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Tailored merocyanine dyes for solution-processed BHJ solar cells

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1. Materials and methods

Solvents and reagents were obtained from commercial suppliers and purified and dried according to standard procedures.[S1] 2-(3-Oxo-indan-1-ylidene)-malononitrile **4**,[S2] 1,1-dimethyl-2-methylene-1,2,4,5-tetrahydro-pyrrolo[3,2,1-*hi*]indole **3a**[S3] and 1,1-dimethyl-2-methylene-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline **3b**[S3] were synthesized according to literature.

Column chromatography was performed with commercial glass columns using silica gel (particle size 0.063-0.2 mm) as stationary phase. ^{1}H NMR spectra were recorded with a Bruker Advance 400 spectrometer at 25 °C using residual solvent peaks as internal standard. High resolution ESI mass spectroscopy was carried out on a microTOF focus instrument (Bruker Daltronik GmbH) in positive mode with MeCN or $CHCl_3$ as solvent. UV/Vis spectra were measured on a Perkin Elmer Lambda 950 UV/Vis spectrophotometer using a conventional quartz cell (light path 1cm). Temperature was regulated by a PTP-1 Peltier element (Perkin Elmer).

CV was performed on a standard commercial electrochemical analyzer (EC epsilon; BAS Instrument, UK) in a three electrode single-compartment cell under argon. Dichloromethane (HPLC grade) was obtained from J. T. Baker (Mumbai, India) and dried over calcium hydride and degassed prior to use. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was synthesized according to literature,[S4] recrystallized from ethanol/water and dried in high vacuum. The measurements were carried out under exclusion of air and moisture at a concentration of 10^{-4} M with ferrocene as internal standard for the calibration of the potential. Working electrode: Pt disc; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire.

Charge carrier mobilities were determined in organic field effect transistors, where a spin-coated layer of the respective MC dye from chlorobenzene solution (20 mg/mL) was deposited on a pre-fabricated heavily doped p-type Si++/SiO–$_x$ substrate with patterned source and drain gold contacts. The doped silicon substrate acts as the gate contact followed by a 230 nm thick SiO–$_x$ insulating layer with a capacitance of 15 nF cm^{-2}. Channel length and width were 2.5, 10 or 20 µm and 1 cm, respectively. Devices were measured in a dry nitrogen atmosphere with a Keithley 4200-SCS semiconductor characterization system. Mobilities were calculated from the transconductance in the linear regime.

Solar cell fabrication: All devices were fabricated on commercial indium-tin oxide (ITO) coated glass. The ITO was etched with acid and subsequently cleaned using chloroform, acetone, mucasol detergent and de-ionized water in an ultrasonic bath. Next, the ITO substrates were exposed to ozone for 20 min and immediately spin-coated with poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron P AL 4083, HC Starck; ca. 40 nm). Afterwards, the samples were heat treated for 2 min at 110 °C to remove residual water and transferred into a N_2 glove box for further fabrication processing and measurement. PCBM was obtained from Nano-C (Westwood, MA, USA), the merocyanine (MC) dyes were synthesized according to synthetic procedures described below. The active layers were spin-coated from heated (75 °C) chlorobenzene containing a mixture of MC and PCBM with a concentration of 20 mg mL^{-1}. The substrates were moved to a high-vacuum chamber where the top electrode was evaporated through a mask (120 nm Al), leading to seven solar cells on each substrate with an active area of 0.08 cm^2. The *JV* characteristics of the solar cells were measured using a Keithley 2425 source measurement unit. The AM1.5 light was provided by a filtered Xe-lamp. The intensity of 100 mW cm^{-2} of the AM1.5 light was determined by using a calibrated inorganic solar cell from the Fraunhofer Institute for solar research in Freiburg (Germany) and a reference PCBM:P3HT cell measured by the same institution. No spectral mismatch factor was included in the calculation of the efficiency. A

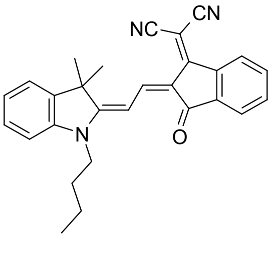
Dektak surface profiler (Veeco) was used to determine the active layer thicknesses. The active layer thickness was 50-60 nm. UV/vis spectra were taken with a Varian Cary 50 spectrometer.

2. Synthesis and characterization

General procedure for the three-component condensation reaction:

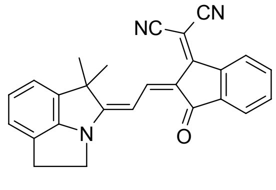
One equivalent of 1-butyl-3,3-dimethyl-2-methylene-2,3-dihydro-1*H*-indole or 1,1-dimethyl-2-methylene-1,2,4,5-tetrahydro-pyrrolo[3,2,1-*hi*]indole **3a** or 1,1-dimethyl-2-methylene-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline **3b** and 1 equivalent of 2-(3-oxo-indan-1-ylidene)-malononitrile **4** and 1.5 equivalents of ethyl orthoformate in 1 mL ethanol /equivalent were heated to reflux for 1 h. After removal of solvent, the product was isolated by column chromatography (CH_2Cl_2) and further purified by precipitation from dichloromethane solution by adding *n*-hexane.

2-{2-[2-(1-*n*-Butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-ethylidene]-3-oxo-indan-1-ylidene}-malononitrile (MD376)



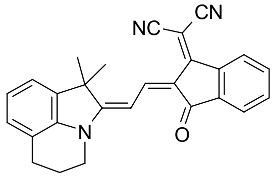
Yield: 50%, green-brown solid. m.p. 173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.05$ (d, $^3J = 13.9$ Hz, 1H), 8.57 (m, 1H), 8.07 (d, $^3J = 13.8$ Hz, 1H), 7.73 (m, 1H), 7.59 (m, 2H), 7.37 (m, 2H), 7.24 (m, 1H), 7.07 (m, 1H), 4.06 (t, $^3J = 7.5$ Hz, 2H), 1.88 (m, 2H), 1.80 (s, 6H), 1.53 (m, 2H), 1.04 (t, $^3J = 7.4$ Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 190.94, 176.66, 161.55, 143.42, 142.20, 141.88, 139.79, 137.38, 133.57, 132.95, 128.58, 125.32, 124.61, 122.49, 122.24, 117.56, 116.76, 114.99, 110.49, 99.64, 61.46, 49.41, 44.47, 29.41, 27.71, 20.57, 13.99. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 477 (21000), 576 (66400 M^{-1} cm^{-1}). HRMS (ESI): calcd for $C_{28}H_{26}N_3O$ $[M+H]^+$: 420.2070, found: 420.2071.

2-{2-[2-(1,1-Dimethyl-4,5-dihydro-1*H*-pyrrolo[3,2,1-*hi*]indol-2-ylidene)-ethylidene]-3-oxo-indan-1-ylidene}-malononitrile (HB193)



Yield: 19%, brown solid. m.p. 277 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ= 8.55 (d, ^3J = 14.0 Hz, 1H), 8.34 (m, 1H), 7.58-7.73 (m, 4H), 7.39 (m, 1H), 7.31 (m, 1H), 7.22 (t, ^3J = 7.3 Hz, 1H), 4.64 (m, 2H), 3.77 (t, ^3J = 6.2 Hz, 2H), 1.65 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 190.56, 174.17, 161.79, 141.98, 139.92, 137.21, 133.47, 132.85, 126.79, 124.51, 123.45, 122.17, 121.46, 117.74, 116.90, 114.72, 98.24, 60.46, 59.67, 51.73, 34.80, 26.25. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 486 (20300), 586 (51100 M^{-1} cm^{-1}). HRMS (ESI): calcd for $C_{26}H_{20}N_3O$ $[M+H]^+$: 390.1600, found: 390.1599.

2-{2-[2-(1,1-Dimethyl-5,6-dihydro-1*H*,4*H*-pyrrolo[3,2,1-*ij*]quinolin-2-ylidene)-ethylidene]-3-oxo-indan-1-ylidene}-malononitrile (HB194)



Yield: 60%, brown solid. m.p. 291 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.00 (d, ^3J = 14.0 Hz, 1H), 8.56 (m, 1H), 7.92 (d, ^3J = 13.8 Hz, 1H), 7.70 (m, 1H), 7.58 (m, 2H), 7.15 (m, 3H), 4.05 (br, 2H), 2.90 (t, ^3J = 6.1 Hz, 2H), 2.25 (m, 2H), 1.79 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 190.82, 175.54, 161.39, 142.84, 139.81, 138.67, 137.34, 133.50, 132.84, 127.32, 125.34, 125.34, 124.55, 123.32, 122.13, 120.14, 117.70, 116.87, 114.54, 99.27, 61.03, 50.66, 43.65, 27.32, 23.92, 21.83. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 482 (21700), 578 (60300 M^{-1} cm-^{1}). HRMS (ESI): calcd for $C_{27}H_{21}N_3O$ $[M]^+$: 403.1685, found: 403.1679.

3. UV/Vis spectroscopy

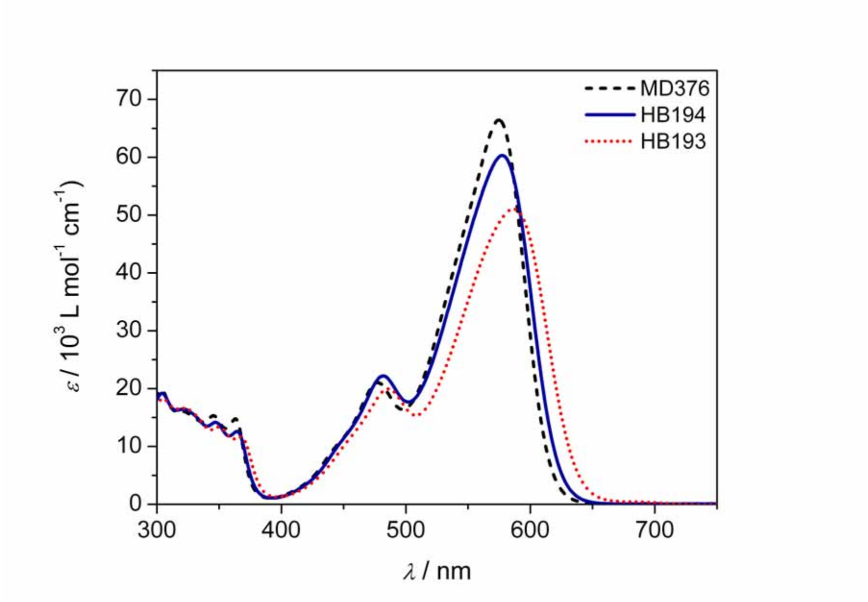


Figure S1. UV/Vis-absorption spectra of the investigated MC dyes in CH_2Cl_2 ($c = 2 \times 10^{-5}$ M) at room temperature.

4. CV measurements

Table S1. CV measurements in CH_2Cl_2 calibrated against the ferrocene/ferrocenium couple as internal standard.

	$E_{1/2}^{ox}$ (V)	$E_{1/2}^{red}$ (V)
MD376	0.65	-1.52
HB193	0.56	-1.54
HB194	0.60	-1.55

5. EOA measurements

Dipole moments of the ground state μ_g and the dipole moment differences $\Delta\mu = \mu_e - \mu_g$ (μ_e: excited state dipole moment) of chromophores have been determined by means of electro-optical absorption (EOA) spectroscopy by which the difference of absorption of a solution with ($\varepsilon^{\mathrm{E}}(\varphi, \tilde{\nu})$) and without ($\varepsilon(\tilde{\nu})$) an externally applied electric field E is measured with light parallelly (φ = 0°) and perpendicularly (φ = 90°) polarized to the direction of E.[S5] For uniaxial phases, induced in a solution by both an alternating and a constant electric field of about $3 \cdot 10^6$ V m^{-1}, the dichroism $\varepsilon^{\mathrm{E}}(\varphi, \tilde{\nu}) - \varepsilon(\tilde{\nu})$ depends on the orientational order of the molecules due to their ground state dipole moment μ_{g}, the shift of the absorption band proportional to the dipole moments difference $\Delta\mu$, and on the electric field dependence of the electric transition dipole moment $\mu_{\mathrm{eg}}(E)$. UV/Vis spectra, required for the evaluation of the integral absorption (μ_{eg}^2), were recorded with a Perkin-Elmer Lambda 900 spectrophotometer at 298 K.

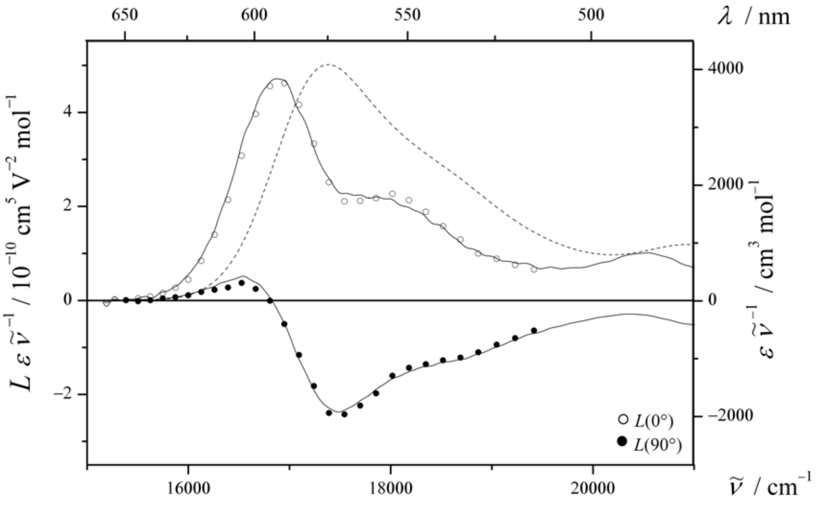


Figure S2: UV/Vis (----) and EOA spectra (φ = 0°: ○; 90°: ●) of **HB194** and the multi linear regressions (—) measured in 1,4-dioxane at 298 K.

Table S2. Optical and electro-optical properties of **HB194** determined by analysis of the UV/Vis and EOA spectra measured in 1,4-dioxane at 298 K.

	λ_{max} (nm)	$\varepsilon_{\mathrm{max}}$ (M^{-1} mol^{-1})	μ_{eg} (D)	μ_{e} (D)	μ_{g} (D)	$\Delta\mu$ (D)	c^2 [a]

HB194	574	7100	10.0	10.8	6.8	4.0	0.403

[a] For the definition of c^2, see ref S5b.

6. Crystal structure of HB194

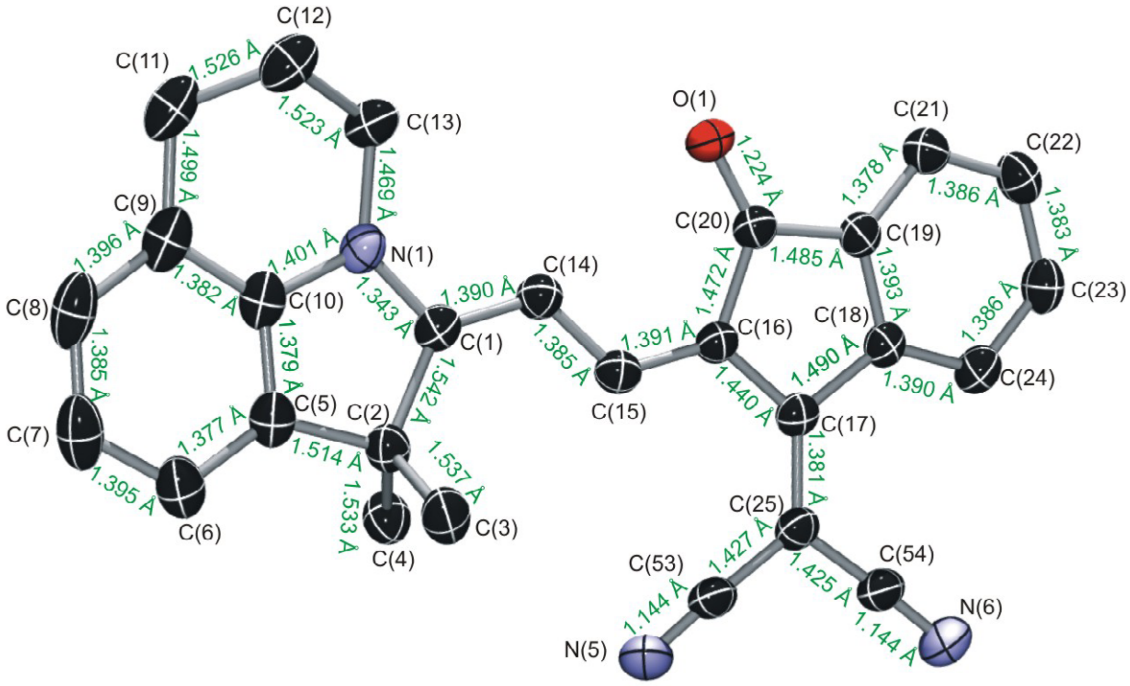
Crystal structure determination. The crystal data of **HB194** were collected at Bruker APEX diffractometer with CCD area detector and graphite monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with SHELX software package (G. Sheldrick, University of Göttingen, Germany 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factors calculations.

Crystal data for **HB194**: $C_{27}H_{21}N_3O$, $M_r = 403.47$, dark block-shaped crystal, 0.09×0.2×0.26, monoclinic space group P2(1)/n, $a = 8.1678(6)$Å, $b = 21.9108(17)$Å, $c = 23.0033(18)$Å, $\alpha = 90.00°$, $\beta = 94.1810(10)°$, $\gamma = 90.00°$, $V = 4105.8(5)$Å^3, $Z = 8$, $\rho_{calcd} = 1.305$ g·cm^{-3}, $\mu = 0.081$ mm^{-1}, $F(000) = 1696$, $T = 173(2)$ K, $R_1 = 0.0863$, $wR^2 = 0.1309$, 10265 independent reflections [$2\theta \leq 56.76°$] and 567 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-740220. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Two repetitive units were found in the unit cell (Fig. S8), which vary only slightly from each other. For the compound depicted in Figure S8b a disorder concerning C(37) was observed. This molecule shows a larger distortion angle of 7.4° between the donor and acceptor plane compared to 3.5° of the other molecule (Fig. S8a). The bond length alternation of the methine bridge is also slightly larger for the disordered repetitive molecule (1.379 Å vs 1.399 Å) compared to the other one (1.385 Å and 1.391 Å).

a)


C(12)
C(11)
1.526 Å
1.523 Å
C(13)
1.499 Å
1.469 Å
O(1)
1.224 Å
C(21)
C(22)
1.378 Å
1.386 Å
1.383 Å
C(9)
1.396 Å
1.401 Å
N(1)
C(20)
1.485 Å
C(19)
C(14)
1.390 Å
C(8)
1.382 Å
C(10)
1.343 Å
C(1)
1.472 Å
C(16)
C(18)
1.393 Å
C(23)
1.386 Å
1.385 Å
1.379 Å
1.385 Å
1.391 Å
1.490 Å
C(24)
1.390 Å
1.542 Å
1.440 Å
C(7)
C(5)
1.377 Å
C(2)
C(15)
C(17)
1.514 Å
1.537 Å
1.381 Å
1.395 Å
1.533 Å
C(6)
C(4)
C(3)
C(25)
C(53)
1.427 Å
C(54)
1.425 Å
1.144 Å
1.144 Å
N(5)
N(6)

b)

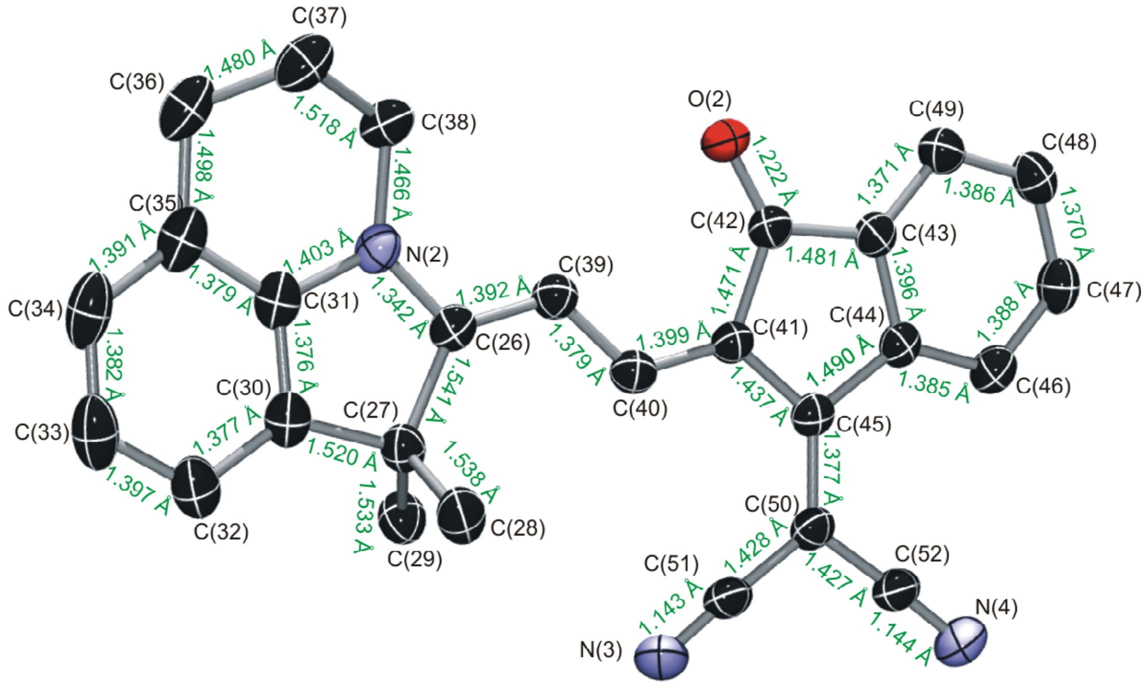

C(37)
C(36)
1.480 Å
1.518 Å
C(38)
1.498 Å
1.466 Å
O(2)
1.222 Å
C(49)
C(48)
1.371 Å
1.386 Å
1.370 Å
C(35)
1.391 Å
1.403 Å
N(2)
C(42)
1.481 Å
C(43)
C(39)
1.392 Å
C(34)
1.379 Å
C(31)
1.342 Å
C(26)
1.471 Å
C(41)
C(44)
1.396 Å
C(47)
1.388 Å
1.382 Å
1.376 Å
1.379 Å
1.399 Å
1.490 Å
C(46)
1.385 Å
1.541 Å
1.437 Å
C(33)
C(30)
1.377 Å
C(27)
C(40)
C(45)
1.520 Å
1.538 Å
1.377 Å
1.397 Å
1.533 Å
C(32)
C(29)
C(28)
C(50)
C(51)
1.428 Å
C(52)
1.427 Å
1.143 Å
1.144 Å
N(3)
N(4)

Figure S3. Repetitive units of **HB194** depicted with all bond lengths. a) Repetitive unit without disorder, b) repetitive unit with disorder concerning C(37).

7. Kelvin probe force microscopy images

KPFM images were recorded with a commercial AFM system (MultiMode AFM with Nanoscope IV controller, Veeco) operating in Lift Mode (typical lift height 15 nm) employing sharp silicon tips with Pt coating (Olympus OMCL-AC240TM-B2, apex radius <15 nm, k ≈ 2 N m^{-1}, cone angle 25°, resonant frequency ~70 kHz). The images were taken from areas of the solar cell devices where the active layer is not covered by the metal cathode.

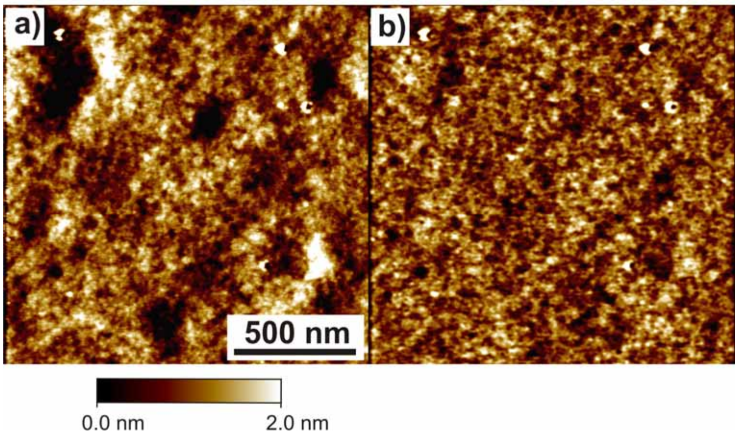


Figure S4. KPFM images of a **HB194** (45 wt%):PCBM (55 wt%) blend spin-coated from chlorobenzene solution on ITO/PEDOT:PSS: a) Topography, b) work function in the dark.

8. Powder X-ray diffractograms

X-ray powder diffraction (XRD) patterns were acquired on a STOE transmission diffractometer (STADI P) in a 2θ range of 5-30° by using Cu$_{K\alpha}$ radiation with a scanning rate of 1 deg min^{-1} in the case of **HB193** and **MD376** and a scanning rate of 0.075 deg min^{-1} in the case of **HB194**. A 8 mm aperture was used for all measurements.

The samples for powder XRD were prepared as follows: A thick film was prepared by drop-casting a chlorobenzene solution of the corresponding dye or MC:PCBM mixture on a glass substrate. The film was then scratched off from the substrate and pestled to produce a homogeneous powder.

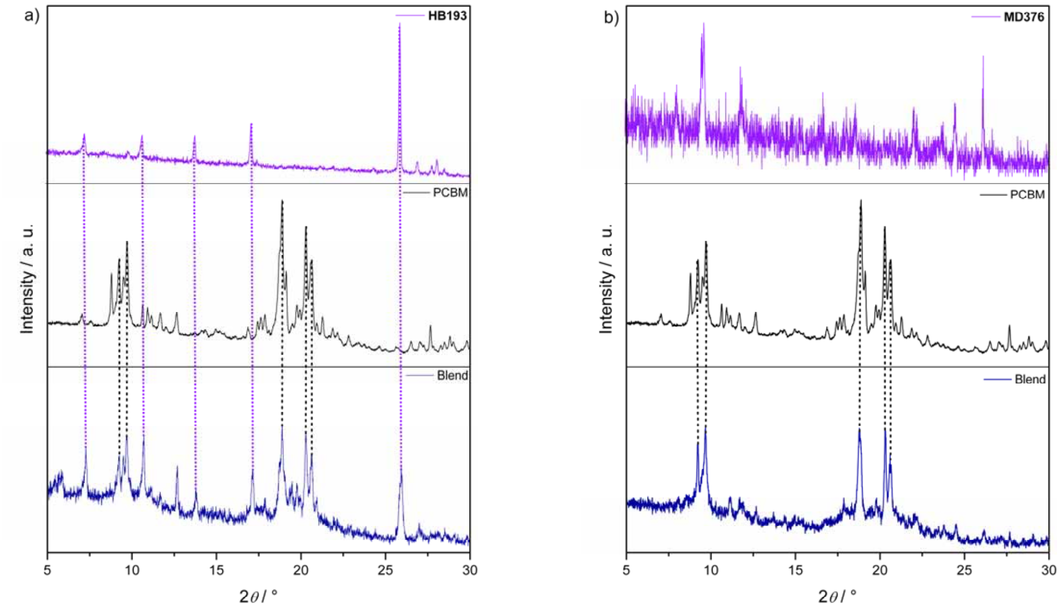


Figure S5. Powder X-ray diffractograms of a) **HB193** (top), PCBM (middle) and a **HB193** (35 wt%):PCBM (65 wt%) film (bottom) and b) **MD376** (top), PCBM (middle) and a **MD376** (25 wt%):PCBM (75 wt%) film drop-cast onto a glass substrate (bottom).

9. Differential scanning calorimetry measurements (DSC)

DSC measurements were performed with a TA Q1000 calorimeter using a heating/cooling rate of 10 °C min^{-1} in a nitrogen atmosphere. Two heating-cooling cycles were performed for each compound.

The samples for DSC were prepared in the same way as for powder XRD.

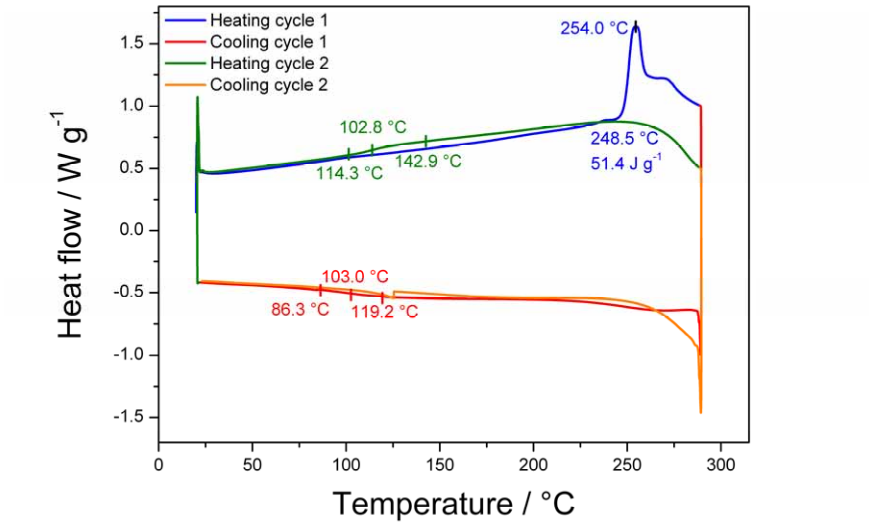


Figure S6. DSC measurement of a **HB194** (45 wt%):PCBM (55 wt%) film.

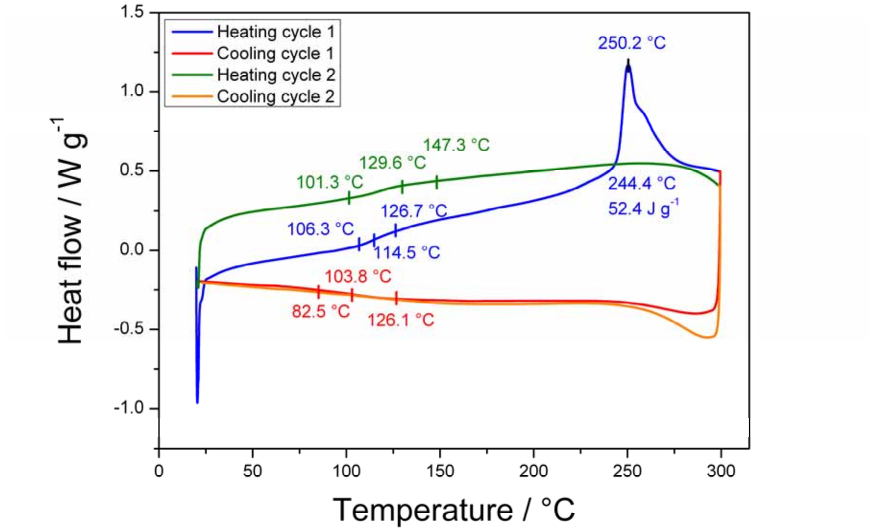


Figure S7. DSC measurement of a **HB193** (35 wt%):PCBM (65 wt%) film.

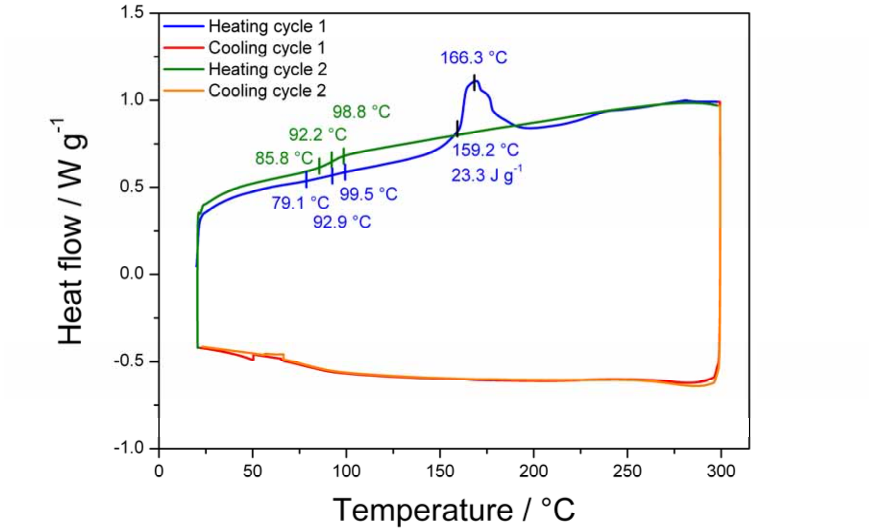


Figure S8. DSC measurement of a **MD376** (25 wt%):PCBM (75 wt%) film.

10. Additional References

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