

Electronic Supplementary Information for

**Triisopropylsilylethynyl-Functionalized Dibenzo[*def,mno*]Chrysene:
A Solution-Processed Small Molecule for Bulk Heterojunction Solar
Cells**

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General: ^1H NMR and ^{13}C NMR spectra were recorded in deuterated solvent on a Bruker ADVANCE 300 NMR. ^1H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. MALDI-TOF-MS were determined on a Bruker BIFLEX III Mass spectrometer. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. THF was freshly distilled from sodium prior to use.

1. Synthesis and Characterization of TIPS-DBC

To a solution of triisopropylsilylacetylene (5.94g) in dry THF (250 ml), 11.9 mL of 2.5M n-BuLi (29.7 mmol) at 0 °C was added dropwise. The solution was allowed to stir for 1 h at 0°C before the addition of anthanthrene quinone^[1](1g). The mixture was warmed to room temperature and stirred over night. A solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (3 g) in 3M HCl (15 ml) was added to the solution at room temperature, and it was then stirred for 3h and then poured into water (500 ml), extracted with chloroform, and dried over MgSO_4 . The crude product was purified by a short silica chromatographic column (Hexane/dichloromethane 10:1) to provide red, needle-like crystals. Yield: 82%. M.p: 244-245°C. ^1H NMR (CDCl_3 , 300MHz): σ 9.12(d, 2H), 8.80(d, 2H), 8.29(d, 2H), 1.32(m, 42H). ^{13}C NMR (CDCl_3 , 300) σ 11.65, 19.00, 106.40, 106.50, 120.00, 124.60, 125.30, 125.63, 135.70; MALDI-TOF: 636.81. Anal.Calcd for $\text{C}_{44}\text{H}_{52}\text{Si}_2$: C, 82.96%; H, 8.23%; Found: C, 83.31; H, 8.40%.

2. CV spectra of TIPS-DBC

Cyclic voltammograms (CVs) were recorded on a 1000B model electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/Ag^+ electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) dissolved in THF was employed as the supporting electrolyte. THF was freshly distilled over LiAlH_4 prior to use.

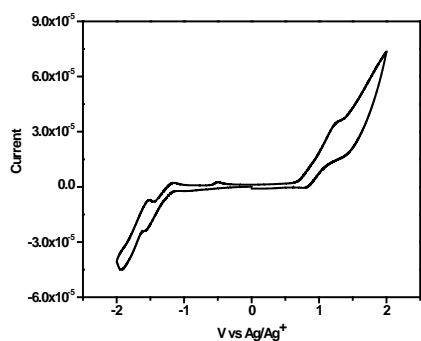


Figure 1. Cyclic voltammogram of TIPS-DBC.

3. DSC measurement of TIPS-DBC

Sample: A
Size: 2.6200 mg
Method: Ramp

DSC

File: G:\dsc recently\Feng\2011-0510\lei-a.004
Operator: Feng
Run Date: 10-May-11 13:58
Instrument: DSC Q200 V24.9 Build 121

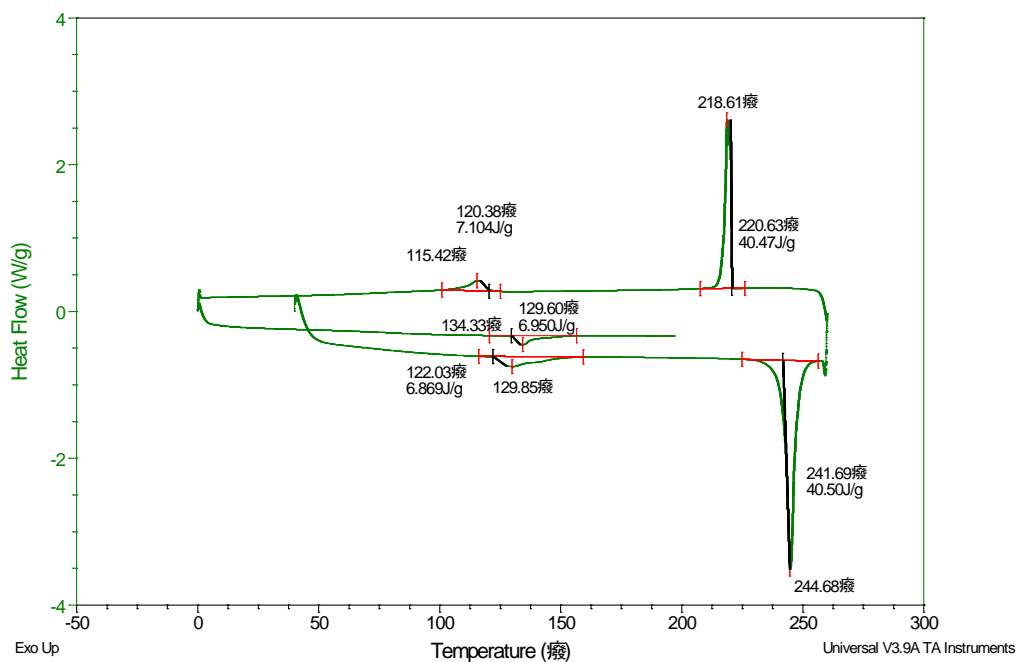


Figure 2. Differential scanning calorimetry (DSC) thermogram of TIPS-DBC.

4. ¹HNMR Stability Spectrum of TIPS-DBC/PCBM (1:1, w/w)

TIPS-DBC (2 mg) and PCBM (2 mg) were dissolved by 0.7 ml deuterated chloroform and monitored by ¹HNMR under ambient temperature over several days. Additionally, a film containing equal weight percents of TIPS-DBC and PCBM was cast, and subsequently annealed

for 5 min at 150°C. It was washed then off by deuterated chloroform and analyzed by ^1H NMR.

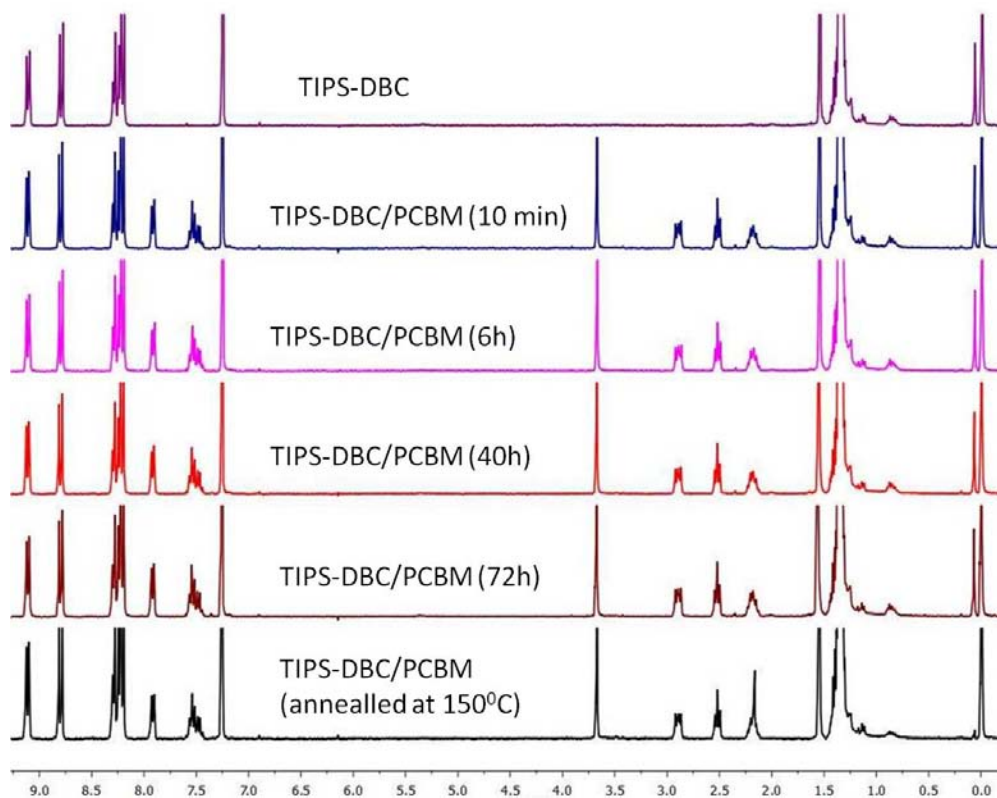


Figure 3. ^1H NMR spectra of TIPS-DBC and PCBM deuterated chloroform at different temperatures.

5. Devices Fabrication and Characterization

Solar Cells: [6,6]-phenyl- C_{60} -butyric acid methyl ester, [6,6]-phenyl- C_{71} -butyric acid methyl ester were obtained from American Dye source. The indium tin oxide (ITO)-coated glass substrates (20 ± 5 ohms/sq) were bought from Thin Film Devices Inc., and were cleaned through ultrasonic treatment in detergent, DI water, acetone, and isopropyl alcohol and then dried in an oven overnight. PEDOT: PSS (Baytron P VP A1 4083) (~ 40 - 50 nm) was spin-coated onto ultraviolet ozone-treated ITO substrates. After annealing at 140 - 150 °C for 30 min in air, the substrates were transferred to a glove box. The TIPS-DBC (10 mg): PC_{71}BM (10 mg)/1 mL chloroform solution was spin-coated on top of the PEDOT: PSS layer at 3000 rpm. The thickness of film was 80 - 100 nm (KLA-TENCOR Alpha-Step IQ Surface Profiler). An 80 - 100 nm thick Al cathode was deposited (area 6 mm 2) on the active layer under high vacuum (2×10^{-4} Pa) using a thermal evaporator. For thermal annealing, spin coated films were placed directly onto a digitally controlled hot plate and heated to the desired temperatures 2 minutes, after which they

were transferred to a room temperature surface to cool. All current-voltage (I-V) characteristics of the devices were measured under simulated AM1.5G irradiation (100 mW cm^{-2}) using a Xe lamp-based Newport 91160 300-W Solar Simulator. A Xe lamp equipped with an AM1.5G filter was used as the white light source. The light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter or KG1 optical. Quantum efficiencies were measured with a Xe lamp, monochromator, optical chopper and lock-in amplifier; photon flux was determined by a calibrated silicon photodiode. AFM images were collected in air under ambient conditions using an Innova scanning probe microscope (Veeco). Silicon probes with resonant frequencies of 75 KHz (Budget Sensors) were used for tapping mode AFM measurements.

1) TIPS-DBC: PC₆₀BM 50:50 (w/w)

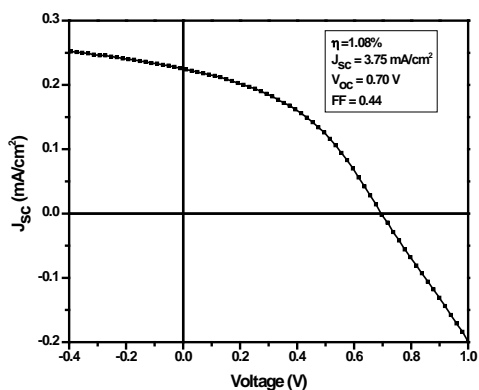


Figure 4. (a): J-V Curves of solar cells based on the blend of TIPS-DBC/PC₆₀BM (50:50, w/w).

2) TIPS-DBC: PC₇₁BM 30:70 (w/w)

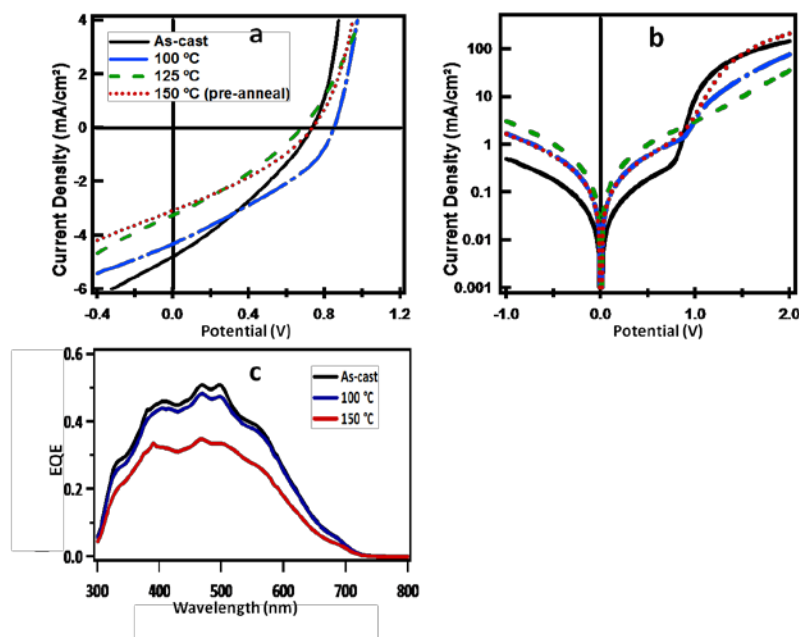


Figure 5. (a): J-V Curves of solar cells based on the blend of TIPS-DBC/PC₇₁BM (30:70, w/w); (b): Dark current measurement of the TIPS-DBC/PC₇₁BM (30:70, w/w); (c): EQE spectra of solar cells based on the blend of TIPS-DBC/PC₇₁BM (30:70, w/w) under different conditions.

Table 1. The best performance of selected solar cells based on the blend of TIPS-DBC/PC₇₁BM (30:70, W/W).

	As-Cast	100°C	125°C	150°C
$R_{series}(\Omega\text{cm}^2)$	7.1	7.8	14.6	3.8
$R_{parallel}(\Omega\text{cm}^2)$	3776	1178	712	1192
$J_{sc}(\text{mA}/\text{cm}^2)$	4.805	4.328	3.250	3.075
$V_{oc}(\text{V})$	0.735	0.850	0.680	0.738
$FF(\%)$	0.309	0.342	0.306	0.328
$PCE(\%)$	1.091	1.257	0.677	0.744

3) TIPS-DBC: PC₇₁BM 70:30 (w/w)

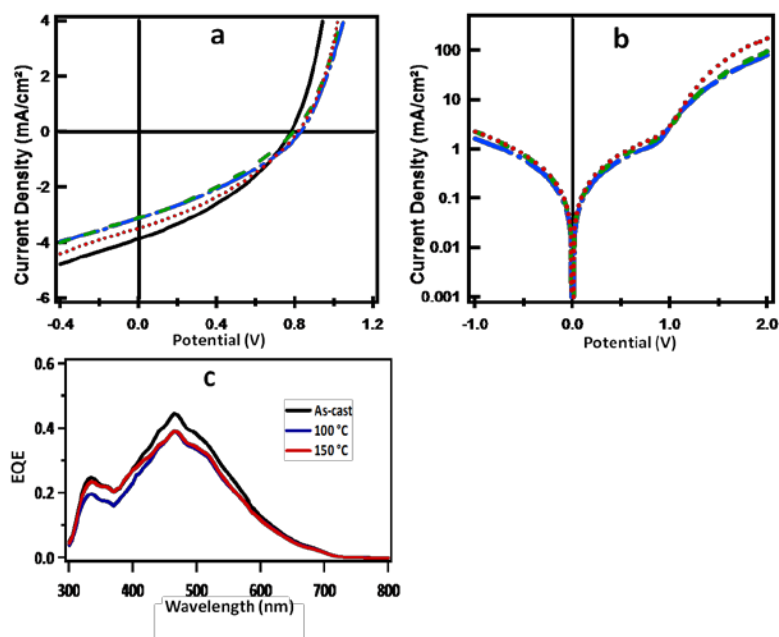


Figure 6. (a): J-V Curves of solar cells based on the blend of TIPS-DBC/PC₇₁BM (70:30, w/w); (b): Dark current measurement of the TIPS-DBC/PC₇₁BM (70:30, w/w); (c): EQE spectra of solar cells based on the blend of TIPS-DBC/PC₇₁BM (70:30, w/w) under different conditions.

Table 2. The best performance of selected solar cells based on the blend of TIPS-DBC/PC₇₁BM (70:30, W/W).

	As-Cast	100°C	125°C	150°C
$R_{series}(\Omega cm^2)$	--	7.6	6.2	3.5
$R_{parallel}(\Omega cm^2)$	--	1101	950	886
$J_{sc}(mA/cm^2)$	3.858	3.122	3.103	3.477
$V_{oc}(V)$	0.780	0.830	0.794	0.816
$FF(\%)$	0.357	0.332	0.332	0.344
$PCE(\%)$	1.074	0.860	0.820	0.975

4) TIPS: PC₇₁BM 50:50 (w/w)

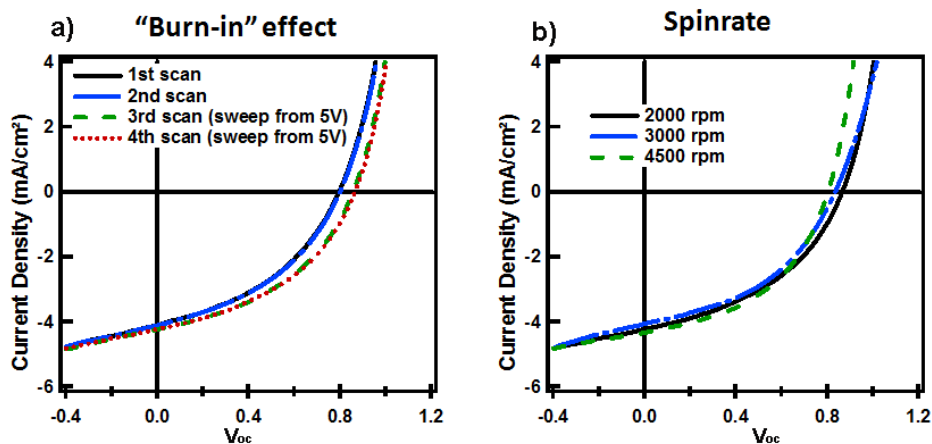


Figure 7. (a): The effect of scan voltages on J-V Curves (from 795 mA to 865 mA). (b): The effect of spin rates on J-V Curves (from 3000 rpm to 2000 rpm or 4500 rpm).

6. AFM Images of the Blends

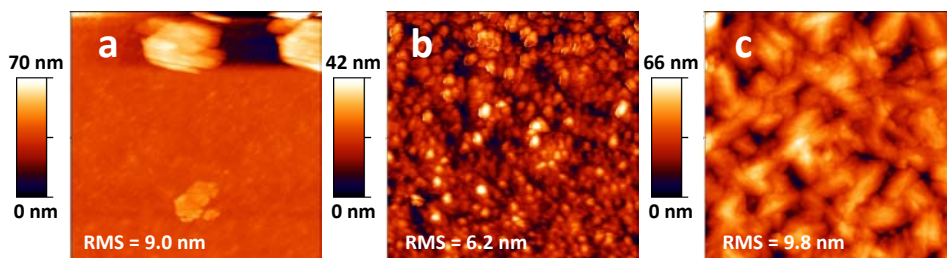


Figure 8. AFM images of TIPS-DBC:PC₇₁BM films with different ratios. a–c) Height images of as-cast film, a) 30:70 (w/w); b) 50:50 (w/w); c) 70:30 (w/w); All images are 2 µm × 2 µm.

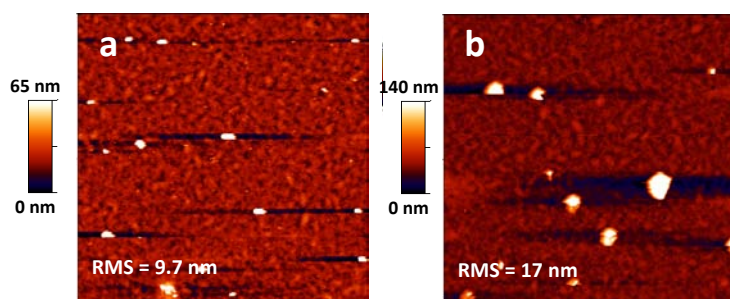


Figure 9. AFM height images of TIPS-DBC:PC₇₁BM films (50:50, w/w). a) as cast; b) after annealing at 150 °C. All images are 10 µm × 10 µm.

7. GIXD Patterns of TIPS-DBC Thin Film

Grazing incidence X-ray scattering characterization of the TIPS-AA films was performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam lines 2-1, and 11-3. The scattering intensity was recorded on a 2-D image plate (MAR-345) with a pixel size of $150\ \mu\text{m}$ (2300×2300 pixels). The samples were ~ 10 mm long in the direction of the beam path, and the detector was located at a distance of 400 mm from the sample center (distance calibrated using a Lanthanumhexaboride standard). The incidence angle was chosen in the range of $0.10\text{--}0.12^\circ$ to optimize the signal-to-background ratio. The beam size was $50\ \mu\text{m} \times 150\ \mu\text{m}$, which resulted in a beam exposure on the sample $150\ \mu\text{m}$ wide over the entire length of the 10 mm long sample. The data were distortion-corrected (θ -dependent image distortion introduced by planar detector surface) before performing quantitative analysis on the images using the software WxDiff.[S.C.B. Mannsfeld, M.L Tang, Z. Bao, “Thin Film Structure of Triisopropyl-silylethynyl-Functionalized Pentacene and Tetraceno[2,3-b]thiophene from Grazing Incidence X-ray Diffraction “, *Adv. Mater.* **23**, 127 (2011).] The overall resolution in the GIXD experiments, dominated by the sample size, was about $0.01\ \text{\AA}^{-1}$.

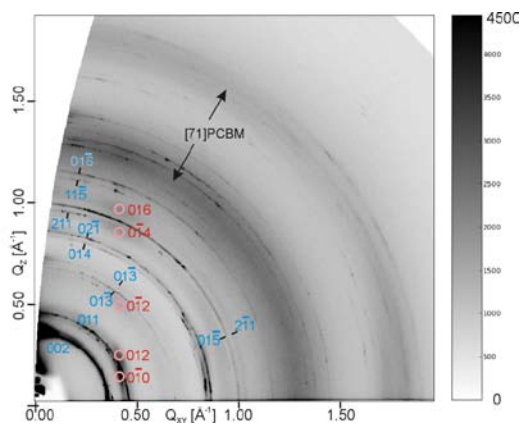


Figure 10. GIXD image of the TIPS-DBC:PC₇₁BM blend (100 nm). The diffraction image indicates that the blended film is composed of randomly oriented crystallites of the TIPS-DBC bulk lattice structure (prominent lines indexed in blue), a substrate-near thin film polymorph of TIPS-DBC ($\{01\}$ Bragg rods clearly visible; red indices), and nanocrystalline PC₇₁BM particles that produce broad 3D powder rings.

The GIXD image (Fig. 11) of the TIPS-DBC:PC₇₁BM is composed of scattering signals from both TIPS-DBC crystallites and PC₇₁BM nanocrystals. TIPS-DBC forms a 3D powder (producing diffraction rings) of large crystallites. These lines are quite narrow (~ 1 mrad), indicating crystallite sizes with coherence lengths of at least several micrometer (lower limit). The diffraction lines were successfully indexed consistent with the TIPS-DBC bulk unit cell:

$|a|=13.89 \text{ \AA}$, $|b|=15.17 \text{ \AA}$, $|c|=35.46 \text{ \AA}$, $\alpha=88.9^\circ$, $\beta=79.7^\circ$, $\gamma=84.14^\circ$. In addition to the 3D powder diffraction signal, the $\{01\}$, $\{10\}$ Bragg rods of a bulk-like thin film phase are visible at an in-plane momentum transfer value of $Q_{xy}=0.42 \text{ \AA}^{-1}$ (indices in red in Fig. 11; this phase has been clearly identified in evaporated thin films). The existence of these Bragg rods and their faint appearance suggests that TIPS-DBC crystallites in the layers closer to the substrate grow in an oriented thin film phase (which is buried thus strongly attenuated), with its basal plane parallel to the substrate surface. With increasing distance from the substrate, the orientation of the crystallites becomes more random and the lattice becomes that of the bulk phase (forming the more intense 3D powder lines).

PC₇₁BM produces broad powder rings at 1.3 \AA^{-1} and 1.8 \AA^{-1} that are in agreement with values reported in literature. [Ref.: "The Role of Alkane Dithiols in Controlling Polymer Crystallization in Small Band Gap Polymer:Fullerene Solar Cells"]. The large breadth of these rings indicates very small crystallites of completely random orientation throughout the entire film thickness. Using the Debye-Scherrer formula, [ref: Patterson, A. "The Scherrer Formula for X-Ray Particle Size Determination". Phys. Rev. 56, 978–982 (1939).] the PC₇₁BM particle size can be estimated as 2 nm (note that this estimates the coherent particles size).

8. Reference

1. D. Thetford, A. P. Chorlton, *Dyes and Pigments*, **2004**, 61, 49.