## **Electronic Supplementary Information**

## Increased Thermal Stabilization of Polymer Photovoltaic Cells with Oligomeric PCBM

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#### Equipment

<sup>1</sup>H (400.6 MHz), <sup>13</sup>C (100.16 MHz), and 2-D NMRs were recorded on a Bruker<sup>®</sup> Avance 400 spectrometer at ambient temperature using solvents as indicated. Characterisations using size exclusion chromatography (SEC) were performed at 30 °C with THF as eluent at a flow rate of 1 mL min<sup>-1</sup> and toluene flow marker; calibration was against polystyrene standards and samples (0.5 to 4 mg mL<sup>-1</sup>) were pre-filtered. UV-visible spectra were recorded on a Shimadzu UV-2450PC spectrophotometer. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. Differential scanning calorimetry was performed on a Perkin Elmer DSC8000 with solid samples in aluminium crucibles at a heating/cooling rate of 10 °C min<sup>-1</sup> under a flux of N<sub>2</sub> maintained at 20 mL min<sup>-1</sup>. Data treatment was performed with Pyris<sup>™</sup> series DSC8000 software. X-Ray and Ultraviolet Photoelectron Spectroscopy (XPS, UPS) measurements were performed using a multi-chamber UHV-system (base pressure 2 x10<sup>-10</sup> mbar), equipped with a Phoibos 150 cylindrical hemispherical analyzer (SPECS), a monochromatic Al Kα source and a high-flux He discharge lamp (UVS 300, SPECS). The energetic resolution determined from the width of the Fermi edge for XPS and UPS was about 400 meV and 100 meV, respectively. The binding energy (BE) scale of the spectra was calibrated to reproduce the BE of Au4f7/2 (84.0 eV), Ag 3d5/2 (368.3 eV) and Cu2p3/2 (932.5 eV).



**Figure S1**. XPS overview spectrum of OPCBMMB on ITO. The OPCBMMB film was prepared by doctor blade casting. From the attenuation of the substrate related In 3d core level signal we estimate the film thickness to be about 5 nm. Beside the substrate related features only C1s and O1s signals of the oligomer were found. Catalysts were not detectable (detection limit 0.5-1%).

Peak	OPCBMMB			
	expected conc.	Experimental		
	(%)	conc. (%)		
C1s	95.8	87.9/96.7*		
O1s	4.2	12.1/3.4*		

Table S1. Atomic concentration as determined from the overview spectrum.

\* value obtained subtracting the contribution of ITO determined by O1s peak fitting.

The atomic concentration was determined using sensitivity factors from Wagner.<sup>S1</sup> The contribution of ITO to the O1s signal was subtracted (*cf.* Figure S2). The O-content of 3.4% is significantly less than the expected value of 4.2% for the OPCBMMB and points thus to a significant contribution of PCBM in agreement with GPC data discussed in the paper.



**Figure S2**. O1s core level spectrum for OPCBMMB on ITO. The signals shown in dark yellow are related to the ITO substrate. They contribute to about 72% to the total intensity. We ascribe the peak at 532 eV to C=O from the methoxycarbonyl group, whereas the peak at higher binding energy is related to C-O-C of the methoxycarbonyl group overlapping with oxygen from benzene-O-alkyl. The peak fit analysis was performed using the program Unifit.<sup>S2</sup>



Figure S3. TGA thermograms of OPCBMMB and PCBM.



**Figure S4**. DSC thermograms of OPCBMMB (red and labelled here HHR25) and PCBM (black): top, 1<sup>st</sup> cycle, below, 2<sup>nd</sup> cycle; left, heating, right, cooling.

### Calculations and discussion on the relative thermal stability of polyC<sub>60</sub> and OPCBMMB

This can be demonstrated by considering **Table 1**, which shows the various temperatures, molecules and broken bonds.  $T_0$  is a temperature at which neither C<sub>60</sub>-methylenephenylene system (A) nor PCBM-methylenephenylene system (B) are as yet dissociated. At  $T_0$  the thermal energy is of the order of  $k_{\rm B}T_0$ . This energy is, completely or in part, absorbed by a number  $(m_A)$  of vibrators in (A) and a number  $(m_B)$  of vibrators in (B). At a temperature  $(T_1)$ the system (A) breaks at the weakest bond i.e., the methylene-C<sub>60</sub> bond, to give the molecules shown. At this temperature, system (B) does not break as part of the available energy is distributed over certain vibrators of the phenyl butyric acid methyl ester side group. Finally, at a temperature  $T_2$ , (B) breaks at the same PCBM-methylene bond.

At  $T_0$ , the energies dissipated over (A) and over (B) are, respectively, as in equations (1 and 2):

$$k_{B}T0 = \sum_{i=1}^{m_{A}} hc_{\omega_{i}}exp^{\frac{-h\omega_{i}}{RT}} \qquad k_{B}T0 = \sum_{i=1}^{m_{B}} hc_{\omega_{i}}exp^{\frac{-h\omega_{i}}{RT}} \qquad \text{with } m'_{A} \ge m_{A} \text{ and } m_{B} \ge m_{A}$$
  
and at  $T_{1}$  these expressions become equations (2 and 3):

$$k_{B}T1 = \sum_{i=1}^{m_{A}} hc_{\omega_{i}}exp^{\frac{-n\omega_{i}}{RT}} + E_{diss} \text{ and } k_{B}T1 = \sum_{i=1}^{m_{A}} hc_{\omega_{i}}exp^{\frac{-n\omega_{i}}{RT}} + E_{diss}$$

with  $m''_A \ge m'_A$  and  $m_B \le m_B$ 

At  $T_2$  the expression for system (B) becomes:

 $k_B T 2 = \sum_{i=1}^{m''_B - 1} h c_{\omega_i} exp^{\frac{-h\omega_i}{RT}} + E_{diss}$  with  $m''_B \ge m'_B$ (5) Equation

We have thus estimated the contribution of the additional vibrators present on (B) with respect to (A) using a simple semi-empirical AM1 calculation. The vibrational results are reported in Table S2. They indicate that at 100 °C the thermal energy that is available is calculated at 69 cm<sup>-1</sup> or 0.2 kcal mol<sup>-1</sup>. The PCBM-methylenephenylene system (B) possesses, at this energy,  $m''_{B} - m'_{A} = 6$  vibrators more than C<sub>60</sub>-methylenephenylene system (A). The sum of these vibrators represents around 0.6 kcal mol<sup>-1</sup>. An identical calculation can be performed for a much higher temperature, for example, at 500 °C, there are  $m'_{B} - m'_{A} = 21$ additional vibrators that contribute to the absorption, equivalent to 11.6 kcal mol<sup>-1</sup>. The contribution of these vibrators, at 500 °C, is thus estimated to be approximately 25% of the energy necessary to break the most fragile bond in the two systems i.e., the C<sub>60</sub>-methylene bond. This same contribution was only 1.5% at 100 °C.

Another simple calculation can be carried out to estimate the energy range over which system (B) is protected by its vibrators. System (A) possesses 174 vibrators with an average energy per vibrator of 1074 cm<sup>-1</sup>. System B, however, has 258 vibrators with an average energy per vibrator estimated at 1135 cm<sup>-1</sup>. The average contribution of the additional vibrators is thus 61 cm<sup>-1</sup> or ca 42 °C. It should be stated that the aim of this calculation is not to determine the difference  $T_1$ - $T_2$ , but rather to give an approximate estimation of the effect of the additional vibrators. The chosen model will not take into account coupling between modes (and thus the mechanical anharmonicity) nor does it recognize that the communal modes of (A) and (B) are not exactly identical due to the numerous couplings arising from the phenyl butyric acid methyl ester group. Finally, it should be similarly noted that such changes may not be observed in the TGA due to the fact that the  $C_{60}$  will not escape the matrix of the material.



**Table S2.** Denotation of temperatures and the ruptured bonds studied.

PCBM	C <sub>60</sub>	573	574	887	904	1324	1326
11		575	574	889	904	1328	1326
23		579		894	904	1329	1326
31		589		901	904	1339	
42		608	611	901	904	1352	
46		611	611	902	904	1360	
50		617	611	903	908	1369	
76		618	623	905	908	1374	
102		618	623	906	908	1378	
112		622	623	906		1379	1383
140		628	628	908		1381	1383
159		631	628	912		1384	1383
181		634	628	946		1386	1390
212		639	628	958		1391	1390
236		651	660	966		1393	1390
265		656		986	990	1394	1390
275	284	677		988	990	1395	1390
276	284	693		990	990	1397	1405
286	284	716		994	990	1401	1405
289	284	723	730	1005	990	1404	1405
304		725	730	1009	1018	1407	
312		732	730	1014		1410	
357	376	737	730	1048		1424	
366	376	742	730	1059		1429	
367	376	752		1083		1433	
371	376	769	776	1109		1443	1442
373	379	774	776	1135		1447	1443
376	379	776	776	1155		1450	1443
383	379	779	782	1162	1169	1452	1443
386		781	782	1164	1169	1456	1443
390		782	782	1170	1169	1457	1459
425	432	782	782	1173	1169	1457	1459
425	432	783	782	1181		1463	1459
433	432	783	782	1193		1464	1466
437	432	787	782	1196		1468	1467
439	432	795	782	1197		1469	1467
454	463	815	829	1213		1472	1467
459	463	821	829	1215		1477	1481
461	463	822	829	1223	1224	1483	1481
462	463	825	829	1227	1224	1487	1481
471	463	827	830	1229	1224	1492	1481
482		829	830	1236		1497	1500
490		830	830	1239		1499	1500
506	515	833	830	1251		1501	1500
514	515	835	830	1282		1502	1500
517	515	847	852	1290		1508	1500
	-		-				

534	515	849	852	1295		1510	1502
560	573	851	852	1299	1297	1511	1502
566	573	852	852	1303	1297	1512	1502
567	573	860	867	1307	1297	1530	
570	573	867	867	1310	1297	1565	
572	573	867	867	1313	1326	1621	1652
573	574	870	904	1323	1326	1643	1652
573	574	887	904	1324	1326	1657	1652
1660	1652	1811	1816				
1661	1686	1814	1817				
1682	1686	1822	1817				
1683	1686	1824	1817				
1685	1686	1826	1817				
1688	1686	1828					
1698		2076					
1716		2999					
1729	1728	3015					
1729	1728	3030					
1744	1728	3073					
1745	1728	3075					
1752	1753	3086					
1757	1753	3091					
1761	1753	3099					
1779	1787	3155					
1782	1787	3178					
1787	1787	3182					
1787	1787	3186					
1791	1787	3190					
1794	1799	3199					
1795	1799						
1800	1799						
1802	1799						



Figure S5. Normalized UV-visible spectra of films of OPCBMMB (black) and PCBM (red).

	J <sub>sc</sub> (mA cm <sup>-2</sup> )	V <sub>oc</sub> (V)	FF (%)	PCE (%)
РСВМ	7.27 (± 0.342)	0.537 (± 0.004)	47.4 (± 3.55)	1.85 (± 0.111)
ОРСВММВ	7.37 (± 0.521)	0.528 (± 0.006)	45.7(± 3.30)	1.79 (± 0.213)



**Figure S6**. UPS spectrum of OPCBMMB on ITO. A negative bias of 12 V was applied to the sample in order to determine the work function  $\mathbb{P}$  from the high binding energy cut-off of the spectrum. We obtain  $\mathbb{P}$  = 4.5 eV and the onset of the highest occupied molecular orbital (HOMO) is 1.5 eV, giving an ionization potential ( $\mathbb{P}$  + HOMO) of 6.0 ± 0.1 eV. The value is very similar to that of PCBM (6.10 eV) reported in the literature.<sup>S3</sup>



**Figure S7.** Change in PCE values for P3HT:PCBM devices fabricated on glass and PET as a function of annealing time at 120 °C.



**Figure S8**. Normalised (a)  $J_{SC}$ , (b)  $V_{OC}$  and (c) FF values for P3HT:PCBM (red) and P3HT:OPCBMMB (black) devices as a function of annealing time at 120 °C. Note that although all parameters are changing under the influence of thermal stress it is the observed change in extracted current that accounts for the loss in PCE most strongly.



**Figure S9**. (left to right) Absorption spectra of P3HT, P3HT:PCBM and P3HT:OPCBMMB films after various stages of annealing. Note that after some time PCBM absorption is decreased and scattering is observed to increase in samples containing PCBM (after 5 h) and OPCBMMB (after 25 h) corresponding to aggregation of the acceptor species.



**Figure S10**. (a)  $J_{SC}$ , (b)  $V_{OC}$ , (c) FF and (d) PCE values for Si-PCPDTBT:PCBM (green) and Si-PCPDTBT:OPCBMMB (black) devices as a function of annealing time at 120 °C.



**Figure S11**. (a)  $J_{SC}$ , (b)  $V_{OC}$ , (c) FF and (d) PCE values for PCDTBT:PCBM (purple) and PCDTBT:OPCBMMB (black) devices as a function of annealing time at 120 °C.

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