Supplementary Information for:

A facile protect-deprotect route for obtaining indigo pigments as thin films and in organic bulk heterojunctions

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Synthetic Procedures and analytical data:

General preparative information. Both Di-*tert*-butyl dicarbonate (*t*BOC$_2$O) and N,N'-dimethylaminopyridine (DMAP) were purchased from *Aldrich*. Indigo (**1a**) was obtained from *BASF (Ludwigshafen*). The indigo derivatives 4,4'-dichloroindigo (**2a**), 4,4'-dibromoindigo (**3a**) and 6,6'-dibromoindigo (**6a**) were synthesized from 6-chloro-2-nitrobenzaldehyde, 6-bromo-2-nitrobenzaldehyde, and 4-bromo-2-nitrobenzaldehyde, respectively, according to Baeyer and Drewsen.[1] A historic sample labeled as 5-Bromoindigo, CI 73055 [a statistical mixture of indigo (**1a**), 5-bromoindigo (**4a**) and 5,5'-dibromoindigo (**5a**)] was obtained from the dyestuff collection of the *Technical University* of *Dresden*. 5-Bromoindigo (**4a**) was synthesized according to Clark et al.[2] from 5-bromoisatin and indoxyl-acetate. All solvents were distilled before use. Column filtration: *Merck* silica gel 60 (0.040-0.063 mm). TGA: a) *Netzsch 200* (heating rate 10 °C/min), b) *Perkin Elmer* 4000 (heating rate 20 °C/min). Inflection points of the TGA curves are taken as the decomposition temperature. IR [$\tilde{\nu}$(cm^{-1})]: *Perkin-Elmer Paragon 1000 FT*. NMR [in CDCl$_3$, δ (ppm), *J* (Hz)]: *Bruker 300* (^{1}H: 300 MHz, ^{13}C: 75.5 MHz). ^{13}C-NMR experiments: C13APT (Attached Proton Test using J_{mod} pulse program). EI-MS: Varian-MAT-312 at 70 EV. Elemental analysis: *Thermo Electron Corporation*. CHNS-O Analyzer, Flash EA 1112 Series.

The following are references for the substituted indigo pigment compounds **2a-6a**:

2a 4,4'-Dichloroindigo

L. Gindraux, *Helv. Chim. Acta*, 1929, **12**, 921–934.

3a, 5a, 6a 4,4'-Dibromoindigo, 5,5'-Dibromoindigo, 6,6'-Dibromoindigo

P. Friedlaender, S. Bruckner, G. Deutsch, *Justus Liebigs Ann. Chem.* 1912, **388**, 23 – 49.

4a 5-Bromoindigo (CI 73055)

R.J.H. Clark, Ch. J. Cooksey, *New. J. Chem.* 1999, 323–328.

General Procedure (*GP*). The bis-*t*BOC indigos **1b** – **6b** were prepared by stirring the pigments **1a** – **6a** in dichloromethane (CH_2Cl_2) at room temp. with ≥ two equivalents of *t*BOC_2O and about one equivalent of DMAP for 1-3 d (TLC). The reaction mixtures were concentrated almost to dryness and filtrated on the 80-fold amount of silica gel with toluene/AcOEt (9:1) to give the products in yields up to 90%. For analysis the samples were recrystallized from AcOEt.

1,1'-Bis(tert-butoxycarbonyl)-bis-indolidene-3,3'-dione[3] (*Bis-tBOC-indigo*; **1b**). Prepared according to *GP* from 3.14 g (12 mmol) **1a**, 9.90 g (45 mmol) *t*BOC_2O and 2.27 g (18 mmol) of DMAP in 600 ml of dichloromethane gave 4.9 g (89%) **2a**. Recrystallization from 14 ml of AcOEt resulted in 4.5 g of red crystalline solid. R_f = 0.18 (cyclohexane/AcOEt, 9:1) and 0.44 (toluene/AcOEt, 9:1). Dec.p. (a): 206.3 °C (Ref.3 193-5 °C). IR: among others 3107 (vw, C-H_{ar}), 2979, 2929 (all w, C-H_{al}) 1731 (s, C=O_{BOC}), 1678 (s, C=O_{ring}), 1601 (s). - ^{1}H-NMR: 1.64 (*s*, CH_3, 18 H), 7.23 (brd *t, J* = 7.0 Hz, 2 H, H-5,5'), 7.63 (*td,* ^3J = 8.0 Hz, ^4J = 1.5 Hz, 2 H, H-6,6'), 7.78 (brd *d, J* = 7.0 Hz, 2 H, H-4,4'), 8.04 (*d, J* = 8.0 Hz, 2 H, H-7,7'). - ^{13}C-NMR: 28.1 (*q*, 6 CH_3), 84.5 *s,* 116.6 (*d*, C-7,7'), 122.9 *s*, 124.0 (*d*, C-4,4'), 124.2 (*d*, C-5,5'), 125.0 *s*, 136.9 (*d*, C-6,6'), 149.0 *s*, 150.0 *s*, 183.7 *s*. - EI-MS: among others 462 (10, M^+), 362 (7 $[M - CO_2 - C_4H_8]^+$), 262 (100 $[M - 2\ CO_2 - 2\ C_4H_8]^+$).

1,1'-Bis(tert-butoxycarbonyl)-bis(4,4'-dichloro-indolidene)-3,3'-dione (*Bis-tBOC-4,4'-dichloroindigo*; **2b**). Prepared according to *GP* from 340 mg (1.0 mmol) **2a**, 545 mg (2.5 mmol) *t*BOC_2O and 120 mg (1.0 mmol) DMAP in 100 ml of dichloromethane. 388 mg (73%) of **2b**. Red solid. R_f = 0.22 (cyclohexane/AcOEt, 9:1). Dec.p. (a): 188.3 °C. IR: among others 3109 (vw, C-H_{ar}), 2963, 2928 (all w, C-H_{al}) 1746 (s, C=O_{BOC}), 1682 (s, C=O_{ring}), 1591, 1581 (all s). - ^{1}H-NMR: 1.52 (*s*, CH_3, 18 H), 7.29 (*d, J* = 8.1 Hz, 2 H, H-5,5'), 7.70 (*t, J* = 8.1 Hz, 2 H, H-6,6'), 7.95 (*d, J* = 8.1 Hz, 2 H, H-7,7'). - ^{13}C-NMR: among others 28.0 (*q*, 6 CH_3), 114.8 (*d,* C-7,7'), 125.7 (*d,* C-5,5'), 135.9 (*d,* C-6,6'). - EI-MS: among others 532 (3, M^+), 530 (4, M^+), 332 (93 $[M - 2\ CO_2, - 2\ C_4H_8]^+$), 330 (100 $[M - 2\ CO_2 - 2\ C_4H_8)]^+$), 57 (95).

Found: C 58.74, H 4.52, N 5.00%. Calc. for $C_{26}H_{24}Cl_2N_2O_6$: C 58.77, H 4.55, N 5.27%.

1,1'-Bis(tert-butoxycarbonyl)-bis(4,4'-dibromo-indolidene)-3,3'-dione (*Bis-tBOC-4,4'-dibromoindigo;* **3b**). Prepared according to *GP* from 1.26 g (3.0 mmol) of **3a**, 1.8 g (8.0 mmol) *t*BOC_2O and 420 mg (3.4 mmol) DMAP in 300 ml of dichloromethane. 1.70 g (90%) of **3b**. Red solid. R_f = 0.27 (cyclohexane/AcOEt, 9:1). Dec.p. (a): 198.2 °C. - IR: among others 3106 (vw, C-H_{ar}), 2963, 2933 (all w, C-H_{al}) 1746 (s, C=O_{BOC}), 1679 (s, C=O_{ring}), 1589, 1574 (all s). - ^{1}H-NMR: 1.58 (*s*, 6 CH_3, 18 H), 7.34 (*d, J* = 7.9 Hz, 2 H, H-5,5'), 7.40 (*t, J* = 7.9 Hz, 2 H, H-6,6'), 8.03 (*d, J* = 7.9 Hz, 2 H, H-7,7'). - ^{13}C-NMR: among others 28.0 (*q*, 6 CH_3), 115.4 (*d,* C-7,7'), 129.0 (*d,* C-5,5'), 136.0 (*d,* C-6,6'). - EI-MS: among others 622 (2, M^+), 620 (3, M^+), 618 (2, M^+), 422 (62 $[M - 2\ CO_2, - 2\ C_4H_8]^+$), 420 (100 $[M - 2\ CO_2 - 2\ C_4H_8)]^+$), 418 (60 $[M - 2\ CO_2, - 2\ C_4H_8]^+$), 58 (67). -

Found: C 50.25, H 3.89, N 4.17%. Calc. for $C_{26}H_{24}Br_2N_2O_6$: C 50.34, H 3.90, N 4.52%.

1,1'-Bis(tert-butoxycarbonyl)-[(5-bromo-indolidene)indolidene]-3,3'-dione (Bis-tBOC-5-bromoindigo; **4b**). Prepared according to *GP* from 1.65 g (3.4 mmol) of **4a**, 2.23 g (10 mmol) *t*BOC_2O and 415 mg (3.4 mmol) of DMAP in 400 ml of dichloromethane. 1.3 g (72%) of **4b**. Red solid. R_f = 0.27 (cyclohexane/AcOEt, 9:1) and 0.62 (toluene/AcOEt, 9:1). Dec.p. (b): 200.4 °C. IR: among others 2979 (s, C-H_{al}), 2884 (m, C-H_{al}), 1732 (s, C=O_{BOC}), 1673 (s, C=O_{ring}), 1598 (all s). – ^{1}H-NMR: 1.62 (*s*, 3 CH_3, 9 H), 1.64 (*s*, 3 CH_3, 9 H), 7.24 (*t, J_1* = 7.5 Hz, 1 H, H-5'), 7.64 (brd *t, J* = 8.3 Hz, 1 H, H-6'), 7.71 (*dd, J_1* = 8.7 Hz, *J_2* = 1.9 Hz, 1 H, H-6), 7.78 (brd *d, J* = 7.5 Hz, 1 H, H-4'), 7.89 (*d, J* = 1.9 Hz, 1 H, H-4), 7.95 (*d, J_1* = 8.7 Hz, 1 H, H-7), 8.03 (*d, J* = 8.3 Hz, 1 H, H-7'). - ^{13}C-NMR: among others 28.08 (*q*, 3 CH_3), 28.12 (*q*, 3 CH_3), 116.6 (*d*, C-7'), 118.4 (*d*, C-7), 124.2, 124.4 (2*d*, C-4',5'), 126.6 (*d*, C-4), 136.1 (*d*, C-6'), 138.2 (*d*, C-6). - EI-MS: among others 542 (7, M^+), 540 (7, M^+), 342 (100 [M – 2 CO_2, - 2 C_4H_8] $^+$), 340 (100 [M – 2 CO_2 - 2 C_4H_8)]$^+$), 58 (87). - Found: C 57.63, H 4.31, N 5.10%. Calc. for $C_{26}H_{25}BrN_2O_6$: C 57.68, H 4.65, N 5.17%.

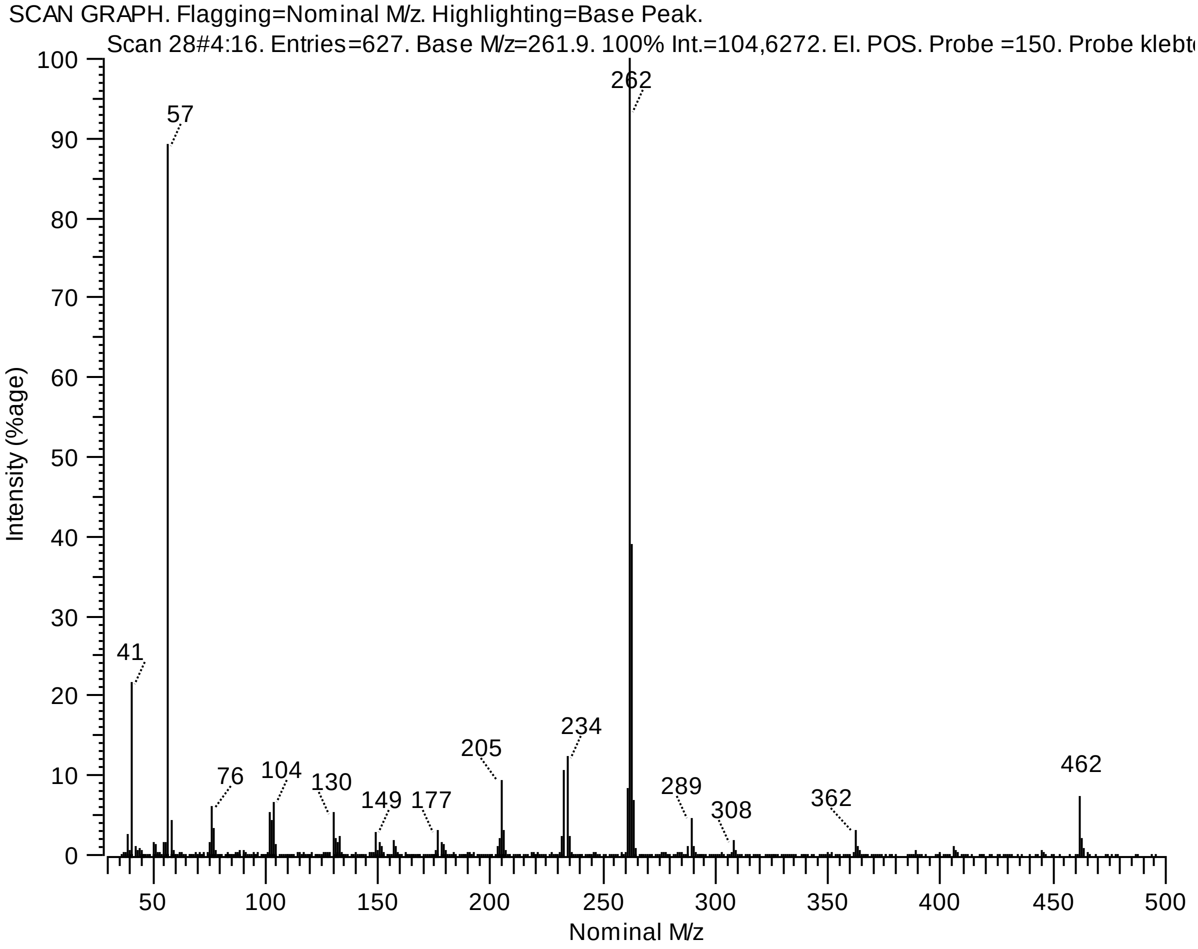
1,1'-Bis(tert-butoxycarbonyl)-bis(6,6'-dibromo-indolidene)-3,3'-dione (Bis-tBOC-6,6'-dibromoindigo; **6b**). Prepared according to *GP* from 420 mg (1.0 mmol) of **6a**, 655 mg (3.0 mmol) *t*BOC_2O and 120 mg (1.0 mmol) of DMAP in 250 ml of dichloromethane, 3 days stirring. 540 mg (87%) of **2e**. Red solid. R_f = 0.35 (cyclohexane/AcOEt, 9:1). Dec.p. (a): 196.0 °C. - IR: among others 3105 (vw, C-H_{ar}), 2966, 2928 (all w, C-H_{al}) 1737 (s, C=O_{BOC}), 1674 (s, C=O_{ring}), 1596 (s). - ^{1}H-NMR: 1.59 (*s*, 6 CH_3, 18 H), 7.35 (*d, J* = 8.2 Hz, 2 H, H-5,5'), 7.60 (*d, J* = 8.2 Hz, 2 H, H-4,4'), 8.42 (*s*, 2 H, H-7,7'). - ^{13}C-NMR: among others 28.0 (*q*, 6 CH_3), 120.2 (*d*, C-7,7'), 125.0 (*d*, C-5,5'), 127.8 (*d*, C-4,4'). - EI-MS: among others 622 (2, M^+), 620 (3, M^+), 618 (2, M^+), 422 (60 [M – 2 CO_2, - 2 C_4H_8] $^+$), 420 (100 [M – 2 CO_2 - 2 C_4H_8)]$^+$), 418 (60 [M – 2 CO_2, - 2 C_4H_8] $^+$), 57 (97). - Found: C 50.79, H 3.96, N 4.32%. Calc. for $C_{26}H_{24}Br_2N_2O_6$: C 50.34, H 3.90, N 4.52%.

From a historic dye sample (*TU Dresden, Dyestuff Museum*; statistical mixture of **1a**, **4a** and **5a**). We ran the protection reaction according to GP in order to chromatographically separate the mixture and verify what it contained. Thus the following dyes were prepared as mixture *1,1'-Bis(tert-butoxycarbonyl)-bis-indolidene-3,3'-dione* (**1b**), *1,1'-Bis(tert-butoxycarbonyl)-[(5-bromo-indolidene)indolyden]-3,3'-dione* (**4b**) and *1,1'-Bis(tert-butoxycarbonyl)-bis(5,5'-dibromo-indolidene)-3,3'-dione (***5b**) according to *GP* from 1.2 g **1a**, **4a** and **5a** (about 3.5 mmol of the sample), 3.3 g (15 mmol) of *t*BOC_2O and 610 mg (5.0 mmol) of DMAP in 400 ml of dichloromethane gave a mixture of **1b**, **4b** and **5b** (red solid). Filtration on 270 g silica gel with cyclohexane/AcOEt (9:1) gave 40 mg of **1b**, 30 mg of **5b** and 1.2 g of a red mixture again. A second chromatography with toluene/EcOEt 19:1 and final crystallization from AcOEt did result in the pure compounds **1b** (30 mg), **4b** (55 mg) and **5b** (40 mg), all red solids. The physical and spectroscopical data of **1b** and **4b** are identical with those of independently prepared samples, see above.

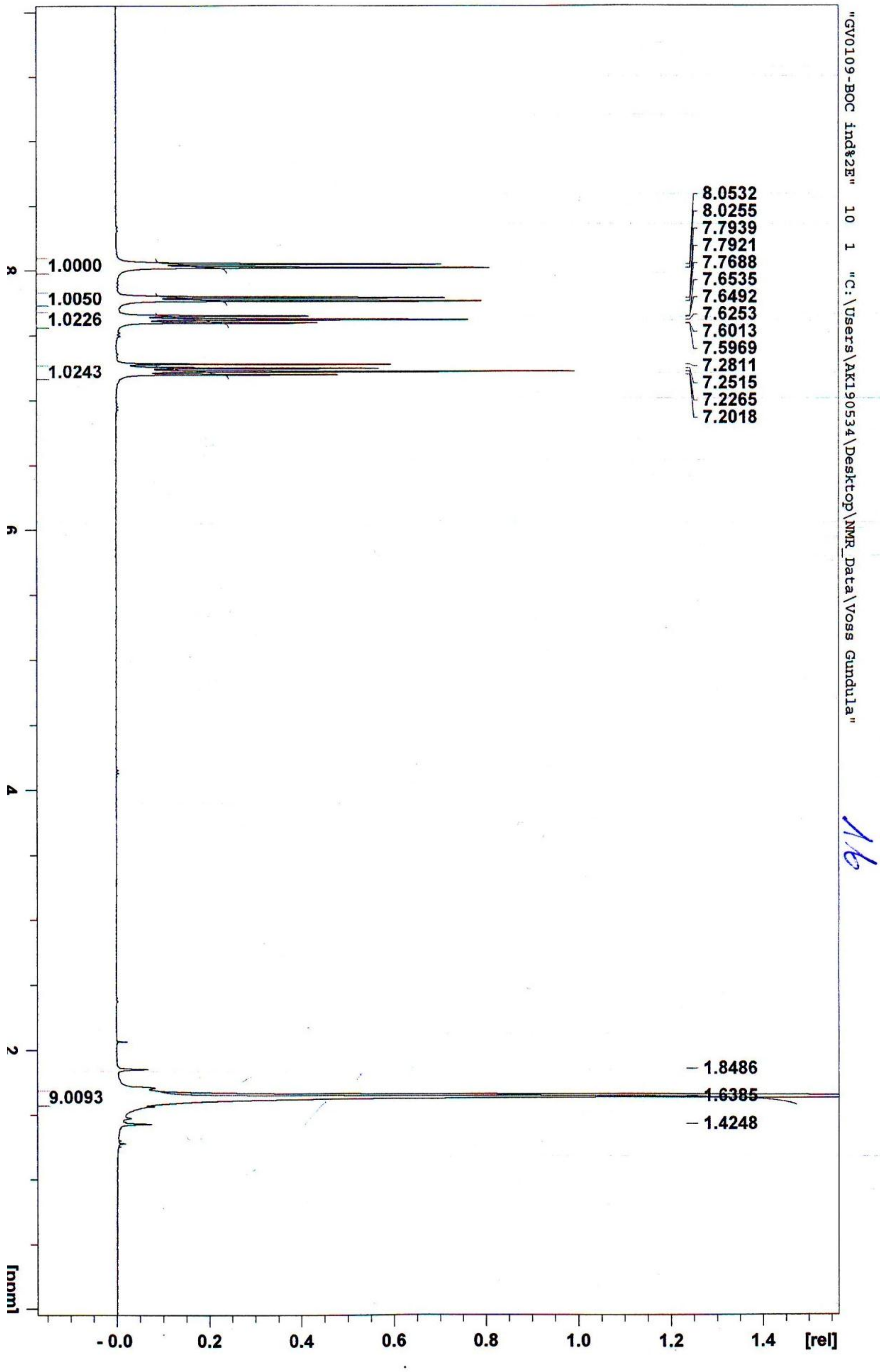
1,1'-Bis(tert-butoxycarbonyl)-bis(5,5'-dibromo-indolidene)-3,3'-dione (**5b**). R_f = 0.42 (cyclohexane/AcOEt, 9:1) and 0.74 (toluene/AcOEt, 9:1). Dec.p. (b): 191.4 °C. IR: amoung others 3110 (vw, C-H_{ar}), 2978 (s, C-H_{al}) 1740 (s, C=O_{BOC}), 1674 (s, C=O_{ring}), 1600 (s). - ^{1}H-NMR: 1.61 (*s*, 6 C*H*$_3$, 18 H), 7.72 (*dd, J_1* = 8.8 Hz, J_2 = 2.1 Hz, 2 H, H-6,6'), 7.89 (*d, J* = 2.1 Hz, 2 H, H-4,4'), 7.93 (*d*, *J* = 8.8 Hz, 2 H, H-7,7'). – ^{13}C-NMR: among others 28.1 (*q*, 6 *C*H$_3$), 118.4 (*d,* C-7,7'), 126.7 (*d,* C-4,4'), 138.4 (*d,* C-6,6'). - EI-MS: among others 622 (1, M^+), 620 (2, M^+), 618 (1, M^+), 422 (30 $[M - 2\ CO_2, - 2\ C_4H_8]^+$), 420 (60 $[M - 2\ CO_2 - 2\ C_4H_8)]^+$), 418 (29 $[M - 2\ CO_2, - 2\ C_4H_8]^+$), 58 (100). -

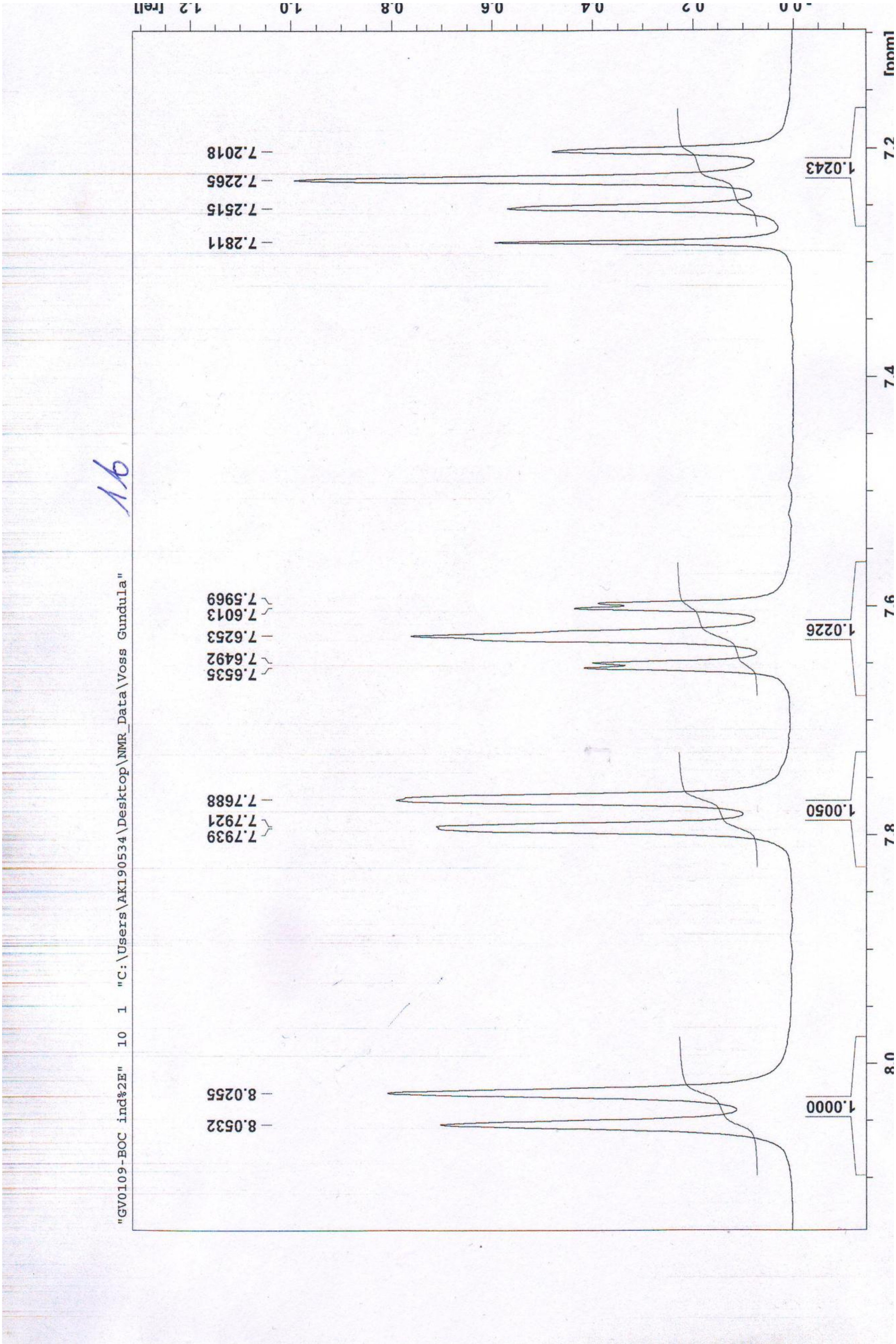
Found: C 50.47, H 3.86, N 4.39%. Calc. for $C_{26}H_{24}Br_2N_2O_6$: C 50.34, H 3.90, N 4.52%.

Mass spectrum for 1b

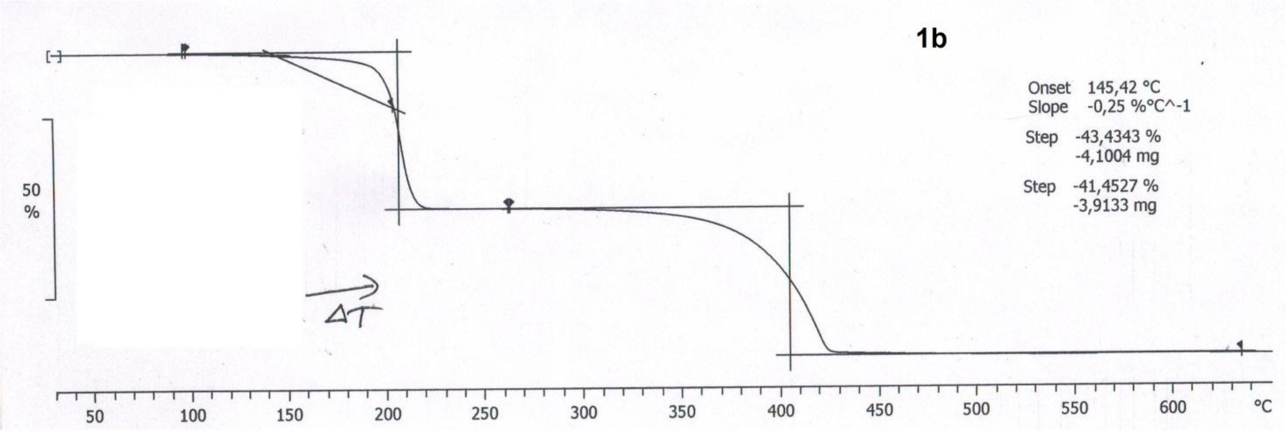


1H NMR for compound 1b




"GV0109-BOC ind%2E" 10 1 "C:\Users\AK190534\Desktop\NMR_Data\Voss Gundula"
1b
7.2018
7.2265
7.2515
7.2811
7.5969
7.6013
7.6253
7.6492
7.6535
7.7688
7.7921
7.7939
8.0255
8.0532
1.0243
1.0226
1.0050
1.0000
7.2
7.4
7.6
7.8
8.0
[ppm]
1.2
1.0
0.8
0.6
0.4
0.2
-0.0
[rel]

TGA for compound 1b (10 °C/min)



Crystallographic data

Table 1 Crystal data, data collection and structure refinement for compounds **1b** and **5b**.

	1b	**5b**
Empirical Formula	$C_{26}H_{26}N_2O_6$	$C_{26}H_{24}Br_2N_2O_6$
M_W [g mole^{-1}]	462.49	620.29
Crystal size [mm]	0.70 × 0.60 × 0.40	0.58 × 0.38 × 0.32
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2/*c*
a [Å]	21.07(1)	18.25(1)
b [Å]	7.368(3)	10.38(1)
c [Å]	17.19(1)	14.37(1)
α [°]	90	90
β [°]	113.66(1)	111.22(1)
γ [°]	90	90
V [Å^3]	2444(2)	2537(2)
ρ_{calc} [g cm^{-3}]	1.257	1.624
Z	4	4
μ [mm^{-1}]	0.09	3.24
T [K]	300	200
Θ range [°]	2.6-25.1	2.0-25.2
Reflections collected	10227	24402
Unique reflections	2162	4535
Observed reflections [I > 2σ(I)]	1647	3068
Parameters refined /*restraint*	158	331
Absorption correction	multi-scan	multi-scan
T_{min}; T_{max}	0.94; 0.96	0.26; 0.42
σ_{fin} (max/min) [e·Å^{-3}]	-0.13; 0.18	-0.68/1.28
R_1 [I≥2σ(I)]	0.042	0.058
wR_2	0.114	0.141
CCDC number	918485	918486

Photochromism of 1b

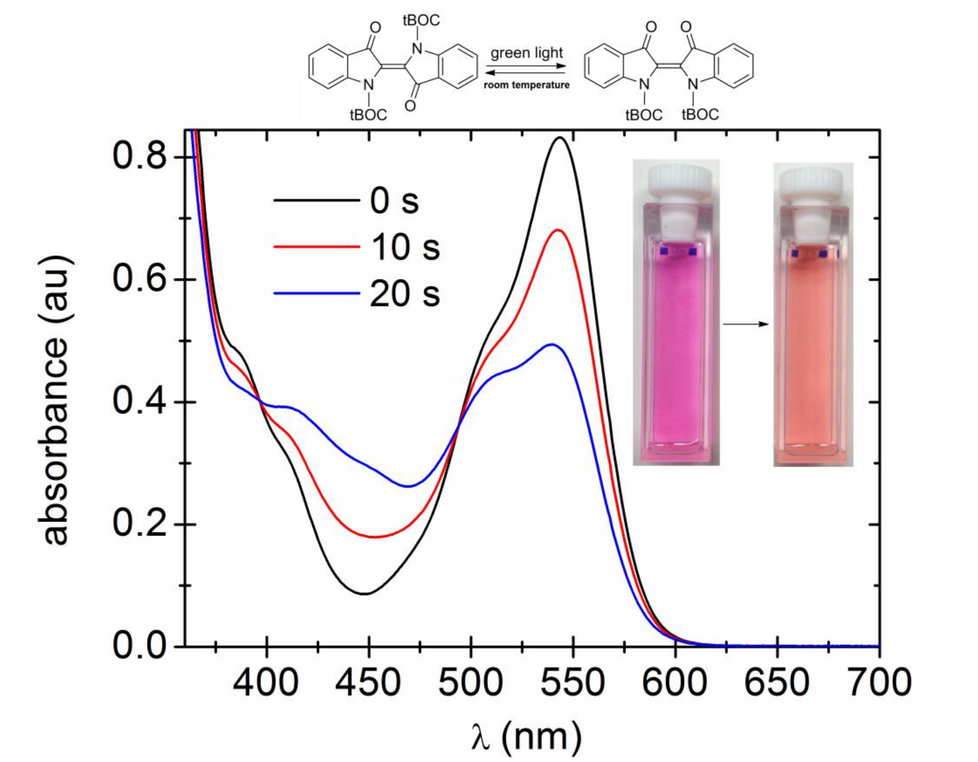


Figure S1. Photochromism of **1b** in chloroform solution, 0.2 mM. The sample was irradiated with a laser diode, peak 532 nm, with incident power of 20 mW/cm^2. Keeping the sample in the dark for 1h restored the original spectrum. These results are very similar to those obtained for N,N'-diacetylindigo, ref. 4.

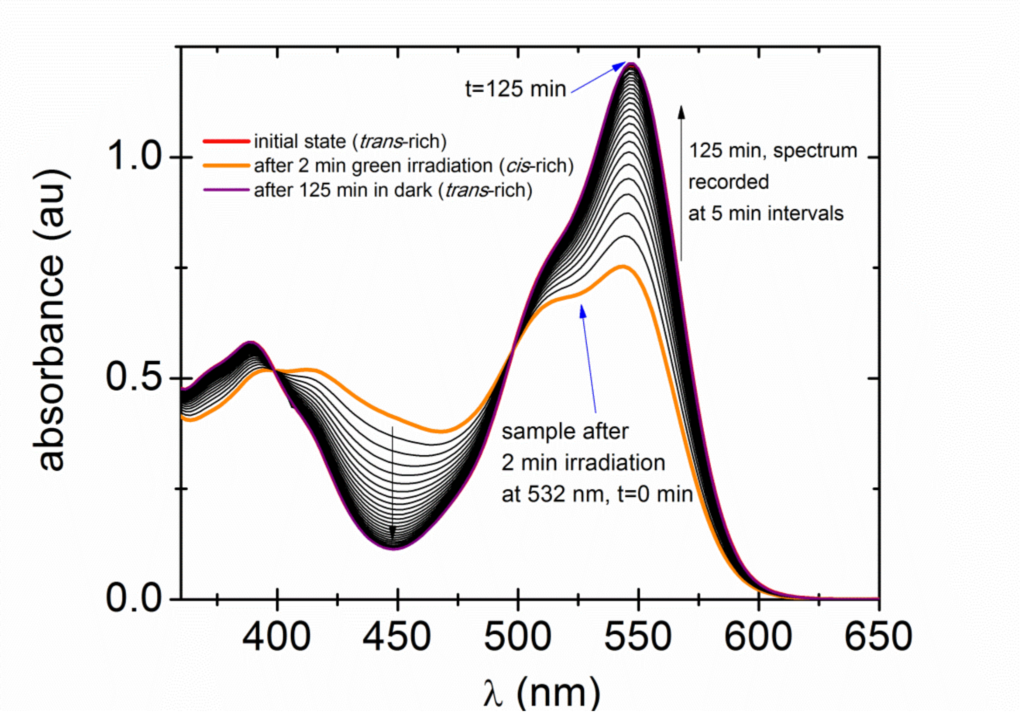


Figure S2. UV-Vis absorption showing the reverse *cis*-*trans* thermal isomerization following irradiation. The initial *trans*-rich solution (red trace) is irradiated at 532 nm for 2 min, then a spectrum is measured (orange trace) showing the sample has increased *cis* population. The thermal recovery of the *trans* state is measured over time at 5 minute intervals. 125 min in dark is sufficient to return the system back to a UV-Vis spectrum (violet trace) identical with that of the initial state. The red and violet trace overlap completely, demonstrating that the photochemical isomerization reaction appears to be fully reversible.

Supplementary AFM data

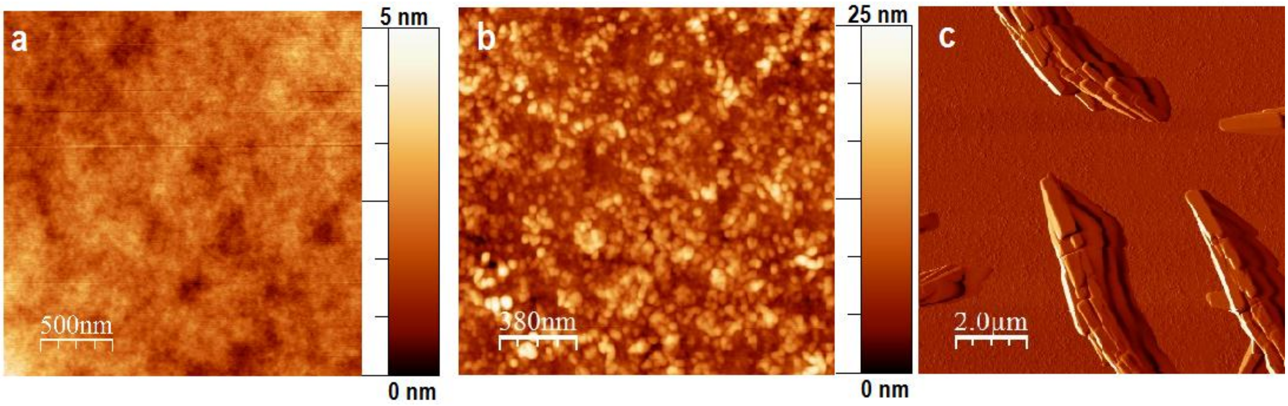


Figure S3. AFM images of a) spin-cast film of **3b**, b) film of **3a** created by heating sample (a). c) AFM Piezovoltage image of a film of **3a**, showing large crystallites on top of the continous film of (b).

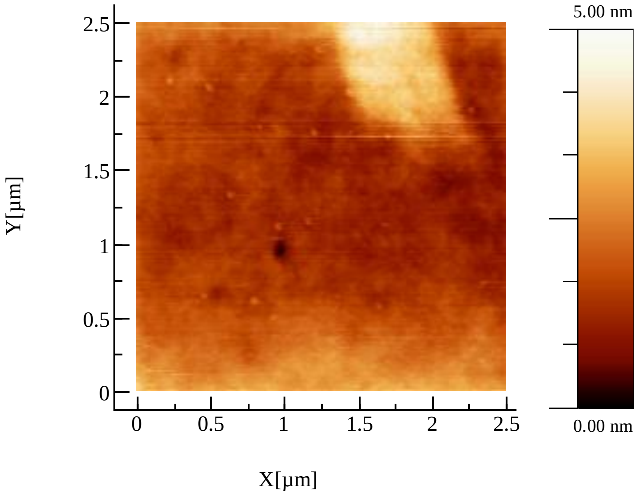


Figure S4. Spin-cast film of **2b** on glass substrate. The film was cast from chloroform solution, concentration 10 mg/ml, 1500 rpm spin-speed. Film thickness ~140 nm. RMS roughness = 1.4 nm.

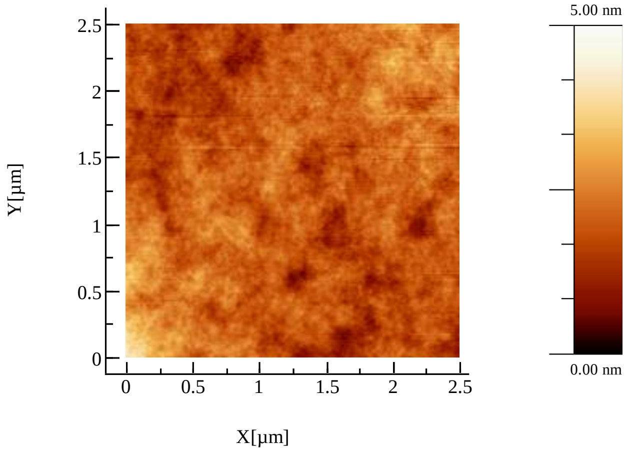


Figure S5. Spin-cast film of **3b** on glass substrate. The film was cast from chloroform solution, concentration 10 mg/ml, 1500 rpm spin-speed. Film thickness ~125 nm. RMS roughness = 0.4 nm.

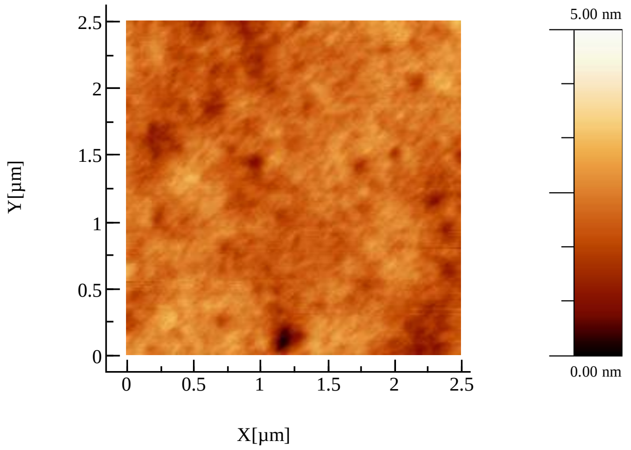


Figure S6. Spin-cast film of **4b** on glass substrate. The film was cast from chloroform solution, concentration 10 mg/ml, 1500 rpm spin-speed. Film thickness ~145 nm. RMS roughness = 0.4 nm.

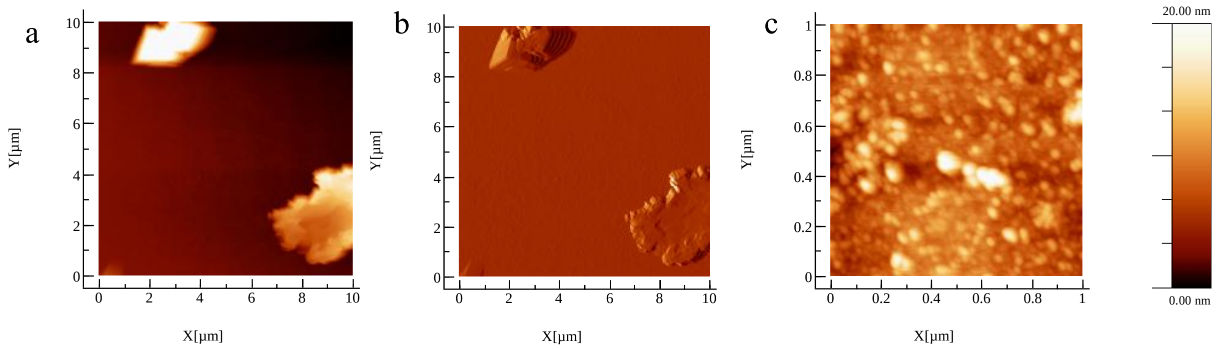


Figure S7. Film of **2a** on glass substrate following deprotection at 200 °C. a) AFM image showing large crystallites of several microns size. b) same field of view, piezovoltage image. c) AFM image zoomed in between large crystallites, showing that the space between is filled with a continuous film of smaller crystallites.

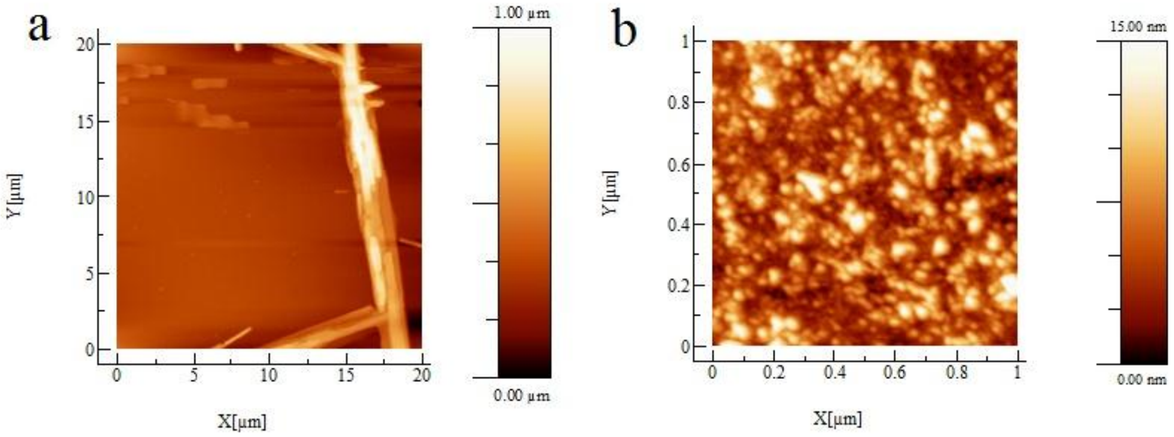


Figure S8. Film of **4a** on glass substrate following deprotection at 200 °C. a) AFM image showing large crystallites of several microns size. b) AFM image zoomed in between large crystallites, showing that the space between is filled with a continuous film of smaller crystallites.

Light-induced Electron Spin Resonance (L-ESR)

Samples for L-ESR were prepared by injecting a quartz ESR tube with a 1:1 P3HT:**5b** solution in $CHCl_3$ and then evaporating the solvent under reduced pressure. The tube was then heated to 150 °C using an oil bath, yielding a thin-film of P3HT:**5a** covering the walls of the ESR tube. ESR spectra were obtained using a Bruker EMX X-band spectrometer at 9.45 GHz and 30 dB of microwave power (0 dB = 200 mW) with a rectangular TE_{102} cavity. A modulation amplitude of 1G was used. For illumination, a diode laser with peak emission at 532 nm was used, while for red, a laser with peak emission at 690 nm with a 650 nm long-pass filter was used. The sample temperature was controlled with an ESR 900 liquid He cryostat from Oxford Instruments. Measurements shown here for dark/light were obtained at 60K. To obtain g-values for the two photoinduced species, fitting function was applied assuming two Lorentzian peaks. The data with fitting is shown in S9.

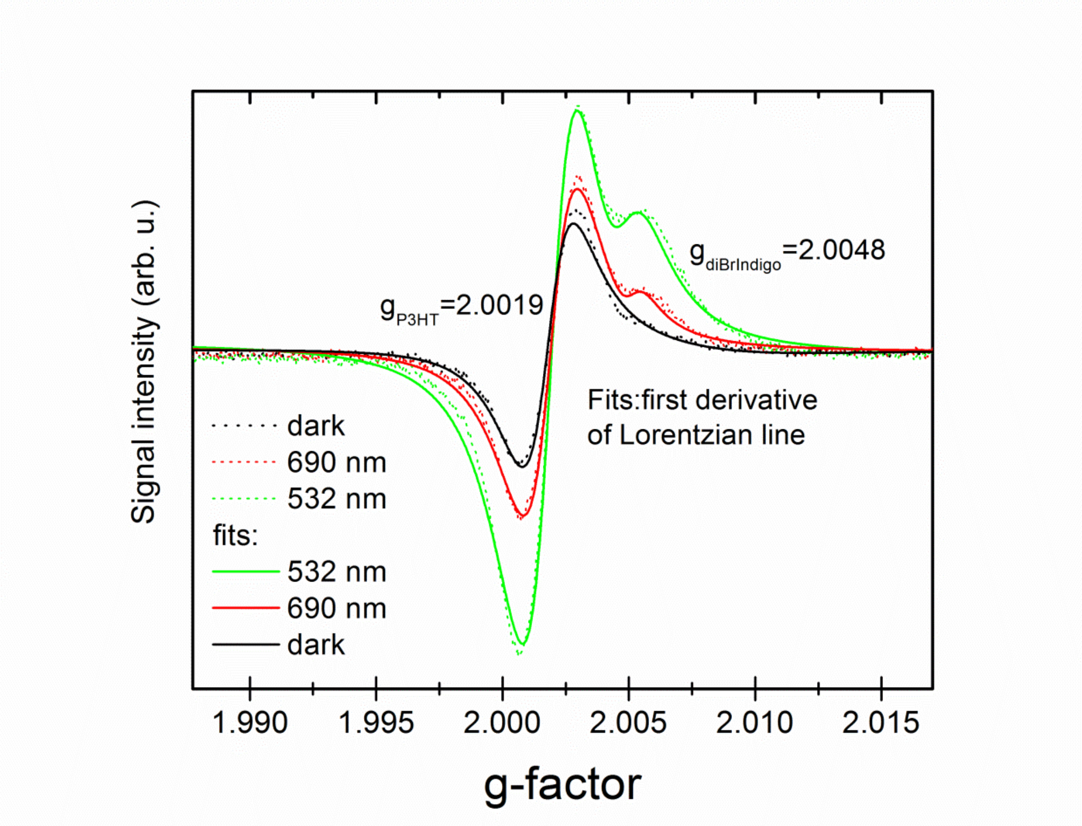


Figure S9. L-ESR spectra of a 1:1 P3HT/**5a** blend

Device fabrication and measurement

Organic diodes were fabricated using P3HT and 5,5'-dibromoindigo (5a) as the active layer. 5a was chosen due to the fact that it yielded uniform-sized crystallites in thin-films following deprotection, and also had an absorption significantly red-shifted relative to P3HT, as verifying hole-transfer from 5a to P3HT upon selective photoexcitation of 5a was of substantial fundamental interest to us. The devices were prepared as follows:

ITO-coated glass was cleaned with successive sonication in acetone, isopropanol, detergent, and DI water followed by O_2 plasma treatment. Branched polyethyleneimine ethylenediamine (PEIE) spin-cast from 2-methoxyethanol was used to modify the ITO surface to have a low work-function.[5] Blends of P3HT:5b in chlorobenzene were then spin-cast onto the ITO substrates, and were heated to 185°C for 5 minutes to afford conversion of 5b into pigment 5a. MoO_x (8 nm) followed by 80 nm of Ag were then thermally-evaporated to provide the high work function back-contact. These devices were thus "inverted" type. We likewise fabricated "normal" devices, using ITO modified with PEDOT:PSS as the bottom contact, and Al as a top contact. These devices demonstrated the same photocurrent and open-circuit voltage as the inverted ones. We prefer to work with inverted structures due to their air stability. The device area used was 0.15 cm^2 and 80 mW/cm^2 simulated solar illumination was used to test solar cell performance.

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[1] A. Baeyer, V. Drewsen, *Ber. Dtsch. Chem. Ges.* 1882, **15**, 2856-2864.

[2] R.J.H. Clark, Ch. J. Cooksey, *New. J. Chem.* 1999, 323-328.

[3] K. Ichimura, K. Arimitsu, M. Tahara, *J. Mater. Chem.* 2004**, 14**, 1164-1172.

[4] G. M. Wyman, *Chem. Rev.*, 1966, **55**, 625–657.

[5] Y. Zhou, C. Fuentes-Hernandez, J. Shim, J. Meyer, A. J. Giordano, H. Li, P. Winget, T. Papadopoulos, H. Cheun, J. Kim, M. Fenoll, a. Dindar, W. Haske, E. Najafabadi, T. M. Khan, H. Sojoudi, S. Barlow, S. Graham, J.-L. Bredas, S. R. Marder, a. Kahn, and B. Kippelen, *Science*, 2012, **336**, 327–332.