (32 g, 100 mmol, 1 eq.) in freshly distilled THF (240 mL) at -78 C was added with lithium diisopropylamide (LDA) (50 mL, 100 mmol, 1 eq.) over 30 min. After 1 h stirring at -78 C, the reaction solution was added with anhydrous $CuCl_2$ (52.8 g, 400 mmol, 4 eq.) in portions. After another 1 h stirring at -78 C, the reaction mixture was then warmed to room temperature and stirred overnight. Quenched with saturated aqueous NH_4Cl, the organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated via rotary evaporation. The pure compound was obtained as a pale yellow solid (24 g, 74%) with flush chromatography over silica gel column using hexane as eluent. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.08 (d, J= 5.4 Hz, 2H), 7.41 (d, J= 5.4 Hz, 2H).^{13}C NMR (100

MHz, Chloroform-d) δ 112.65, 127.53, 128.89. 130.81. $C_8H_4Br_2S_2[M^+]$ Exact Mass = 321.8121, MS (ESI-QTOF) = 321.824.

4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one (10). To a solution of (9) (24 g, 46 mmol, 1 eq.) in Et_2O (350 mL), *n*-BuLi 2.5M in hexane (41 mL, 102 mmol, 2.2 eq.) was added dropwise at -78 °C. After keeping at -78 °C for 2 h, dimethyl carbamoyl chloride (5.66 mL, 46 mmol, 1 eq.) was added, then the reaction mixture warmed slowly to RT overnight. The reaction mixture was quenched with water at 0°C, extracted with Et_2O and then washed with saturated ammonium chloride and water. After drying over $MgSO_4$, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (DCM:hexane, 1:1) as eluent to yield 7g of purple solid (79%). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.99 (d, J = 4.8 Hz, 2H), 7.04 (d, J = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 121.7, 127.1, 142.4, 149.2, 182.7. $C_9H_4BOS_2[M^+]$ Exact Mass = 191.9704, MS (ESI-QTOF) = 191.982.

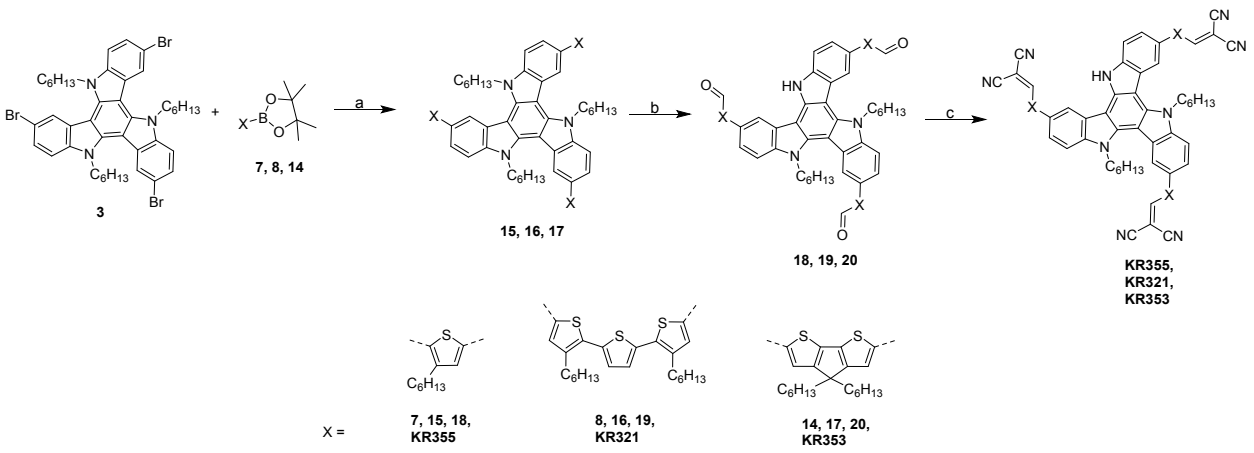
4H-cyclopenta[2,1-b:3,4-b']dithiophene (11). KOH (6 g, 107 mmol, 3.5 eq.) and hydrazine hydrate (12.15 ml) were added to a suspension of compound (10) (6 g, 31 mmol, 1 eq.) in ethylene glycol (200 ml). Reaction mixture was refluxed at 180 °C during 8 h under argon. After cooling down, water (100 ml) with HCl and 300 ml DCM was added. Organic layer was isolated, washed with water (2×200 ml) and dried over anhydrous $MgSO_4$. After removing the solvent by rotary evaporation and purification by column chromatography, using hexane as an eluent, pure product was obtained (3.3 g, 60% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.19 (d, J = 4 Hz, 2H), 7.10 (d, J = 4 Hz, 2H), 3.56 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 149.9, 138.9, 124.7, 123.2, 31.8. $C_9H_6S_2[M^+]$ Exact Mass = 177.9911, MS (ESI-QTOF) = 177.991.

4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (12). To a solution of (11) (1.5 g, 8.4 mmol, 1eq.) in dimethyl sulfoxide (100 mL) was added hexyl bromide (3.5 g, 21.2 mmol, 2.5 eq.) and a catalytic amount of potassium iodide (50 mg). The mixture was cooled to 0 °C, followed by the slow addition of solid potassium hydroxide (1.5 g). The mixture was stirred at room temperature overnight. The mixture was then poured into water and the organic phase extracted with DCM and dried over $MgSO_4$, filtered, and concentrated to give the crude product as yellow oil. Purification via flash chromatography with hexane gave pure product as colorless oil. Yield 2.4 g (82%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.14 (d, J = 4.8 Hz, 2H), 6.92 (d,

J= 4.8 Hz, 2H), 1.81 (m, 4H), 1.13 (m, 12H), 0.94 (m, 4H), 0.81 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 158.08, 136.43, 124.38, 121.59, 53.22, 37.75, 31.60, 29.68, 24.47, 22.58, 14.01. $C_{21}H_{30}S_2[M^+]$ Exact Mass = 346.1789, MS (ESI-QTOF) = 346.192.

2-bromo-4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (13). Compound (12) (2.4 g, 6.9 mmol, 1 eq.) was dissolved in DMF (30 mL) and cooled to -40 °C. NBS (1.23 g, 6.9 mmol, 1 eq.) was added in small portions during the period of 4 h. After stirring the reaction mixture at RT overnight, water was added, and the solution was extracted with DCM. The crude product was purified by column chromatography on silica gel using hexane. Yield 2.3 g (78%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.16 (d, J = 4.8 Hz, 1H), 6.94 (s, 1H), 6.91 (d, J = 4.8 Hz, 1H), 1.79 (m, 4H), 1.18 (m, 4H), 1.13 (m, 8H), 0.91(m, 4H), 0.83 (t, J = 7.2 Hz, 6H). $C_{21}H_{29}BrS_2[M^+]$ Exact Mass = 424.0894, MS (ESI-QTOF) = 424.222.

2-(4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14). Compound (13) (2.3 g, 5.4 mmol, 1 eq.) was dissolved in 30 mL THF. The solution was cooled to -78 °C. *n*-Butyllithium (2.5M in hexane, 2.4 mL, 5.9 mmol, 1.1 eq.) was added dropwise by syringe and the solution was stirred for 1 h at -78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.1 g, 5.9 mmol, 1.1 eq.) was added dropwise by syringe. The solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding 30 mL of water. The organic layer was extracted with DCM (2 x 40 mL), washed with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. After filtration, the organic layer was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 20-30% DCM in hexane. Yield 1.1 g (43%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 (m, 1H), 7.17 (m, 1H), 6.92, (m, 1H), 1.85 (m, 4H), 1.35 (s, 12H), 0.85 (m, 16H), 0.74 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-d: δ 160.97, 144.07, 131.87, 83.97, 52.66, 43.20, 35.13, 33.80, 28.31, 24.77, 22.77, 10.57. $C_{27}H_{41}BO_2S_2[M^+]$ Exact Mass = 472.2641, MS (ESI-QTOF) = 472.252.



(a) $Pd(PPh_3)_4$, 2 M aq. K_2CO_3, THF, 80 °C; (b) $POCl_3$/DMF, DCE, 0 °C–reflux; (c) $CH_2(CN)_2$, Et_3N, DCM, RT.

A general method for Suzuki-Miyaura coupling reaction:

To a degassed mixture of (3) (0.4 g, 0.48 mmol, 1 eq.), 4,4,5,5-tetramethyl-1,3,2-dioxaborolanes (7, 8 or 14) 3.5 eq. in THF (15 mL) and 2 M aqueous K_2CO_3 (3 mL), $Pd(PPh_3)_4$ (20 %) was added under N_2, the resulting solution was heated to 80 ^oC overnight. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The organic layer was concentrated and the residue was purified by column chromatography.

5,10,15-trihexyl-3,8,13-tris(3-hexylthiophen-2-yl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (15). The pure compound was obtained after column chromatography on silica gel using 20% DCM in hexane. Yield 0.52 g (99%). ^1H NMR (400 MHz, Chloroform-d) δ 8.33 (d, J = 8.7 Hz, 3H), 7.73 (s, 3H), 7.47 (d, J = 8.2 Hz, 3H), 7.11 (d, J = 5.2 Hz, 3H), 6.97 (d, J = 4.9 Hz, 3H), 5.15 – 4.76 (m, 6H), 2.87 (m, 6H), 2.65 (m, 6H), 2.09 (s, 6H), 1.89 – 1.60 (m, 6H), 1.50 – 1.11 (m, 21H), 1.07 – 0.69 (m, 27H). $C_{72}H_{93}N_3S_3[M^+]$ Exact Mass = 1095.6532, MS (ESI-QTOF) = 1095.523.

3,8,13-tris(3,3''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)-5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (16). The pure compound was obtained after column chromatography on silica gel using 10% acetone in hexane. Yield 0.7 g (80%). ^1H NMR (400 MHz, Methylene Chloride-d_2) δ 8.15 (d, J = 8.5 Hz, 3H), 7.74 (s, 3H), 7.59 (d, J = 7.9 Hz, 3H), 7.36 (s, 3H), 7.28 (d, J = 5.1 Hz, 3H), 7.22 (d, J = 3.8 Hz, 3H), 7.17 (d, J = 3.7 Hz, 3H), 7.05 (d,

J = 5.2 Hz, 3H), 4.98 – 4.51 (m, 6H), 3.06 – 2.63 (m, 18H), 2.12 – 1.64 (m, 18H), 1.61 – 1.16 (m, 48H), 1.07 – 0.71 (m, 27H). $C_{114}H_{141}N_3S_9[M^+]$ Exact Mass = 1839.8612, MS (ESI-QTOF) = 1839.909.

3,8,13-tris(4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (17). The pure compound was obtained after column chromatography on silica gel using 10% DCM in hexane. Yield 0.58 g (74%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.30 (d, J = 8.8 Hz, 3H), 7.87 (s, 3H), 7.69 (d, J = 8.0 Hz, 3H), 7.38 (s, 3H), 7.24 (d, J = 4.8 Hz, 3H), 7.02 (d, J = 4.7 Hz, 3H), 5.18 – 4.88 (m, 6H), 2.12 – 1.88 (m, 18H), 1.41 – 1.05 (m, 66H), 0.86 (m, 27H). $C_{105}H_{135}N_3S_6[M^+]$ Exact Mass = 1629.8980, MS (ESI-QTOF) = 1630.069.

A general method for Vilsmeier–Haack formylation reaction:

Phosphorous oxychloride (5 eq.) was added dropwise to a stirred *N*,*N*-dimethylformamide (5 eq.) at the temperature of ice water under nitrogen atmosphere. Then the mixture was added to the solution of (15, 16 or 17) 1 eq. in 1,2-dichloroethane (30mL) dropwise at 0 °C. After addition, the mixture was refluxed overnight. The resulting mixture was neutralized to pH = 7-8 with aqueous NaOH solution (20 wt %), extracted with DCM and the residue was chromatographed on a silica gel column.

5,5',5''-(5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-triyl)tris(4-hexylthiophene-2-carbaldehyde) (18). The pure compound was obtained after column chromatography on silica gel using DCM, gradually increasing polarity up to 5% THF in DCM. Yield 0.6 g (86%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.96 (s, 3H), 8.34 (d, J = 8.4 Hz, 3H), 7.77 (d, J = 7.1 Hz, 6H), 7.51 (d, J = 8.1 Hz, 3H), 2.90 (t, J = 7.9 Hz, 6H), 2.07 (m, 6H), 1.72 (m, 6H), 1.50 – 1.11 (m, 42H), 0.98 – 0.67 (m, 18H). $C_{75}H_{93}N_3O_3S_3[M^+]$ Exact Mass = 1179.6379, MS (ESI-QTOF) = 1179.565.

5'',5'''',5''''''-(5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-triyl)tris(3,3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (19). The pure compound was obtained after column chromatography on silica gel using 20-30% acetone in hexane. Yield 0.6 g

(95%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 9.87 (s, 3H), 8.03 (d, J = 8.7 Hz, 3H), 7.64 (d, J = 5.4 Hz, 6H), 7.51 (d, J = 7.9 Hz, 3H), 7.31 (d, J = 3.7 Hz, 6H), 7.20 (d, J = 3.7 Hz, 3H), 4.79 – 4.51 (m, 6H), 3.00 – 2.74 (m, 6H), 1.85 (m, 18H), 1.66 – 1.14 (m, 60H), 0.97 (t, 27H). $C_{117}H_{141}N_3O_3S_9[M^+]$ Exact Mass = 1923.8459, MS (ESI-QTOF) = 1923.736.

6,6',6''-(5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-triyl)tris(4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde) (20). After addition of Vilsmeier complex, the mixture was stirred overnight at room temperature. The pure compound was obtained after column chromatography on silica gel using 15-20% THF in hexane. Yield 0.5 g (73%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.90 (s, 3H), 8.32 (d, J = 8.1 Hz, 3H), 7.89 (s, 3H), 7.72 (d, J = 8.0 Hz, 3H), 7.65 (s, 1H), 7.42 (s, 3H), 5.03 (t, 6H), 2.10 – 1.92 (m, 18H), 1.29 (d, J = 18.1 Hz, 66H), 0.96 – 0.67 (m, 27H). $C_{108}H_{135}N_3O_3S_6[M^+]$ Exact Mass = 1713.8828, MS (ESI-QTOF) = 1714.091.

A general method for Knoevenagel condensation reaction:

Aldehyde (18, 19 or 20) 1 eq. and malononitrile (6 eq.) were dissolved in dry DCM (50 mL) and stirred for 1 h with a few drops of triethylamine at room temperature. After completion of the reaction monitored by TLC, the mixture was acidified with few drops of conc. HCl, washed with water the organic layer extracted with CH_2Cl_2, dried over anhydrous magnesium sulfate and filtered. The column chromatography was performed to purify the final compound. Isolated compound was dissolved in THF and dropped into MeOH, precipitate was collected by filtration, washed with MeOH and dried.

2,2',2''-(((5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-triyl)tris(4-hexylthiophene-5,2-diyl))tris(methanylylidene))trimalononitrile (KR355). The pure compound was obtained after column chromatography on silica gel using 15-20% THF in hexane. Yield 0.6 g (89%). ^{1}H NMR (400 MHz, THF-d_8) δ 8.43 (d, J = 8.3 Hz, 3H), 8.30 (s, 3H), 7.90 (d, J = 15.0 Hz, 6H), 7.58 (d, J = 8.3 Hz, 3H), 5.14 – 4.94 (m, 6H), 2.95 (m, 6H), 2.09 – 1.88 (m, 6H), 1.50 – 1.05 (m, 42H), 1.01 – 0.64 (m, 18H). ^{13}C NMR (100 MHz, THF-d8) δ

151.46, 151.07, 141.66, 140.94, 140.48, 139.94, 133.57, 127.43, 123.73, 121.90, 121.07, 114.18, 113.44, 111.20, 103.24, 75.88, 46.79, 31.65, 31.57, 31.37, 30.58, 29.66, 29.15, 28.96, 28.50, 26.12, 22.54, 22.34, 13.42, 13.28. C84H93N9S3[M+] Exact Mass = 1323.6716, MS (ESI-QTOF) = 1323.837.

2,2',2''-(((5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-triyl)tris(3,3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))tris(methanylylidene))trimalononitrile (KR321). The pure compound was obtained after column chromatography on silica gel starting with pure DCM and switching to 20% hexane in chloroform at the end. Yield 0.4 g (62%). ^{1}H NMR (400 MHz, THF-d_8) δ 8.29 (d, J = 10.2 Hz, 3H), 8.20 (s, 3H), 7.95 (d, J = 6.3 Hz, 3H), 7.76 (s, 6H), 7.67 (d, J = 8.5 Hz, 3H), 7.50 (d, J = 5.0 Hz, 6H), 7.32 (s, 3H), 5.15 – 4.91 (m, 6H), 2.96 (t, J = 7.3 Hz, 18H), 1.98 (m, 6H), 1.62 – 1.09 (m, 60H), 1.06 – 0.49 (m, 27H). ^{13}C NMR (100 MHz, THF-d_8) δ 153.11, 150.40, 144.78, 144.18, 142.41, 142.01, 141.65, 140.35, 139.92, 139.66, 139.60, 138.26, 133.34, 133.24, 133.02, 132.72, 128.95, 128.85, 128.78, 128.39, 126.03, 125.97, 114.12, 113.38, 76.10, 55.89, 52.70, 31.77, 31.66, 31.33, 30.53, 30.01, 29.80, 29.67, 29.39, 29.17, 29.09, 22.63, 22.58, 22.36, 13.52, 13.48, 13.37. $C_{126}H_{141}N_9S_9[M^+]$ Exact Mass = 2067.8796, MS (ESI-QTOF) = 2067.966.

2,2',2''-(((5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-triyl)tris(4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))tris(methanylylidene))trimalononitrile (KR353). The pure compound was obtained after column chromatography on silica gel using 20% THF in hexane. Yield 0.5 g (93%). ^{1}H NMR (400 MHz, THF-d_8) δ 8.40 (d, J = 8.4 Hz, 3H), 8.19 (s, 3H), 8.10 (s, 3H), 7.80 (d, J = 12.0 Hz, 6H), 7.72 (s, 3H), 5.20 – 5.03 (m, 6H), 2.11 (m, 18H), 1.98 (m, 6H), 1.40 – 1.00 (m, 60H), 0.88 (t, J = 6.6 Hz, 27H). ^{13}C NMR (100 MHz, THF-d_8) δ 165.18, 157.91, 152.98, 151.06, 150.83, 141.62, 139.65, 136.12, 134.03, 131.96, 129.37, 123.45, 122.03, 118.12, 117.52, 114.83, 114.42, 107.44, 103.78, 71.27, 54.17, 37.71, 31.58, 31.33, 29.66, 26.15, 22.53, 22.36, 13.39, 13.30. $C_{117}H_{135}N_9S_6[M^+]$ Exact Mass = 1857.9165, MS (ESI-QTOF) = 1858.143.

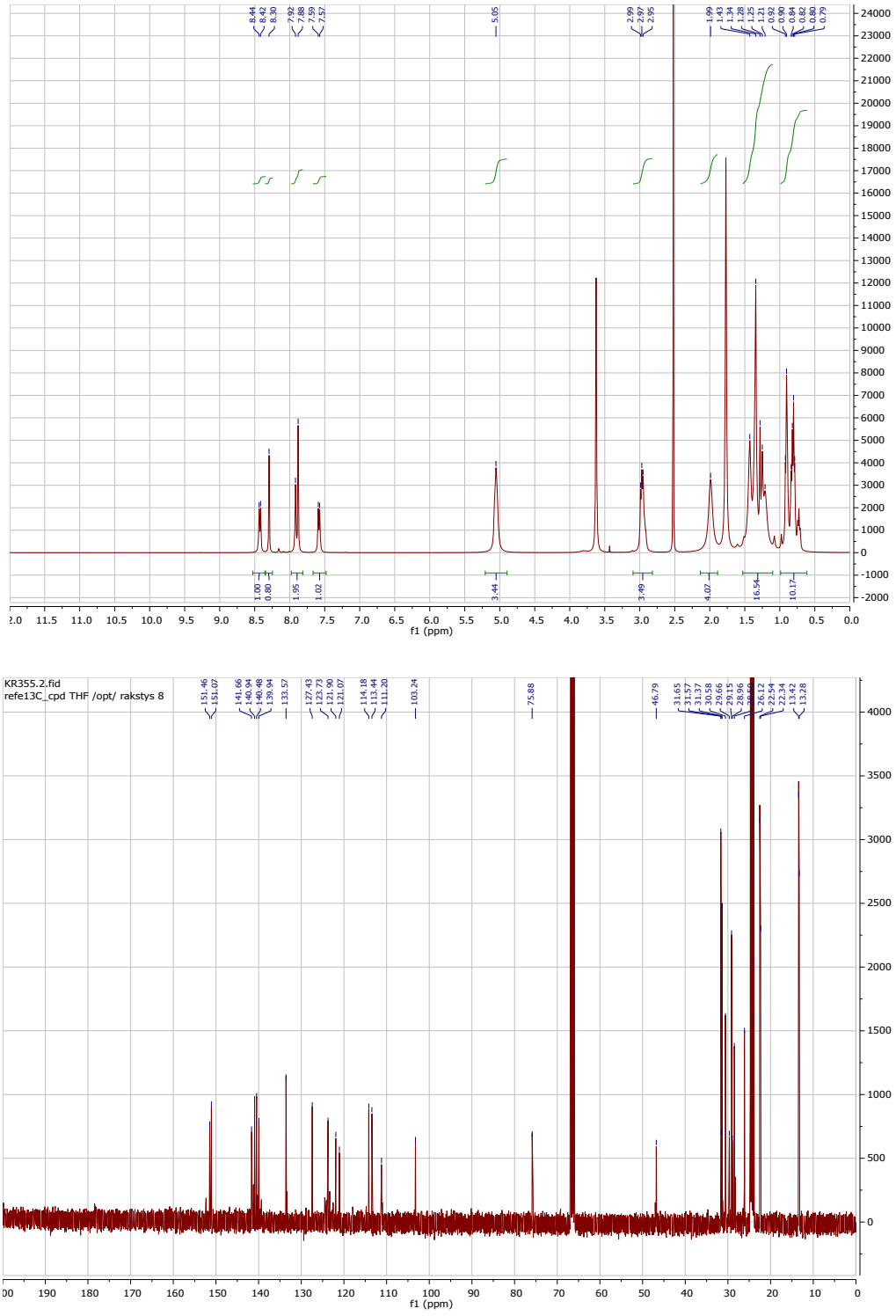


Figure S1. ^{1}H and ^{13}C NMRs of KR355.

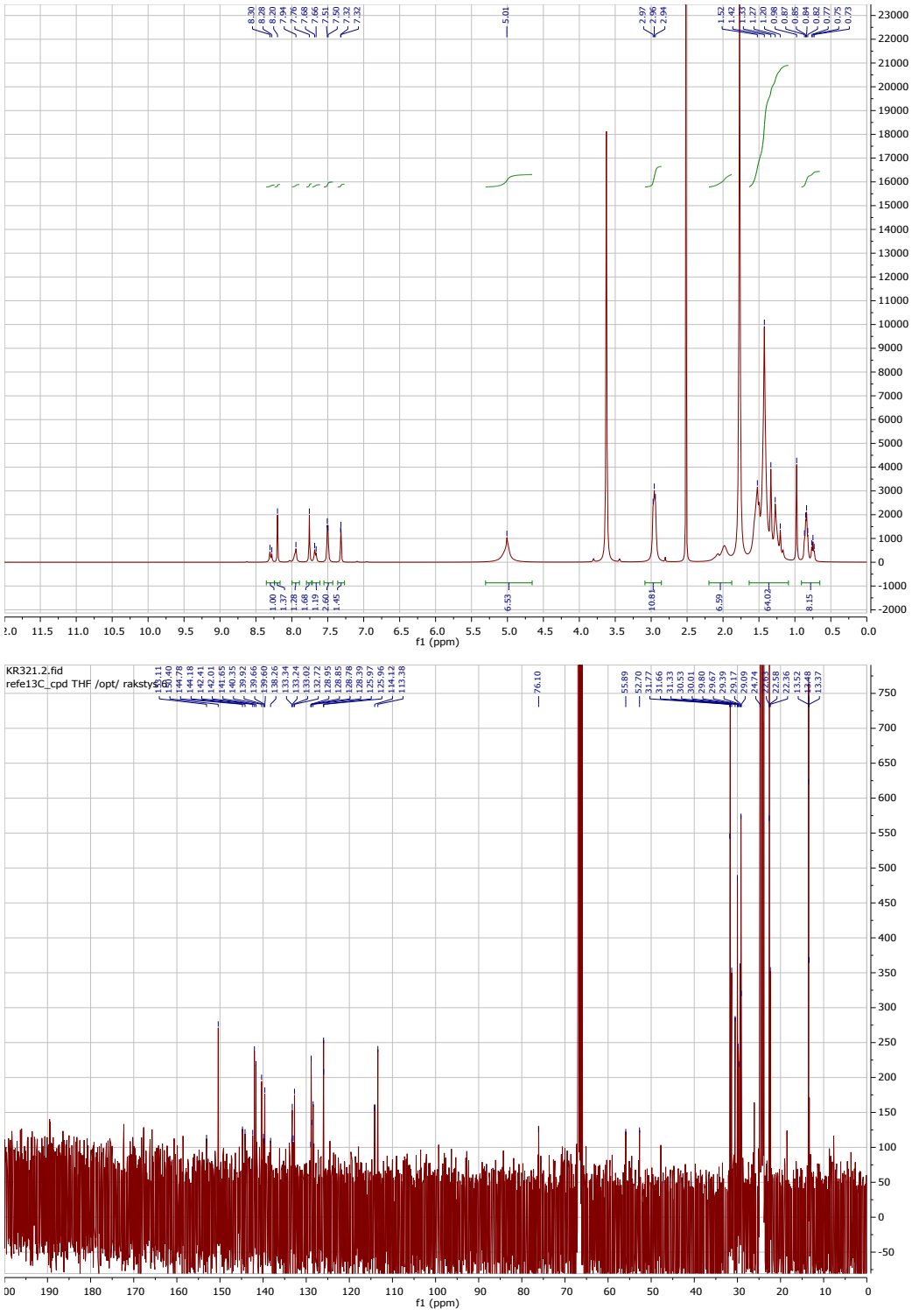


Figure S2. ^{1}H and ^{13}C NMRs of KR321.

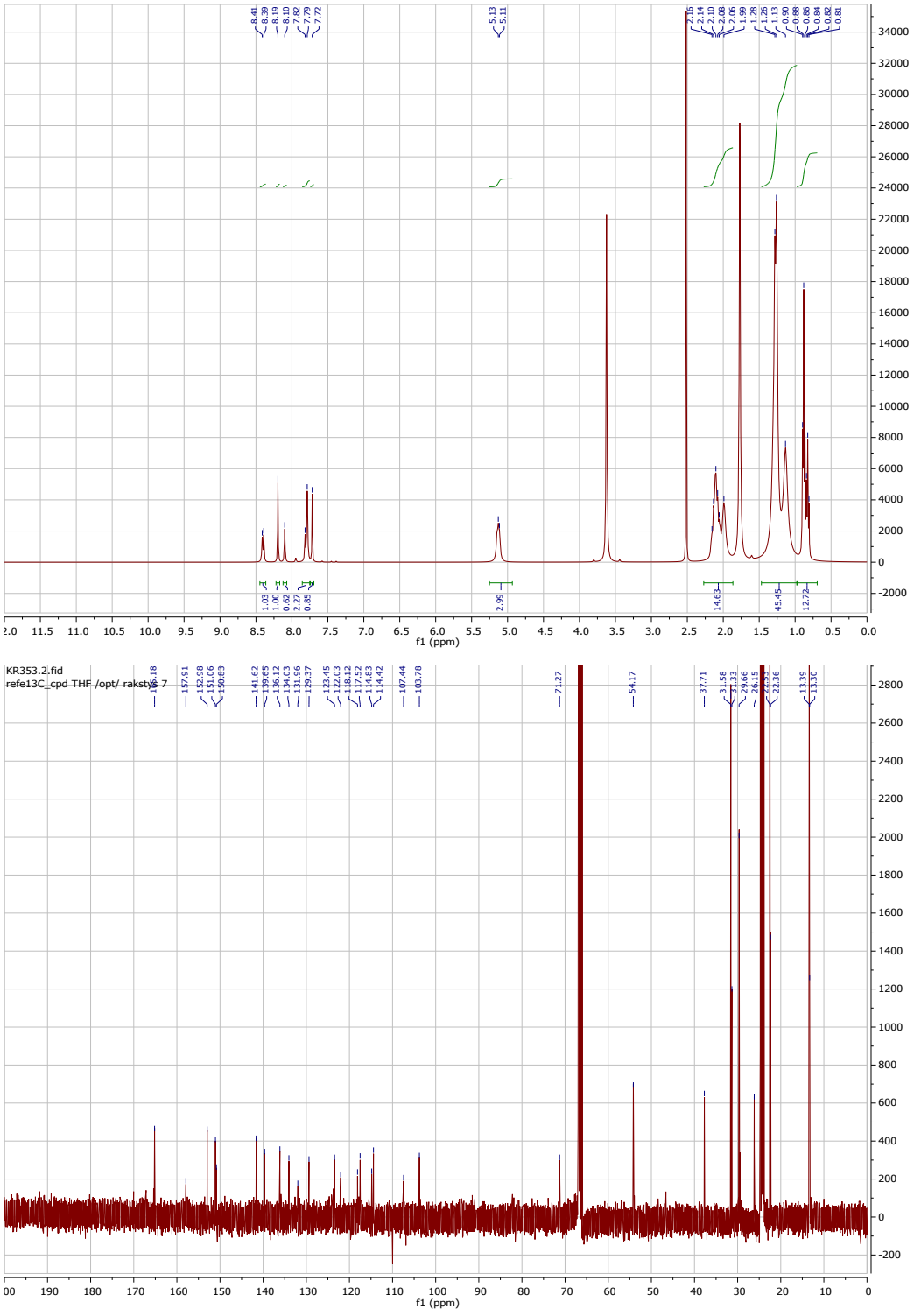


Figure S3. ^{1}H and ^{13}C NMRs of KR353.

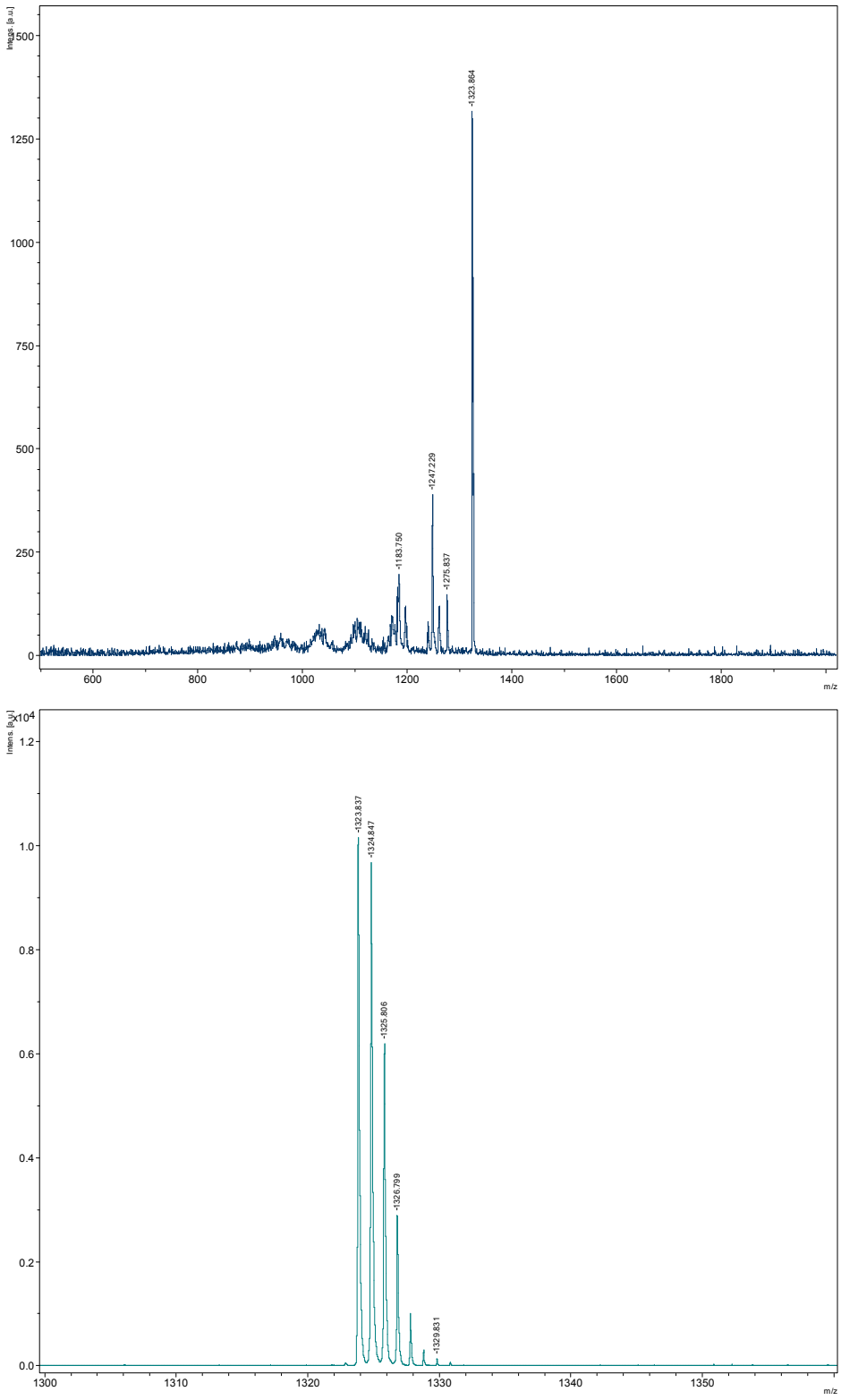


Figure S4. MALDI-TOF-MS spectra in wide and narrow mass ranges of KR355.

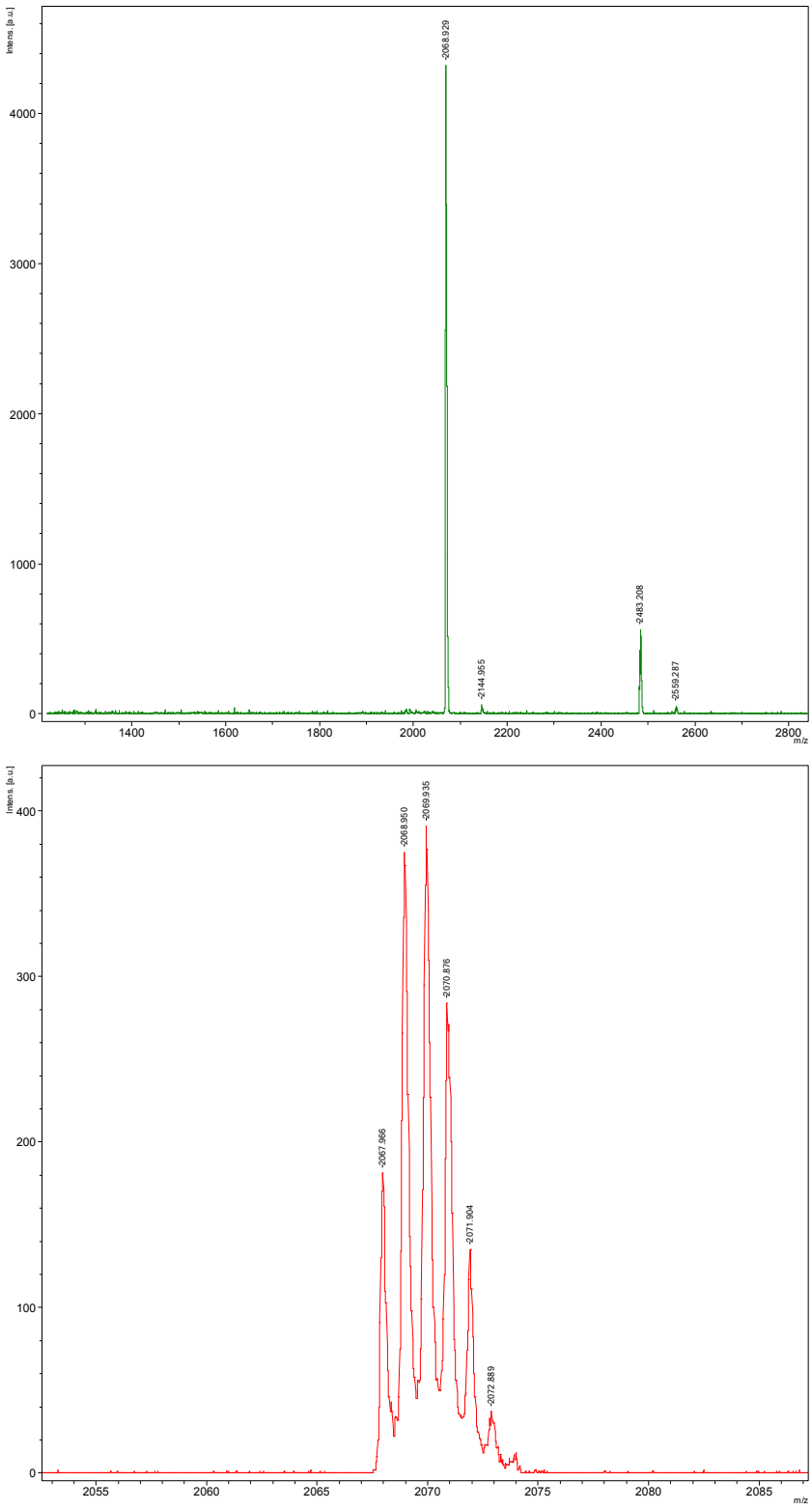


Figure S5. MALDI-TOF-MS spectra in wide and narrow mass ranges of KR321.

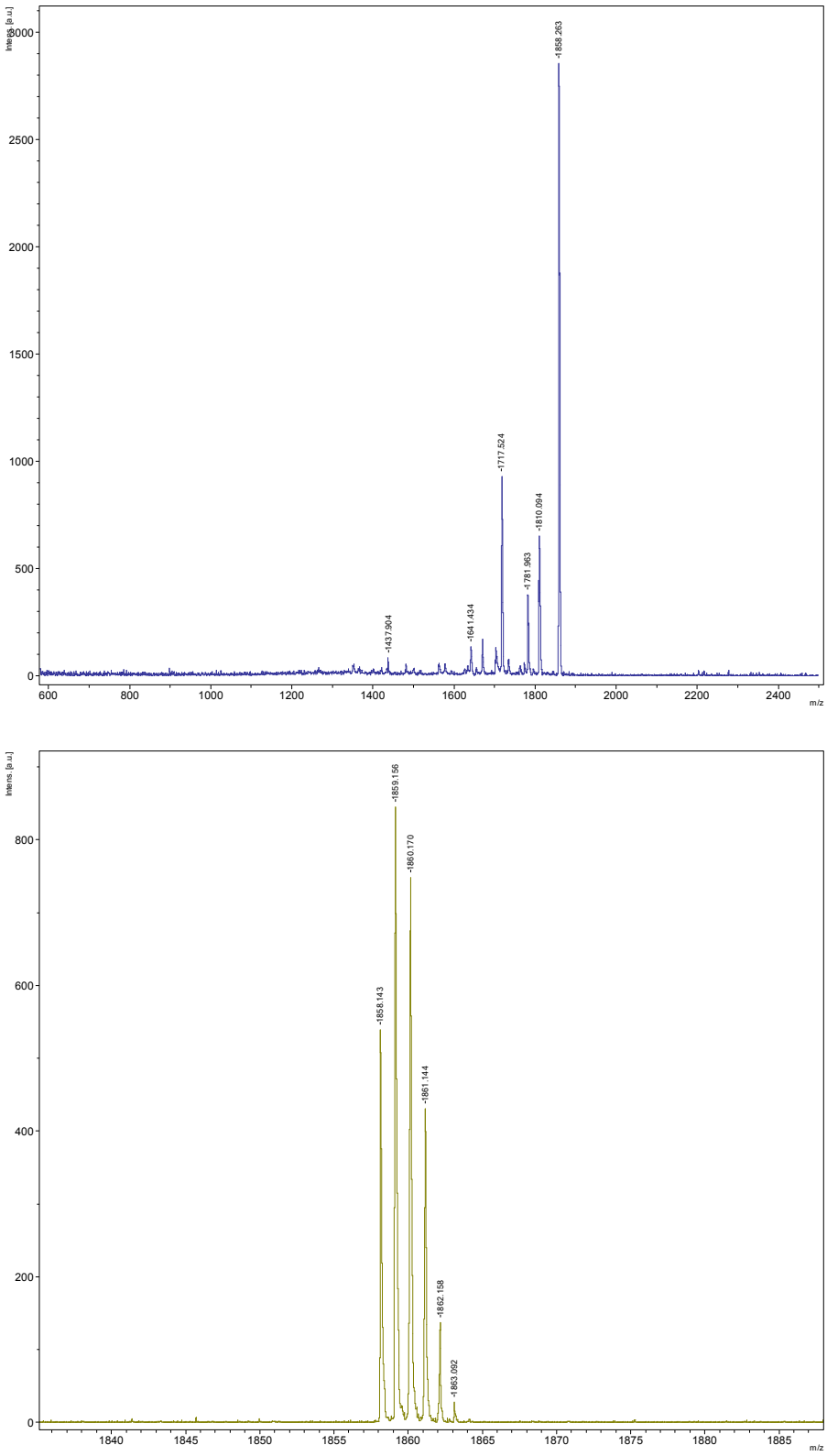
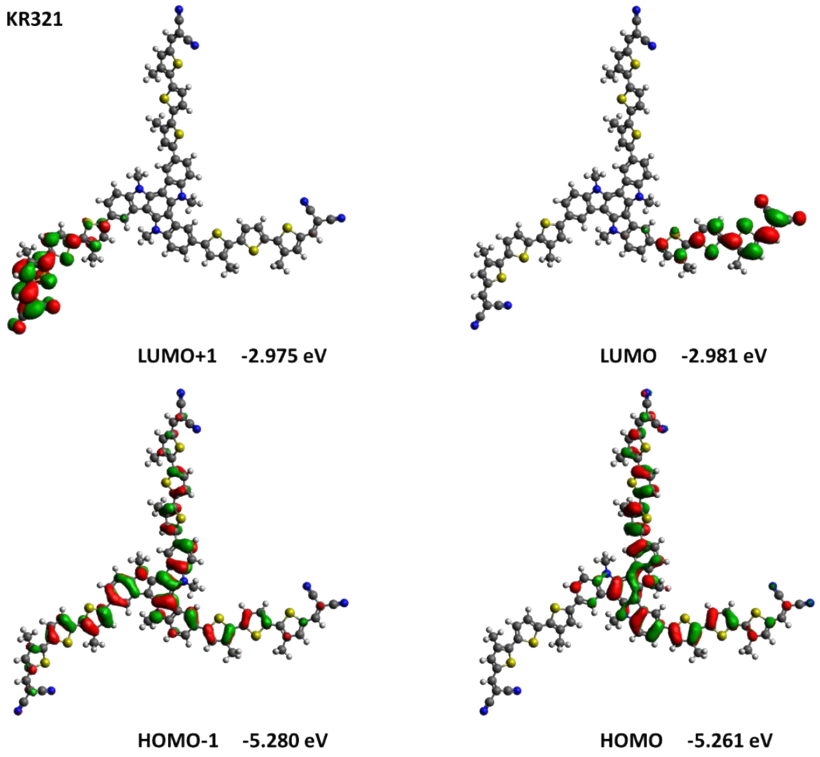


Figure S6. MALDI-TOF-MS spectra in wide and narrow mass ranges of KR353.

DFT calculation

The geometrical and electronic properties of the compound were performed with the Gaussian 09 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals) with the B3LYP/6-31G* atomic basis set. The excitation transitions were calculated using time-dependent density functional theory (TD-DFT) calculations with B3LYP/6-31g*. Molecular orbitals were visualized using Avogadro™.



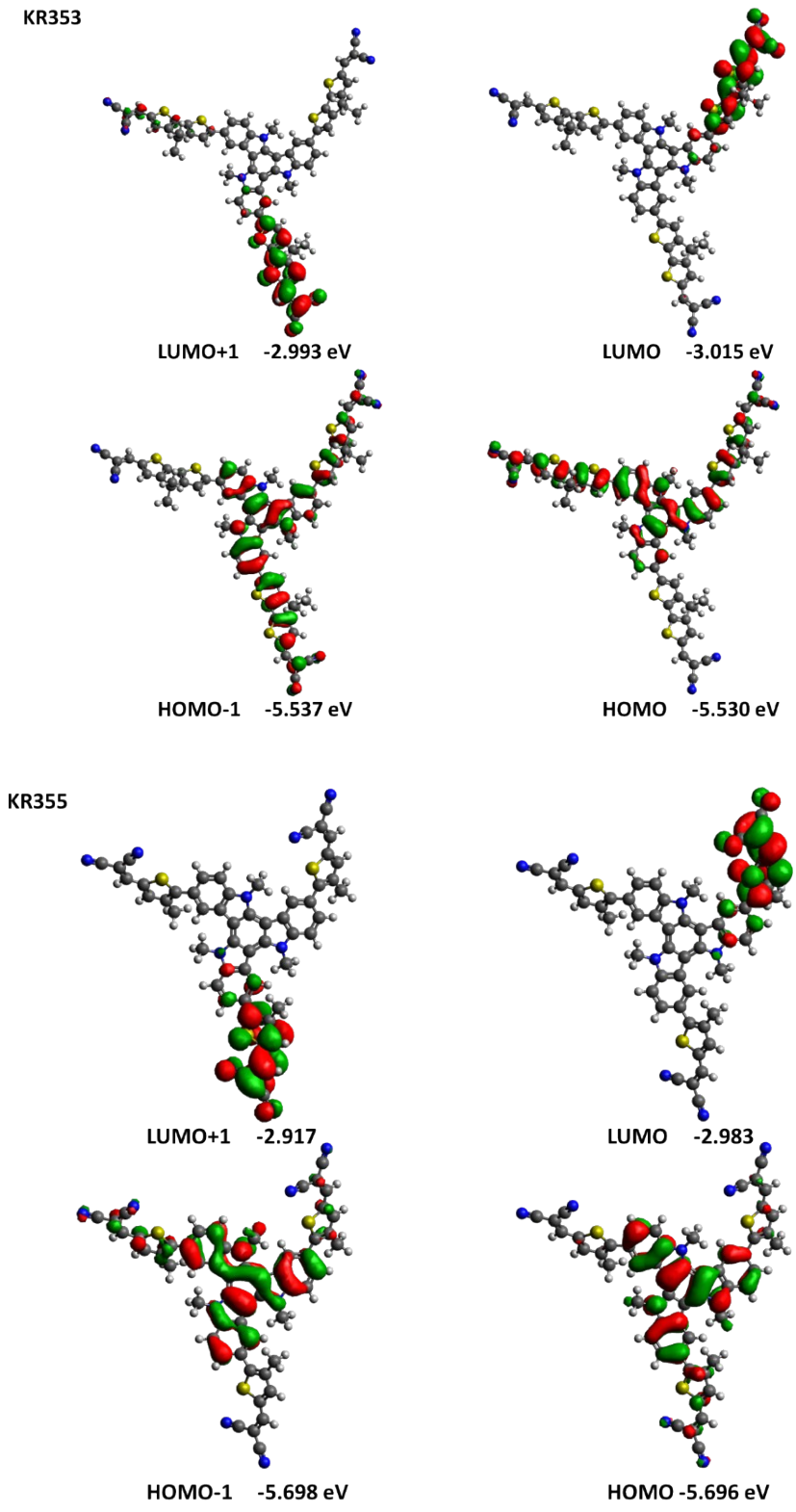


Figure S7. Isodensity surface plots (isovalue of 0.025) and energies calculated for the frontier orbitals of HTMs.

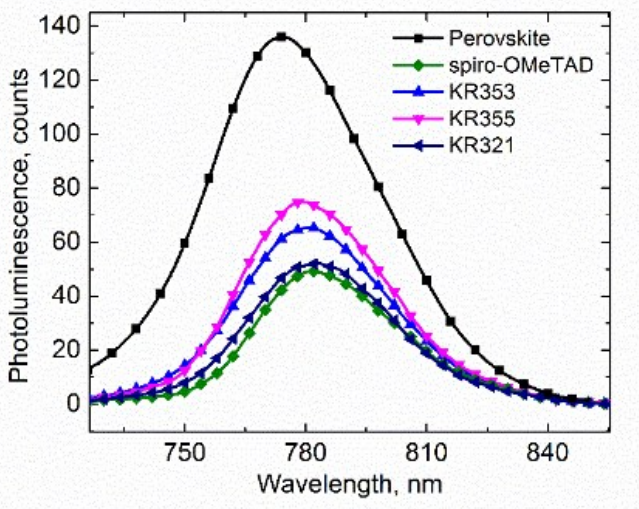


Figure S8. CW photoluminescence spectra, excitation at 650 nm for the pristine perovskite film, perovskite/spiro-OMeTAD sample and perovskite/HTMs as listed in the figure legend. All the samples have been encapsulated with a PMMA layer to prevent degradation or any oxygen/moisture induced effects.

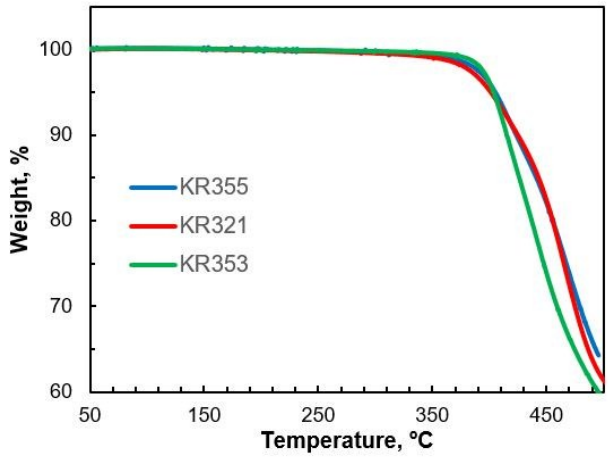


Figure S9. Thermogravimetric analysis (TGA) data of HTMs, heating rate of 10 °Cmin^{-1}, N_2 atmosphere.

2D GIWAXS measurement

To investigate the molecular ordering, GIWAXS experiments were performed by means of a solid anode X-ray tube (Siemens Kristalloflex X-ray source, copper anode X-ray tube operated at 30 kV and 20 mA), osmic confocal MaxFlux optics, X-ray beam with pinhole collimation, and a MAR345 image plate detector. The beam size was 1.0 mm × 1.0 mm (width x height), and samples were irradiated just below the critical angle for total reflection with respect to the incoming X-ray beam (~0.1°). All X-ray scattering measurements were performed under vacuum (~1mbar) to reduce air scattering and beam damage to the sample. All GIWAXS data processing and analysis was performed by using the software package Datasqueeze (http://www.datasqueezesoftware.com).

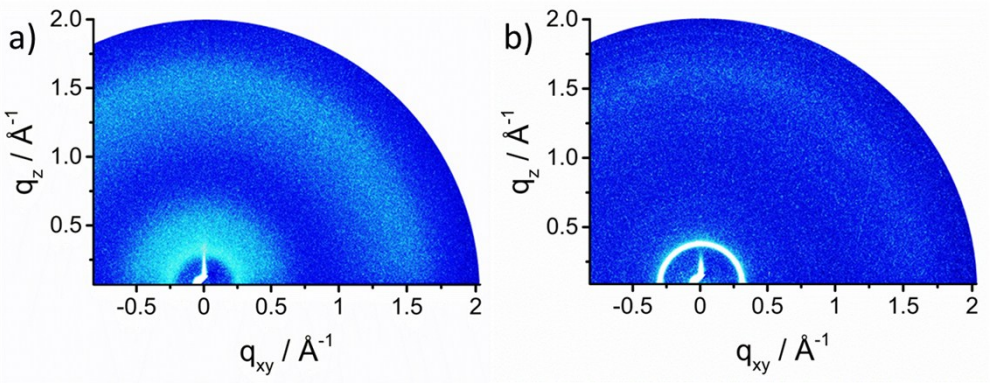


Figure S10. GIWAXS patterns of a) **KR353** and b) **KR355** films spin-coated from tetrachloroethane on silica wafer.

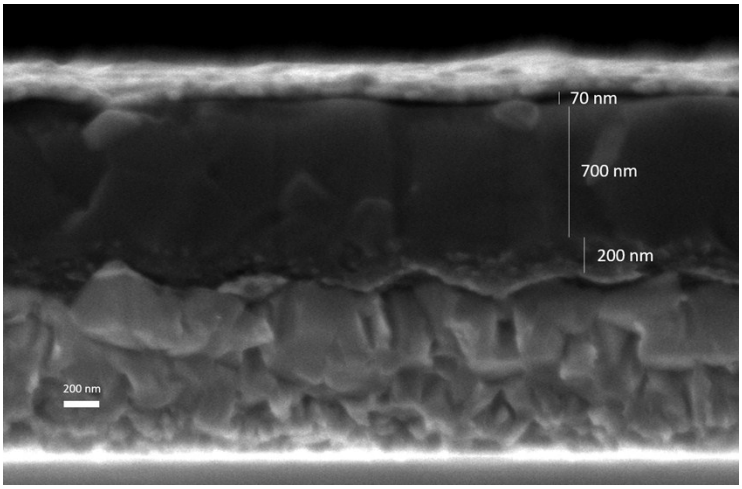


Figure S11. Cross-sectional SEM micrograph of perovskite device containing KR321 HTM.

The ionization potential measurements

The ionization potential values were measured by the photoelectron emission in air method from films, coated on Al subtrates. Ionization potential values were determined as the photon energy at the interception point that resulted from extrapolating the linear relation between $I^{0.5}$ and $h\upsilon$ near the threshold.

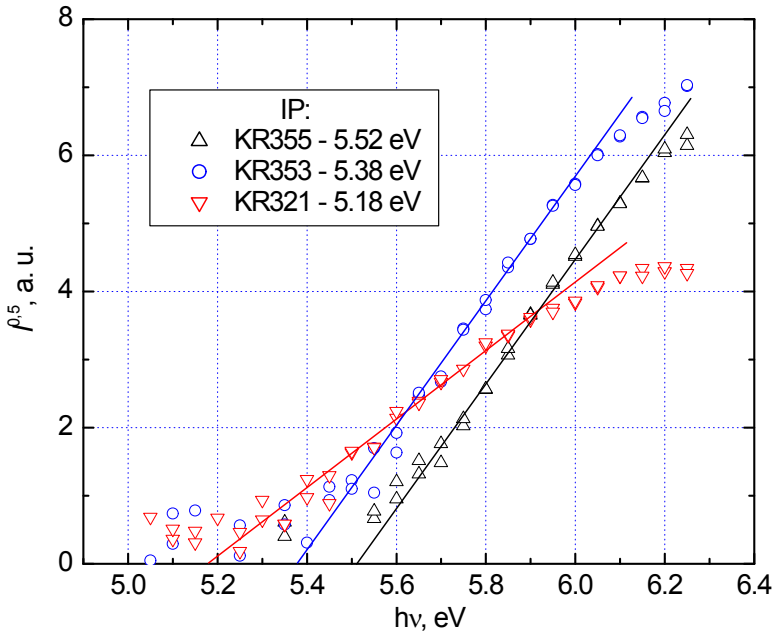


Figure S12. Photoemission in air spectra of the synthesized HTMs.

Space-charge limited current (SCLC) measurement

Hole only device structure: ITO/PEDOT:PSS/HTM/Au

Gold electrode: 7.5mm x 7mm

The data are fitted in the SCLC regime using Mott-Gurney law (slope indicated in the table). The dielectric constant was chosen to be 3 and the built-in potential between PEDOT:PSS and Au to be zero. The films were deposited via spin-coating (2000rpm) inside a nitrogen filled glovebox at 70°C from a 50mM tetrachloroethane solution. The PEDOT:PSS films were spin-coated from a 1:3 (IPA/PEDOT:PSS) solution onto ITO substrates and subsequently heated at 110°C for 30min in air.

$$J = \frac{9\mu_{eff}\varepsilon_0\varepsilon_r}{8}\left(\frac{V^2}{d^3}\right)$$

ID	SCLC hole mobility ($cm^2\ V^{-1}\ s^{-1}$)	PEDOT:PSS thickness (nm)	film thickness (nm)	slope of SCLC regime in log-log plot	R-square
KR355	5.00E-07	40.00	350.00	1.87	0.995
KR353	1.10E-05	40.00	464.00	1.98	0.999
KR321	2.60E-04	40.00	740.00	2.04	0.997

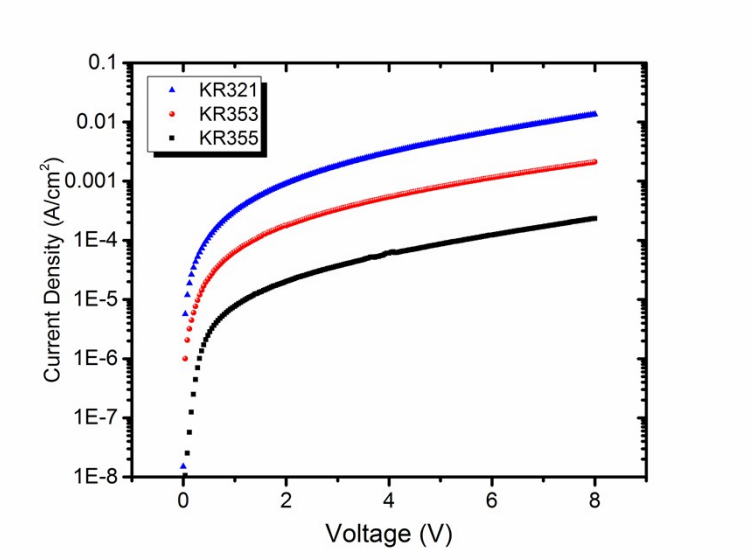


Figure S13. SCLC measurement of the HTMs films.

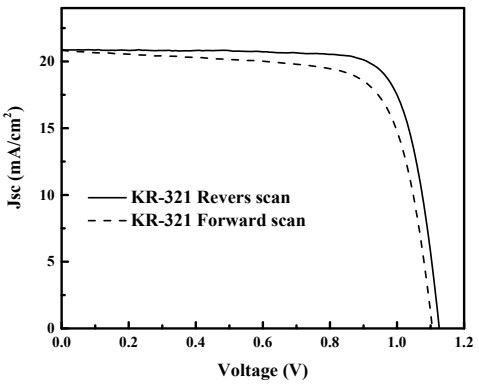
Solar cell fabrication

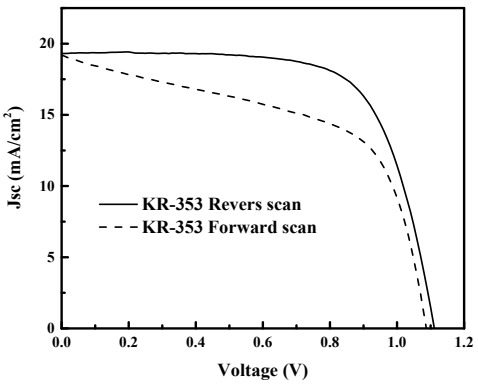
The etched FTO glass (Nippon Sheet Glass) was cleaned sequentially by sonication in a 2 % Hellmanex solution, acetone and ethanol, followed by a 15 min UV-ozone treatment. A 30 nm thick TiO_2 compact layer was deposited by spray pyrolysis at 450°C from a precursor solution of diluted titanium diisopropoxide bis(acetylacetonate) (TAA) solution (Sigma-Aldrich) in isopropanol. On the top of it, a 150 nm mesoporous TiO_2 layer was made by spin coating method using a commercially available TiO_2 paste (Dyesol 30NRD). The Substrates were sintered at 500 ^oC for 30 min in air. Then, Li-doping of the mesoporous TiO_2 is done by spin coating a 0.03 M solution of LiTFSI (in acetonitrile) at 3000 rpm for 20 s, followed by sintering at 500 °C for 20 min before use. The mixed perovskite precursor solution was prepared by dissolving PbI_2 (1.15 M), FAI (1.10 M), $PbBr_2$ (0.2 M), and MABr (0.2 M) in a anhydrous solvent DMF: DMSO = 4 : 1 (volume ratio). The perovskite precursor solution was spin coated at 2000 rpm for 10 s, followed by 6000 rpm for 30 s. Trifluorotoluene (110 µl) was dropped on the spinning substrate at the 20 s in the second step. The films were annealed at 100 °C for 90 min in the glove box. The hole-transporting material, consisting of 15 mM KR321, KR353 and KR355 in tetrachloroethane at 70°C, was spin-coated on the top of the perovskite layer with a spin speed of 4000 rpm. For comparison, the devices using Spiro-OMeTAD as HTM, consisting of 60 mM Spiro-OMeTAD, 30 mM LiTFSI, 198 mM TBP, and 1.8 mM of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(III) tris(bis(trifluoromethyl sulfonyl)imide) (FK209) in chlorobenzene, were prepared by spin coating the corresponding solution with a spin speed of 4000 rpm. Finally, 70 nm of Au was deposited by thermal evaporation as the back electrode.

Photovoltaic characterization

The current-voltage curves were measured under AM 1.5 simulated light source connecting with a source meter (Keithley 2400). The light intensity was calibrated with an NREL certified KG5 filtered Si reference diode. J-V curves were obtained at a scan rate of 10 or 25 mV s^{-1}. The devices were measured by using a black mask with an active area of 0.16 cm^2. The IPCE spectra were measured by using a commercially available instrument ORIEL, IQE 200B.

		Jsc, mA/cm^2	Voc, V	ff	η, %
KR321	Reverse scan	20.89	1.13	0.781	18.36
	Forward scan	20.82	1.11	0.725	16.49
KR353	Reverse scan	19.31	1.11	0.693	14.87
	Forward scan	19.21	1.09	0.567	12.02
KR355	Reverse scan	16.01	1.05	0.528	8.88
	Forward scan	15.95	1.04	0.444	7.41





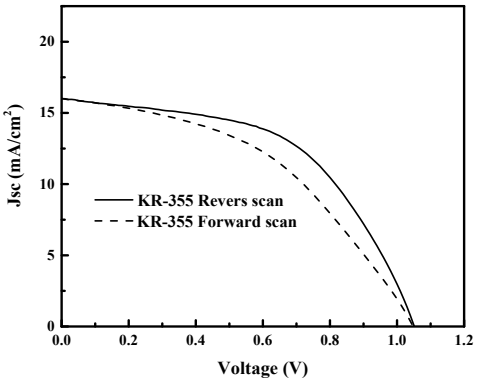


Figure S14. Current-voltage curves of KR321, KR353, and KR355 measured by forward and reverse scans.

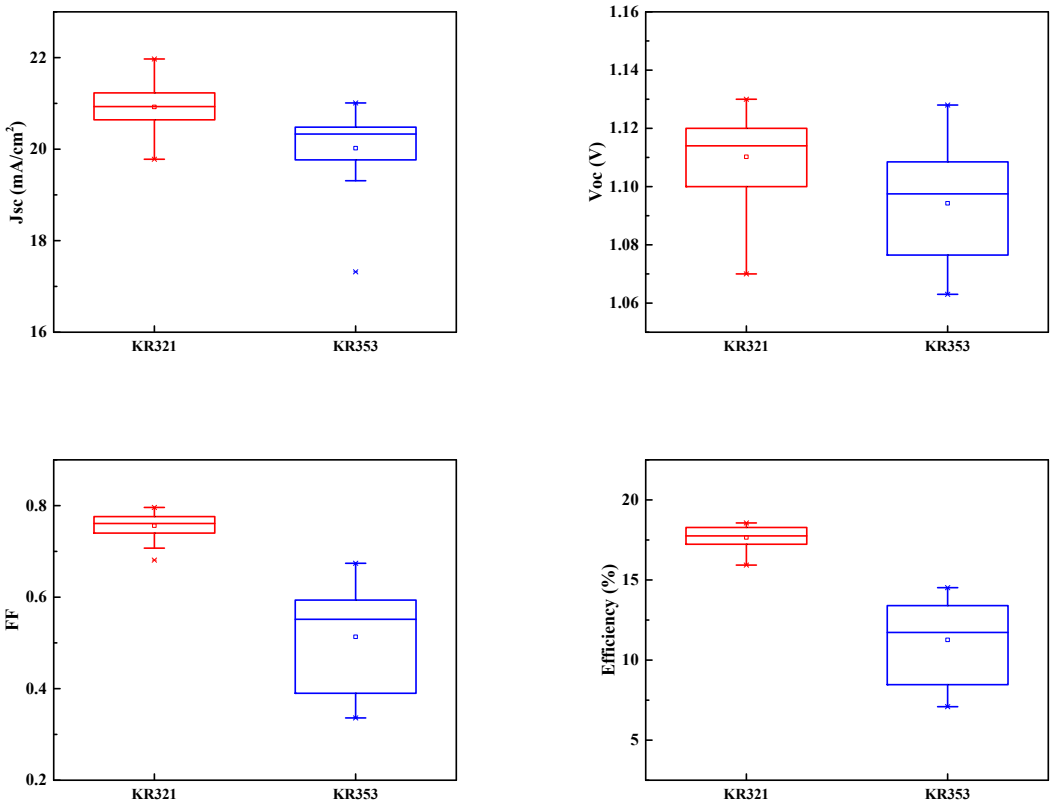


Figure S15. Statistical distribution of perovskite solar cells performance with KR321 and KR353.

Photovoltaic parameters of 45 devices based on KR321 measured under simulated AM 1.5G irradiation:

Device	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
1	21.87	1.12	0.749	18.29
2	21.05	1.13	0.784	18.56
3	21.48	1.11	0.759	18.05
4	21.25	1.12	0.771	18.41
5	20.56	1.09	0.74	17.32
6	21.88	1.09	0.756	18.16
7	19.78	1.09	0.765	16.57
8	20.38	1.07	0.758	16.54

9	20.06	1.10	0.773	17.06
10	20.9	1.09	0.731	16.75
11	20.02	1.12	0.786	17.64
12	21.35	1.08	0.718	16.51
13	20.35	1.1	0.739	16.60
14	21.97	1.11	0.734	17.90
15	20.82	1.09	0.748	17.70
16	20.07	1.11	0.791	18.41
17	20.64	1.11	0.772	18.45
18	21.70	1.13	0.782	19.03
19	20.93	1.12	0.684	16.01
20	20.89	1.13	0.776	18.26
21	21.01	1.12	0.724	17.06
22	21.21	1.12	0.707	16.83
23	21.01	1.11	0.748	17.51
24	21.31	1.12	0.742	17.69
25	21.19	1.12	0.753	17.89
26	21.04	1.11	0.765	17.84
27	21.31	1.12	0.773	18.46
28	21.13	1.09	0.762	17.62
29	20.89	1.11	0.743	17.23
30	21.06	1.13	0.756	17.93
31	21.31	1.13	0.738	17.72
32	21.23	1.11	0.71	16.77
33	21.25	1.11	0.773	18.29
34	21.01	1.12	0.783	18.41
35	21.23	1.12	0.763	18.14
36	21.31	1.12	0.734	17.57
37	20.48	1.12	0.796	18.28
38	20.82	1.12	0.786	18.34
39	20.4	1.10	0.790	17.75
40	20.37	1.10	0.776	17.40

41	20.79	1.12	0.784	18.27
42	20.88	1.10	0.781	17.92
43	20.60	1.12	0.761	17.59
44	20.78	1.13	0.788	18.48
45	20.89	1.13	0.781	18.36
Aver. ± std dev [%]	20.92 ± 0.45	1.11 ± 0.05	0.756 ± 0.25	17.65 ± 0.4

Photovoltaic parameters of 20 devices based on KR353 measured under simulated AM 1.5G irradiation:

Device	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
1	21.01	1.06	0.506	11.29
2	20.37	1.11	0.559	12.62
3	20.61	1.11	0.509	11.69
4	19.58	1.10	0.359	7.7
5	19.6	1.08	0.336	7.09
6	19.93	1.10	0.394	8.61
7	20.41	1.11	0.549	12.43
8	20.42	1.08	0.492	10.8
9	20.62	1.11	0.626	14.36
10	20.53	1.10	0.606	13.66
11	19.31	1.10	0.674	14.37
12	20.77	1.11	0.63	14.52
13	20.25	1.07	0.35	7.6
14	20.27	1.06	0.386	8.32
15	20.43	1.07	0.376	8.22
16	20.36	1.09	0.554	12.3
17	17.32	1.10	0.581	11.03
18	18.07	1.10	0.592	11.76
19	20.30	1.09	0.593	13.22
20	20.25	1.12	0.594	13.58
Aver. ± std dev [%]	20.02 ± 0.68	1.09 ± 0.15	0.513 ± 0.5	11.25 ± 0.5