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Matrix Organization and Merit Factor Evaluation as a Method to Address the Challenge of Finding a Polymer Material for Roll Coated Polymer Solar Cells

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The results presented demonstrate how the screening of 104 light-absorbing low band gap polymers for suitability in roll coated polymer solar cells can be accomplished through rational synthesis according to a matrix where 8 donor and 13 acceptor units are organized in rows and columns. Synthesis of all the polymers corresponding to all combinations of donor and acceptor units is followed by characterization of all the materials with respect to molecular weight, electrochemical energy levels, band gaps, photochemical stability, carrier mobility, and photovoltaic parameters. The photovoltaic evaluation is carried out with specific reference to scalable manufacture, which includes large area (1 cm²), stable inverted device architecture, an indium-tin-oxide-free fully printed flexible front electrode with ZnO/PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate), and a printed silver comb back electrode structure. The matrix organization enables fast identification of active layer materials according to a weighted merit factor that includes more than simply the power conversion efficiency and is used as a method to identify the lead candidates. Based on several characteristics included in the merit factor, it is found that 13 out of the 104 synthesized polymers outperformed poly(3-hexylthiophene) under the chosen processing conditions and thus can be suitable for further development.

1. Introduction

Polymer solar cells (PSCs) are seen as an important solution to the estimated increase in global energy consumption of 1 GW per day due to the low energy pay-back time (EPBT), the potentially high energy return factor (ERF), the small or nonexistent ecotoxicity, and the fully scalable high speed manufacture. This is mainly ascribed to the reduced amount of energy used during production and the avoidance of scarce materials, which has already resulted in an EPBT of 90 days for system-integrated PSCs^[1] with the potential of reaching an EPBT of only 1 day.^[2] The potentially high ERF can be achieved through increased device lifetime, higher device efficiency, and lower energy production cost.

Research into PSCs has increased exponentially over the last decade, with more than 46 500 published papers.^[3]

This increase is partly attributable to the fact that the polymer composition in the active layer has varied due to the use of a large number of different types of conjugated polymers. The most common factor for comparison in the PSC research field is the power conversion efficiency (PCE). In the past decade, the main focus has been on increasing the PCE, and lately efficiencies of over 10% have been reported for small area devices (mm² scale).^[4] Much of the increase in PSC efficiency arises from an optimization of the light-absorbing conjugated polymer applied in the active layer of the device. Low band gap polymers have been developed to absorb light at wavelengths longer than 650 nm and thus have a band gap below 2 eV.^[5] This is done by a very common approach where two monomers, one electron donating and one electron accepting unit, are coupled to produce a low band gap polymer with a charge transfer band at longer wavelengths (lower energy) together with π - π transitions in order to cover a larger part of the solar spectrum. In theory this will give a higher photocurrent compared to, e.g.,

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poly(3-hexylthiophene) (P3HT), which has a band gap of 2 eV, due to an absorption profile that is better matched with the solar spectrum. Thus, a potentially higher PCE of the PSC can be reached, given that the energy level alignment with the acceptor in the active layer is optimal.^[5] For large-area PSC modules, the reported PCE values are significantly lower (2%–3%)^[4] and studies by Jørgensen et al.^[6] clearly demonstrate this. Thus, the 10% efficiency can be viewed as somewhat misleading for several reasons. First of all, interlaboratory measures of efficiency are not necessarily comparable, which has led to a practice of sending the hero devices to be certified at certain trusted laboratories. The same principle has been applied in so-called round robin studies,^[7,8] where the same devices were tested at several laboratories with considerable variation as a result. Another important issue is that an overwhelming majority (95%) of the devices is made with glass substrates, often using indium-tin-oxide (ITO) as the transparent electrode and with a diminutive active area. Any real-world application would probably use flexible plastic substrates, no scarce materials (e.g., indium), roll-to-roll (R2R) fabrication, and considerably larger devices as convincingly demonstrated in the first polymer solar park.^[1] However, less interest has been devoted to these types of devices, even though all indications show that the PCEs obtained in the former laboratory-scale devices cannot be transferred to larger R2R-fabricated devices.^[9] The transfer of any successful PSC from small scale to large scale in a R2R setting requires ambient atmosphere, flexible substrates, freedom from indium and vacuum, and, to complicate matters even further, potentially opens up for a myriad of film forming techniques and inks. Such a transfer, however, has been simplified by the development of the mini roll coater, which applies processing conditions similar to large-scale R2R, but in smaller scale ($100 \times 1 \text{ cm}^2$).^[9] It is essential to note the vast number of choices which can influence the performance of a PSC based on a given active material, and to realize the impossibility of testing all factors for all active polymer materials. Instead, focus should be on settings that are realistic in the context of production and end application. For all the above reasons, the countless scientific studies obtained thus far will only offer a partial answer to the question of whether a given conjugated polymer is suitable for R2R-processed PSCs.

Our main interests lie in developing PSCs to the level of larger-scale fabrication, and we therefore needed a more rational approach. This was in part inspired by how pharmaceutical companies use screening studies to find lead compounds that can later be optimized both with respect to detailed structure and application. They start by building a large library of compounds, which is tested using fairly simple procedures. This gives insights into which chemical structures perform best and should be further elaborated. Even though several thousand different polymer materials have been applied as light-absorbing polymer material in the active layer, to our knowledge such a systematic screening has only been carried out in one instance in the field of PSC using ink jet printing. However, this screening was restricted to two different polymers and two different fullerenes.^[10] Moreover, while many polymer materials have been compared in reviews,^[11–13] one must keep in mind that laboratories using different methods (spin speed,

light source) will generate different PCE measurements of the same polymer as demonstrated in round robin studies.^[7,8] This makes a review based on a comparison of different polymers measured at different laboratories less reliable. In the present study we have utilized a screening strategy comprising the selection of 8 donor and 13 acceptor monomers which give a total of 104 polymers after the combinatorial pairing. This constituted the library that formed the basis for the screening of the photovoltaic properties of roll-coated PSCs and other properties. Our work demonstrates the challenges associated with the design of polymer materials for scaled PSCs, which include a multitude of materials and processing parameters and progress significantly beyond simple criteria such as evaluation according to PCE alone. We conclude on the effort needed for identification of new lead candidates^[14,15] and estimate that only a few percent of all newly reported polymers qualify for further development. We expect that only a small fraction of these will qualify for scaled manufacture of PSCs.

2. Results and Discussion

Table 1 offers a comprehensive overview of all the data collected for the 104 possible polymers based on 13 acceptor monomers (left column) and 8 donor monomers (top row). Each cell in the table represents a unique polymer and contains 8 entries: optical band gap (eV), highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) energies, hole mobility, average PCE and standard deviation together with the highest open circuit voltage (V_{OC}) obtained, PCE values from the literature, photochemical stability, and finally the number of synthetic steps.

2.1. Data Handling

Computer programs and databases were developed in order to handle the enormous amount of data which was produced upon characterization of the 104 polymer materials. For each polymer, 12 different PSC types were prepared (based on 2 different solvents in 2 different polymer/[60]PCBM (phenyl- C_{61} -butyric acid-methyl-ester) ratios coated with 3 different thicknesses). About 50 devices were made for each of these 12 combinations, for which at least 5 of the samples were measured to give the average PCE. This adds up to some 5340 I – V curves measured in total. Each experiment had its own folder and the IV measurement program was set to save the data in the corresponding folder based on the solvent/ratio/thickness combination. On our internal webpage we added a data analysis program, which gave an overview of the data collected during the characterizations. This allowed us to keep track of the progress and gave a clear overview of which polymers performed best. The following measured data were also saved in the database: UV–vis (2 absorption curves for each polymer in solution and as film), square wave voltammetry (SWV; 4 curves for each polymer, i.e., 2 forward and 2 reverse), hole mobility (2 I – V curves in the dark for 2 different active layer thickness), absorption curves used to determine photochemical stability (12 absorption curves are measured per hour, the total number

Table 1. Continued

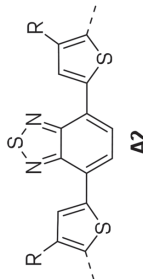
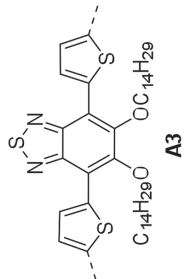
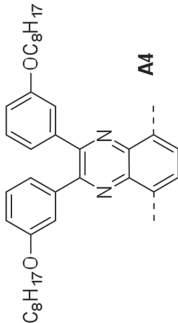
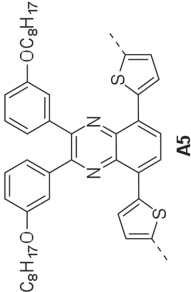
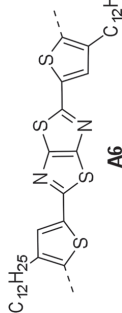
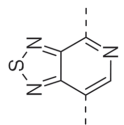
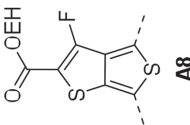
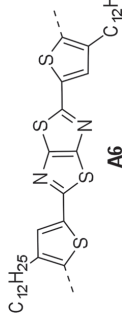
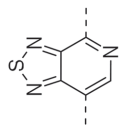
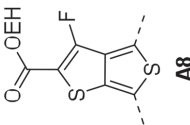
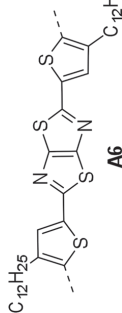
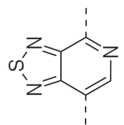
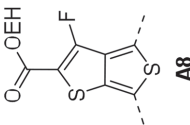
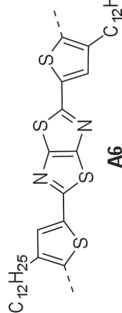
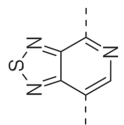
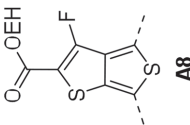
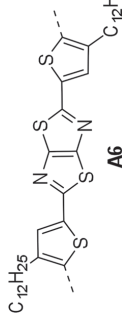
A2	A2 R=C ₁₂ H ₂₅ ; D1 R=hexyl		A2 R=C ₁₂ H ₂₅		A2 R=C ₁₂ H ₂₅ ; D5 R=H		A2 R=H		A2 R=C ₁₂ H ₂₅		A2 and D8 R=C ₁₂ H ₂₅		A2 R=C ₁₂ H ₂₅	
	1. 1.52	2. -5.03/-3.51	1. 1.61	1. 1.69	1. 1.58	1. 1.88	1. 1.65	1. 1.64	1. 1.65	1. 1.64	1. 2.05	1. 1.64	1. 1.65	1. 1.64
	3. 9500; 2.0	4. 4.28E-08	3. 12 400; 11.4	4. 9.75E-10	3. 540 000; 4.2	3. 1860; 2.9	3. 7500; 3.2	3. 9400; 1.8	3. 7500; 3.2	3. 9400; 1.8	3. 8600; 1.5	3. 9400; 1.8	3. 7500; 3.2	3. 9400; 1.8
	5. 0.44 ± 0.03 (0.48); 0.54	6. 2.95 (A2 R=H, PC71BM)	5. 1.02 ± 0.14 (1.3); 0.63	5. 0.5 ± 0.06 (0.61); 0.62	5. 0.07 ± 0 (0.08); 0.50	5. NA	5. 1.24 ± 0.1 (1.38); 0.65	5. NA	5. 1.24 ± 0.1 (1.38); 0.65	5. NA	5. NA	5. NA	5. 1.24 ± 0.1 (1.38); 0.65	5. NA
	7. 16.9 ± 0.5 (0.15)		7. 0.54 ± 0.04 (0.24)	7. 1.17 ± 0.09 (0.26)	7. 0.45 ± 0.05 (0.44)	7. 8.51 ± 0.95 (0.27)	7. 0.83 ± 0.07 (0.60)	7. 5.67 ± 0.29 (0.21)	7. 0.83 ± 0.07 (0.60)	7. 5.67 ± 0.29 (0.21)	7. 20.22 ± 3.05 (0.52)	7. 5.67 ± 0.29 (0.21)	7. 0.83 ± 0.07 (0.60)	7. 5.67 ± 0.29 (0.21)
	8. #14		8. #12	8. #12	8. #8	8. #14	8. #9	8. #11	8. #9	8. #11	8. #11	8. #11	8. #9	8. #11
A3	A3 R=C ₁₂ H ₂₅ ; D1 R=hexyl		A3 R=C ₁₂ H ₂₅		A3 R=C ₁₂ H ₂₅ ; D5 R=H		A3 R=H		A3 R=C ₁₂ H ₂₅		A3 and D8 R=C ₁₂ H ₂₅		A3 R=C ₁₂ H ₂₅	
	1. 1.70	2. NA	1. 1.70	1. 1.83	1. 1.67	1. 1.99	1. 1.83	1. 1.84	1. 1.83	1. 1.84	1. 1.74	1. 1.74	1. 1.83	1. 1.84
	3. 50 000; 10.8	4. NA	2. -5.10/-3.49	2. -5.15/-3.32	2. -4.98/-3.31	2. -5.41/-3.42	2. -4.98/-3.15	2. -5.30/-3.46	2. -4.98/-3.15	2. -5.30/-3.46	2. -4.92/-3.18	2. -4.92/-3.18	2. -4.98/-3.15	2. -5.30/-3.46
	5. 0.21 ± 0.05 (0.32); 0.68	6. 1.99 ^[27]	3. 2 300 000; 6.7	4. 1.99E-07	3. 7300; 1.9	4. 2.11E-07	4. 4.52E-07	4. 5.58E-07	4. 1.99E-07	4. 5.58E-07	3. 2200; 3.1	3. 2200; 3.1	4. 4.52E-07	4. 5.58E-07
	7. 12.0 ± 1.1 (0.13)		8. #15	5. 0.55 ± 0.07 (0.69); 0.68	4. NA	5. 0.19 ± 0.16 (0.21); 0.69	5. 0.35 ± 0.04 (0.43); 0.69	5. 0.23 ± 0.04 (0.31); 0.71	5. 0.35 ± 0.04 (0.43); 0.69	5. 0.23 ± 0.04 (0.31); 0.71	4. 2.11E-07	4. 2.11E-07	5. 0.35 ± 0.04 (0.43); 0.69	5. 0.23 ± 0.04 (0.31); 0.71
	8. #17		8. #15	6. 4.02 (PC ₇₁ BM) ^[38]	5. 0.49 ± 0.06 (0.59); 0.58	6. 5.4 (A3 OC ₈ H ₁₇ , D6 N-C ₈ H ₁₇ , PC ₇₁ BM) ^[40,41]	6. No reference	6. No reference	6. 4.02 (PC ₇₁ BM) ^[38]	6. No reference	5. 0.22 ± 0.05 (0.32); 0.64	5. 0.22 ± 0.05 (0.32); 0.64	6. No reference	6. No reference
Continued														

Table 1. Continued

 A4	1. 1.70 2. -5.16/-3.46 3. 15 000; 2.1 4. 2.07E-08 5. 0.05 ± 0.01 (0.07); 0.66 6. No PCE ^[42]	1. 1.66 2. -5.25/-3.59 3. 22 000; 9.1 4. Unstable 5. 0.17 ± 0.01 (0.2); 0.80 6. No reference	1. 1.82 2. -5.19/-3.39 3. 8000; 6.1 4. Unstable 5. 0.03 ± 3.34 (0.03); 0.59 6. No reference	D5 R=H 1. 1.73 2. -5.28/-3.55 3. 29 000; 9.2 4. 4.58E-10 5. 0.49 ± 0.07 (0.68); 0.94 6. 6.0 (PC ₇₁ BM) ^[43] 7. 1.51 ± 0.11 (0.25) 8. #9	NA 6. No reference 8. #15	1. 1.89 2. -5.24/-3.35 3. 6400; 2.1 4. 1.66E-07 5. NA 6. 2.82 (PC ₇₁ BM) ^[44] 7. 18.1 ± 0.45 (0.1) 8. #10	D8 R=C ₁₂ H ₂₅ NA 6. No reference 8. #12	1. 1.96 2. -5.50/-3.54 3. 7000; 1.5 5. NA 6. No reference 7. 5.81 ± 0.53 (0.17) 8. #12
 A5	1. 1.64 2. -5.03/-3.39 3. 18000; 3.0 4. NA 5. 0.29 ± 0 (0.29); 0.66 6. 2.15 (A5, R in para, PC ₇₁ BM) ^[45] 7. 8.84 ± 0.21 (0.23)	1. 1.73 2. -4.90/-3.17 3. 100700; 3.1 4. 1.20E-08 5. 1.37 ± 0.07 (1.48); 0.65 6. No reference 7. 0.33 ± 0.01 (0.40)	1. 1.59 2. -5.01/-3.47 3. 50 000; 1.3 4. Gel 5. 1.09 ± 0.03 (1.13); 0.64 6. 1.68 (A5, R in para, PC ₇₁ BM) ^[45] 7. 5.71 ± 0.81 (0.10)	D5 R=C ₁₂ H ₂₅ 1. 1.66 2. -5.03/-3.37 3. 119 000; 16.6 4. 6.24E-10 5. 0.18 ± 0.3 (0.21); 0.62 6. No reference 7. 0.56 ± 0.06 (0.80) 8. #11	1. 1.92 2. -5.29/-3.37 3. 11 000; 26.7 4. 2.72E-09 5. 0.1 ± 0 (0.1); 0.8 6. 2.04 (inverted, PC ₇₁ BM) ^[34,46] 7. 1.85 ± 0.01 (0.83)	1. 1.66 2. -5.06/-3.34 3. 34 000; 3.4 4. 2.40E-09 5. 0.57 ± 0.06 (0.65); 0.65 6. No reference 7. 1.01 ± 0.08 (0.31) 8. #12	D8 R=C ₁₂ H ₂₅ 1. 1.70 2. -5.17/-3.32 3. 261 000; 7.6 4. 6.90E-07 5. 0.06 ± 0.05 (0.1); 0.62 6. No reference 7. 3.09 ± 0.06 (0.25) 8. #14	1. 1.82 2. -5.35/-3.53 3. 138 000; 8.0 4. 2.00E-10 5. NA 6. No reference 7. 2.01 ± 0.08 (0.37) 8. #14

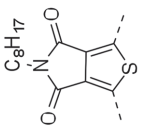
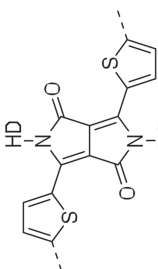
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Table 1. Continued

 A6	1. 1.77	1. 1.95	1. 1.94	D5 R=H	NA	1. 1.92	D8 R=C ₁₂ H ₂₅	1. 1.95
	2. -5.13/-3.36	2. -5.23/-3.28	2. -5.21/-3.27	1. 1.81	6. 2.04 (PC ₇₁ BM, A6 hexyl, inverted) ^[46]	2. -5.00/-3.08	NA (not soluble)	2. -5.28/-3.34
 A7	3. 9600; 2.0	3. 11000; 2.2	3. 4600; 1.9	2. -5.15/-3.30	8. #11	3. 15 000; 1.6	6. No reference	3. 21 600; 2.7
	4. 1.40E-08	4. 3.28E-10	4. 4.15E-08	3. 1800; 1.4	5. NA	4. 7.60E-08	8. #8	4. Gel
 A8	5. 1.03 ± 0.1 (1.14); 0.7	5. 0.85 ± 0.1 (1.05); 0.77	5. 0.61 ± 0.07 (0.72); 0.66	4. 3.20E-09	6. 2.60 (PC ₇₁ BM) ^[49]	5. 0.30 ± 0.07 (0.45); 0.58	5. 0.71 ± 0.07 (0.87); 0.79	6. 3.0 (A6 hexyl) ^[50]
	6. 5.59 (PC ₇₁ BM, A6 hexyl) ^[47]	6. 5.22 (A6 H ₁ PC ₇₁ BM) ^[48]	6. 2.60 (PC ₇₁ BM) ^[49]	5. NA	6. No reference	6. No reference	6. No reference	7. 2.32 ± 0.21 (0.49)
 A9	7. 10.8 ± 0.5 (0.17)	7. 1.03 ± 0.05 (0.61)	7. 0.81 ± 0.07 (0.82)	6. No reference	7. 0.81 ± 0.07 (0.82)	7. 3.58 ± 0.47 (0.32)	7. 2.32 ± 0.21 (0.49)	8. #8
	8. #11	8. #9	8. #9	7. 1.85 ± 0.18 (0.57)	8. #5	8. #6	8. #8	8. #8
 A10	1. 1.35	1. 1.61	1. 1.59	D5 R=C ₁₂ H ₂₅	NA	1. 1.55	D8 R=C ₁₂ H ₂₅	1. 1.87 (solution dewets on glass)
	2. -5.23/-3.88	2. -5.31/-3.70	2. -5.33/-3.74	1. 1.81	6. No reference	2. -5.26/-3.71	NA	2. -5.75/-3.88
 A11	3. 2600; 1.6	3. 3200; 3.5	3. 1200; 2.0	2. -5.62/-3.81	8. #11	3. 1200; 3.3	6. No reference	3. (225; 5.5)
	4. 5.78E-08	4. 5.06E-10	4. 3.12 E-09	3. 1100; 1.6	4. NA	4. 1.48E-09	8. #8	4. NA
 A12	5. 0.02 ± 0.01 (0.03); 0.57	5. NA	5. NA	4. NA	5. NA	5. 0.03 ± 0.93 (0.05); 0.47	5. NA	5. NA
	6. No reference	6. 1.96 (PC ₇₁ BM) ^[51]	6. No reference	5. NA	6. No reference	6. No reference	6. No reference	6. No reference
 A13	7. 0.60 ± 0.04 (0.33)	7. 0.46 ± 0.04 (0.26)	7. 0.31 ± 0.07 (0.19)	6. No reference	7. 0.31 ± 0.07 (0.19)	7. 1.30 ± 0.10 (0.28)	7. NA	7. NA
	8. #11	8. #9	8. #9	7. NA	8. #5	8. #6	8. #8	8. #8
 A14	1. 1.36	1. 1.35	1. 1.36	D5 R=C ₁₂ H ₂₅	NA	1. 1.56	D8 R=C ₁₂ H ₂₅	1. 1.54
	2. -5.01/-3.64	2. -5.21/-3.85	2. -5.09/-3.73	1. 1.27	6. No reference	2. -5.04/-3.48	1. 1.57	2. -5.46/-3.92
 A15	3. 16000; 2.0	3. 14000; 2.4	3. 14 000; 2.2	2. -5.11/-3.83	8. #15	3. 6100; 2.6	2. -5.06/-3.49	3. 1200; 4.8
	4. 7.65E-07	4. 1.72E-08	4. 2.00E-08	3. 5000; 1.4	5. NA	4. 1.15E-07	3. 3700; 2.2	4. 7.82E-09
 A16	5. 0.2 ± 0.03 (0.26); 0.51	5. 0.57 ± 0.06 (0.69); 0.69	5. 0.12 ± 0.02 (0.14); 0.57	4. 2.01E-07	6. No reference	5. 0.04 ± 0.02 (0.07); 0.63	4. 1.23E-08	5. 0.01 ± 0.01 (0.01); 0.56
	6. 6.0 (PC ₇₁ BM, A8 C ₈ H ₁₇) ^[52]	6. 9.0 ^[53-55]	6. 7.4 (PC ₇₁ BM) ^[56]	5. 0.04 ± 0.02 (0.08); 0.82	6. No reference	6. No reference	5. NA	6. No reference
 A17	7. 0.62 ± 0.04 (1.06)	7. 1.27 ± 0.15 (0.48)	7. 0.8 ± 0.04 (0.34)	6. No reference	7. 0.8 ± 0.04 (0.34)	7. 5.17 ± 0.71 (0.33)	6. No reference	7. 12.4 ± 1.5 (0.18)
	8. #15	8. #15	8. #13	7. 7.62 ± 0.51 (0.18)	8. #9	8. #10	7. 3.67 ± 0.26 (0.24)	8. #12
 A18	8. #11	8. #9	8. #9	7. NA	8. #5	8. #6	8. #8	8. #8
	8. #11	8. #9	8. #9	7. NA	8. #5	8. #6	8. #8	8. #8

Continued

Table 1. Continued

 A9	1. 1.73	1. 1.86	1. 1.86	D5 R=H	NA	1. 2.08 (solution dewets on glass)	D8 R=C ₁₂ H ₂₅	1. 2.06 (solution dewets on glass)
	2. -5.37/-3.65	2. -5.43/-3.56	2. -5.35/-3.49	1. 2.07 (solution dewets on glass)	6. No PCE ^[64]	2. -5.41/-3.33	1. 1.79	2. -5.76/-3.70
	3. 9500; 2.8	3. 11000; 3.6	3. 41 000; 14.5	2. -5.53/-3.46	8. #12	3. 7200; 1.7	2. -5.28/-3.48	3. (425; 5.9)
	4. 5.53E-08	4. 7.42E-08	4. 3.40E-09	3. 39 000; 1.5		4. 7.20E-08	3. 3500; 1.3 (not all in solution)	4. NA
	5. 0.23 ± 0.06 (0.38); 0.8	5. 0.67 ± 0.03 (0.74); 0.94	5. 0.47 ± 0.08 (0.64); 0.81	4. 3.90E-09		5. NA	4. 1.80E-11	5. NA
	6. 7.3 (PC ₇₁ BM) ^[57]	6. 6.17 ^[18,58,59]	6. 6.8 ^[60-62]	5. NA	6. No reference			6. No reference
	7. 6.56 ± 0.79 (0.5)	7. 0.56 ± 0.05 (0.37)	7. 0.54 ± 0.03 (0.64)	6. 0.75 (A9 C ₁₂ H ₂₅ , D5 H) ^[63]	7. NA		6. 5.1 (A9 C ₁₂ H ₂₅) ^[65,66]	7. NA
	8. #12	8. #10	8. #10	7. 0.63 ± 0.05 (0.26)	8. #7		7. 0.37 ± 0.02 (0.27)	8. #9
				8. #6				
 A10	1. 1.30	1. 1.35	1. 1.36	D5 R=H	1. 1.71	1. 1.38	D8 R=C ₁₂ H ₂₅	1. 1.52
	2. -5.13/-3.83	2. -5.24/-3.89	2. -5.26/-3.90	1. 1.30	2. -5.27/-3.56	2. -5.07/-3.69	1. 1.34	2. -5.34/-3.84
	3. 21000; 2.5	3. 103000; 3.3	3. 68 000; 3.3	2. -5.15/-3.85	3. 6700; 3.5	3. 34 000; 4.2	2. -5.06/-3.72	3. 2300; 5.4
	4. 7.60E-08	4. 5.20E-09	4. 5.80E-09	3. 233 000; 8.0	4. 9.70E-09	4. 1.73E-06	3. 1200; 2.8	4. 1.80E-09
	5. NA	5. 0.04 ± 0.47 (0.07); 0.58	5. NA	4. 2.08E-06	5. NA	5. NA	4. 1.68E-10	5. NA
	6. 2.10 (PC ₇₁ BM) ^[67]	6. 6.60 (PC ₇₁ BM) ^[59,68,69]	6. 2.83 (PC ₇₁ BM) ^[67,69]	5. NA	6. 2.26 (D6 R=N-CH(C ₁₀ H ₂₁) ₂) ^[71,72]	6. No reference	5. NA	6. No PCE ⁷⁴
	7. 1.71 ± 0.03 (0.76)	7. 2.46 ± 0.05 (1.14)	7. 1.12 ± 0.04 (1.47)	6. 4.7 (D5 R=H, PC ₇₁ BM) ^[70]	7. 22.5 ± 0.94 (0.43)	7. 4.42 ± 0.18 (0.82)	6. 3.2 (different side chains) ^[73]	7. 15.4 ± 0.4 (0.37)
	8. #10	8. #8	8. #8	7. 0.86 ± 0.08 (0.89)	8. #10	8. #5	7. 18.8 ± 0.6 (0.4)	8. #7
				8. #4				
							8. #7	

Continued

Table 1. Continued

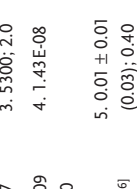
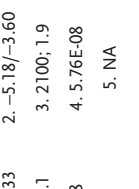
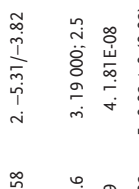
 A12	1. 1.50	1. 1.69	NA	D5 R=C ₁₂ H ₂₅	NA	1. 1.71	D8 R=C ₁₂ H ₂₅	1. 1.67
	2. -5.12/-3.62 3. 6800; 1.9 4. 3.75E-07 5. 1.22 ± 0.03 (1.25); 0.67 6. No reference 7. 0.52 ± 0.02 (0.61)	2. -5.16/-3.47 3. 313000; 10.8 4. 3.13E-08 5. 0.16 ± 0.02 (0.19); 0.74 6. No reference 7. 0.13 ± 0.01 (0.27)	6. No reference 8. #9	1. 1.96 2. -5.76/-3.80 3. 13 000; 3.1 4. Unstable 6. No reference 7. 11.5 ± 0.5 (0.35) 8. #5	6. No reference 8. #9	2. -5.09/-3.38 3. 5600; 2.1 4. 1.77E-07 5. 0.85 ± 1.09 (0.89); 0.70 6. 5.02 (PC ₇₁ BM) ^[36] 7. 0.63 ± 0.06 (0.37) 8. #6 7. 1.84 ± 0.24 (0.31) 8. #8	1. 2.09 2. -5.67/-3.57 3. 5300; 2.0 4. 1.43E-08 5. 0.25 ± 0.02 (0.28); 0.77 6. No reference 7. 32.3 ± 5.1 (0.15) 8. #8	2. -5.57/-3.90 3. 37000; 2.3 4. 9.25E-10 5. 0.25 ± 0.02 (0.28); 0.77 6. No reference 7. 32.3 ± 5.1 (0.15) 8. #8
 A13	A13 R=C ₁₂ H ₂₅	A13 R=C ₁₂ H ₂₅	A13 R=C ₁₂ H ₂₅	A13 R=C ₁₂ H ₂₅ ; D5 R=H	A13 R=C ₁₂ H ₂₅	A13 R=C ₁₂ H ₂₅	A13 R=C ₁₂ H ₂₅ ; D8 R=HD	A13 R=C ₁₂ H ₂₅
	1. 1.50 2. -5.08/-3.58 3. 12000; 7.5 4. 1.96E-08 5. 0.53 ± 0.11 (0.67); 0.65 6. No reference 7. 2.76 ± 0.12 (0.47)	1. 1.65 2. -5.09/-3.44 3. 80000; 18.2 4. 2.12E-08 5. NA 6. 6.21 (A13 R=C ₈ H ₁₇ ; D2 C ₁₂ H ₂₅ , PC ₇₁ BM) ^[75] 7. 0.42 ± 0.03 (0.23)	1. 1.59 2. -5.09/-3.50 3. 66 000; 9.0 4. 9.85E-07 5. NA 6. No reference 7. 0.86 ± 0.09 (0.24) 8. #12	1. 1.52 2. -4.95/-3.43 3. 512 000; 5.3 4. NA 5. NA 6. No reference 7. NA 8. #8	1. 1.72 2. -5.37/-3.65 3. 3200; 2.2 4. 3.12E-08 5. 0.01 ± 0 (0.01); 0.50 6. No reference 7. 0.46 ± 0.04 (0.36) 8. #14	1. 1.58 2. -4.91/-3.33 3. 10 000; 2.1 4. 6.80E-08 5. NA 6. No reference 7. 0.92 ± 0.06 (0.35) 8. #9	1. 1.58 2. -5.18/-3.60 3. 2100; 1.9 4. 5.76E-08 5. NA 6. No reference 7. 1.94 ± 0.08 (0.26) 8. #11	1. 1.53 2. -5.23/-3.70 3. 12 000; 76.7 4. 3.71E-08 5. NA 6. No reference 7. 2.27 ± 0.1 (0.19) 8. #11
 A14	A14 R=C ₁₂ H ₂₅	A14 R=C ₁₂ H ₂₅	A14 R=C ₁₂ H ₂₅	A14 R=C ₁₂ H ₂₅ ; D5 R=H	A14 R=C ₁₂ H ₂₅	A14 R=C ₁₂ H ₂₅	A14 R=C ₁₂ H ₂₅ ; D8 R=C ₁₂ H ₂₅	A14 R=C ₁₂ H ₂₅
	1. 1.37 2. -5.14/-3.77 3. 9800; 1.7 4. 6.07E-08 5. 0.21 ± 0.06 (0.31); 0.59 6. No reference 7. 1.01 ± 0.02 (0.37)	1. 1.47 2. -5.05/-3.58 3. 4600; 4.1 4. 8.94E-08 5. 0.35±0.03 (0.40); 0.60 6. 4.84 (inverted, A14 R=EH) ^[63,76] 7. 0.20 ± 0.01 (0.46)	NA 6. 1.34 (A14 R=hexyl) ^[71] 8. #12	1. 1.33 2. -4.92/-3.59 3. 28 000; 11.1 4. Dewetting 5. 0.02 ± 0.01 (0.03); 0.41 6. No reference 7. 0.38 ± 0.09 (0.42) 8. #8	NA 6. 0.7 (A14 R=H) ^[35] 8. #14	1. 1.46 2. -5.04/-3.58 3. 19 000; 2.6 4. 1.43E-09 5. 0.19 ± 0.02 (0.21); 0.54 6. No reference 7. 1.9 ± 0.2 (0.33) 8. #9	1. 1.49 2. -5.31/-3.82 3. 19 000; 2.5 4. 1.81E-08 5. 0.02 ± 0 (0.02); 0.70 6. No reference 7. 1.55 ± 0.07 (0.24) 8. #11	1. 1.52 2. -5.33/-3.81 3. 1600; 1.9 4. 5.03E-09 (x) 5. 0.06 ± 0 (0.06); 0.45 6. No reference 7. 2.76 ± 0.42 (0.25) 8. #11

Table 2. Manpower and materials consumption.

Manpower	Man months	Materials consumption (PSC)	Amount
Polymer synthesis	8	[60]PCBM	9.7 g
UV-vis, SEC, CV, mobility, stability	4	PEDOT:PSS	2 L
Program development	1	Silver ink	1 kg
Data analysis	6	Solvents	1.3 L
Paper writing	2	Foil	200 m ²
Sum	26		

depends on the lifetime of the polymer), and size exclusion chromatography (SEC; 1 curve per polymer).

2.2. Manpower and Consumption of Material

A large amount of resources, both in terms of manpower and materials, has been expended in the project as listed in **Table 2**.

2.3. Number of Synthetic Steps (Entry 8)

The embedded energy in a PSC is the amount of energy which has been put into the production of the final device, and here the light-absorbing polymer material is responsible for a large part of that energy, which scales with the number of synthetic steps.^[78] Once a high-performing polymer material has been discovered, its application in large-scale R2R processes is the next step and thus large amounts are needed. In order to achieve a low embedded energy in the polymer, the number of synthetic steps has to be as low as possible and the synthetic procedure optimized to give a high yield. The purification (preferably by recrystallization and/or distillation procedures) should be facile and the starting materials have a low cost.^[15] To exemplify this we show the synthetic routes for A8D2 (13 steps, best reported efficiency 9.0%^[55]) and for P3HT (3 steps, best reported efficiency 6%)^[79] in **Scheme 1**. A much higher embedded energy (and cost) for A8D2 compared to P3HT^[80] is clearly indicated.

The polymers in **Table 1** were synthesized by Stille or Suzuki cross coupling polymerizations. The number of synthetic steps from starting materials such as thiophene or benzothiadiazole is shown for each polymer.^[15]

2.4. Synthesis and SEC (Entry 3)

The monomer units were chosen on the basis of high efficiencies reported in the literature and on the complexity of the synthetic route. For example, as A11 (see **Figure 1**) we chose an acceptor monomer, such as naphtha-dithiadiazole, which has been reported to give efficiencies up to 6%.^[82–84] However, the synthesis is highly complicated using tetrasulfurtetranitride (S₄N₄), which is a shock-sensitive compound, and 1,5-dibromo-2,6-dihydroxynaphthalene as starting materials. Even though the latter was claimed to be commercially available, it was

not possible to purchase the final monomer compound. Consequently, in the end it was not chosen as one of the acceptors for the study. As another example, our choice for donor unit D4 (see **Figure 1**) was the benzo[2,1-b;3,4-b']dithiophene with 2-hexyl-decyl as side chains, which has shown PCEs of 4.5%.^[67,85] However, the synthesis was insufficient in large scale and the subsequent purification too challenging to ensure a pure monomer. The side chains were chosen for each monomer to ensure a good solubility of all the resulting polymer materials, even though for some structures a shorter side chain, e.g., hexyl, would have been sufficient. All polymers were prepared by a Stille cross coupling polymerization of a di-stannyl and a di-bromo derivative of the donor and acceptor units, respectively, using a palladium catalyst. The exception was polymers based on D6, which were prepared by a Suzuki cross coupling.

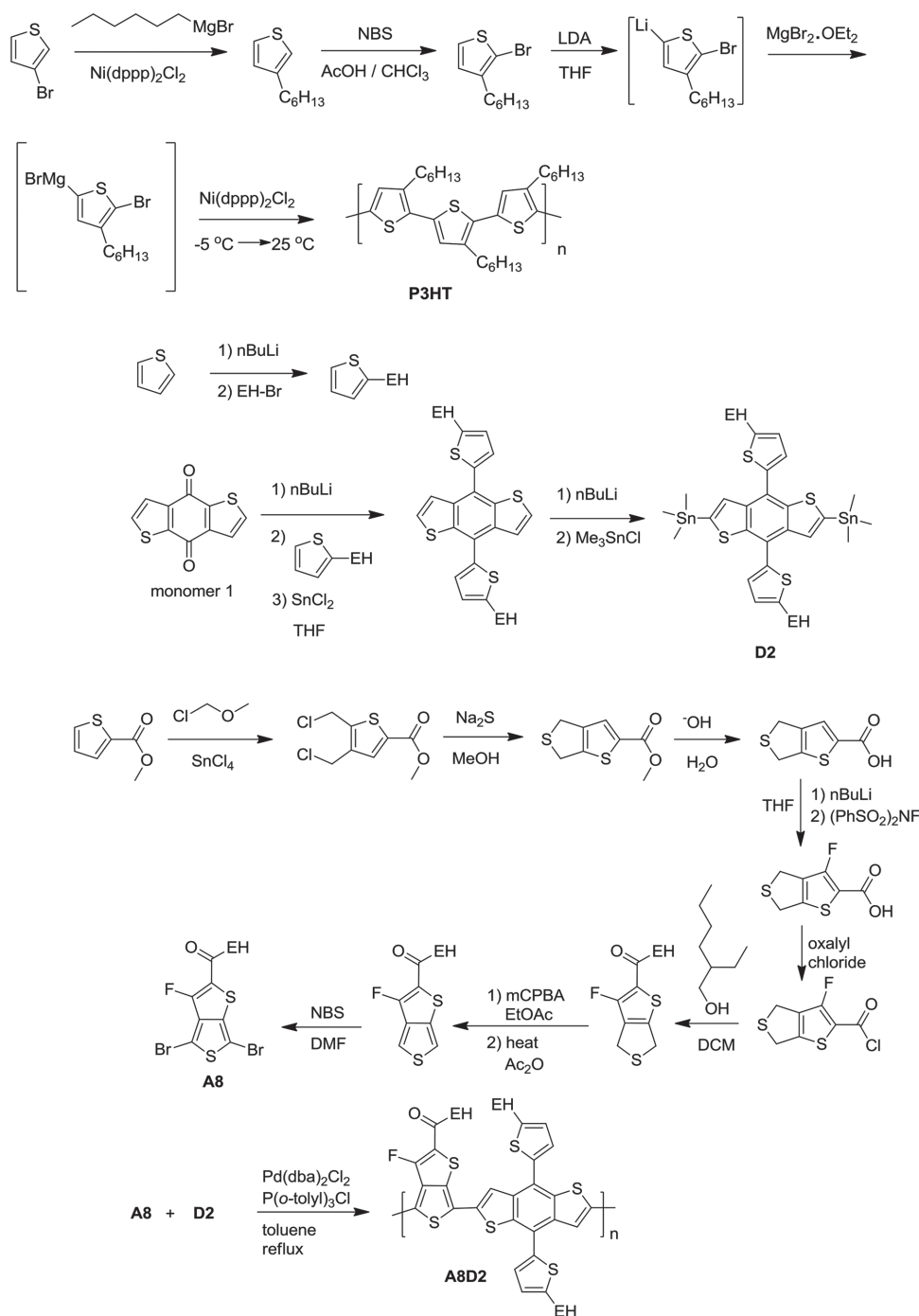
Not all 104 polymers could be successfully synthesized due to low reactivity, or steric hindrance, which is indicated by a NA in the table. The polymers that were successfully synthesized were analysed by SEC (see the Supporting Information), and large variations in the molecular weight (M_n) were found. The low molecular weight polymers are mainly attributed to steric hindrance from side chains, (e.g., A4D8), to a low reactivity of the donor as in the case of D6, and to poor solubility leading to precipitation of oligomers. Finally, some monomers, such as D7, which cannot be purified by recrystallization, may contain minor impurities, which could complicate the polymerization reaction.

2.5. UV-Vis and Optical Band Gap (Entry 1)

The optical band gaps of the polymers were estimated from the onset of the UV-vis absorption spectra (see the Supporting Information) and were within the range of 2.09 to 1.27 eV with only four polymers having a band gap above 2 eV. This corresponds well with the aim of preparing low band gap polymers based on a donor/acceptor approach. The acceptors A8 and A10 produced the polymers with the lowest band gaps.

2.6. Electrochemical Measurements and Energy Levels (Entry 2)

The HOMO levels were estimated from the onset of the SWV curves using ferrocene as reference (see the Supporting Information) and calculated according to literature procedures.^[86–88] The LUMO levels were calculated from the optical band gap and the HOMO level (see the Supporting Information). The HOMO level of P3HT was found to be −4.9 eV, which is somewhat higher compared to the literature value (−5.20 eV).^[89] The LUMO level of [60]PCBM was found to be −3.85 eV, which is a little lower than the literature value (−3.75 eV).^[90] The HOMO level of the polymer has an effect on the V_{OC} , since it is generally proportional to the difference between the HOMO of the donor polymer and the LUMO of the acceptor [60]PCBM. Thus, lowering the HOMO of the polymer will increase the maximum V_{OC} .^[91] This should be considered in view of the fact that lowering the HOMO of the polymer will increase the band gap and thereby potentially also decrease the current. Several polymers, for instance A4D5, A8D5, and



Scheme 1. Comparison of the synthetic routes of P3HT^[81] (top) and the high performing polymer A8D2^[55] (bottom). Monomer 1 is now commercially available in large quantities; it was, however, originally synthesized in two steps from 3-thiophenecarbonyl chloride.

A9D2, showed a very high V_{OC} compared to P3HT, which is a consequence of a low HOMO level. Unfortunately, the current density for these polymers in PSC devices was much lower than for P3HT, and the resulting PCE is therefore also lower (see **Table 3**). The current can be optimized for instance by varying the ratio between polymer and [60]PCBM. Thus, a high V_{OC} is especially important if one would like to use the polymer material in tandem solar cells.^[92]

2.7. Hole Mobility (Entry 4)

The hole mobility was measured in the dark on a polymer film sandwiched between an ITO electrode, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), and an evaporated Al electrode (see the Supporting Information). The hole mobility is highly dependent on the solvent from which the analysed film is spin coated. The values

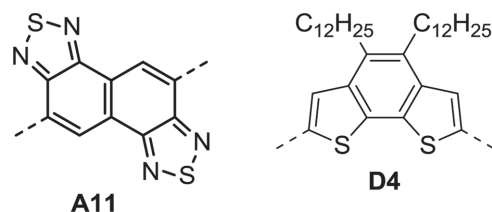


Figure 1. Structures of A11 and D4, which were eliminated from the matrix due to difficulties in the synthesis.

reported here were measured on films prepared from chlorobenzene and were found to be subject to some variation. The hole mobility of P3HT was measured at $1.26 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a 270 nm thick film, which is in good agreement with the literature values (1×10^{-3} – $6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[93] Several polymers, for instance A3D7, A5D8, and A8D1, showed a higher hole mobility than P3HT, but this did not result in a higher PCE (see Table 1), which could be due to poor morphology or insufficient thickness of the active layer film.

2.8. Photochemical Stability (Entry 7)

The photochemical stability of the polymer films was measured as described in the literature by means of an automatic set up that measured the absorption as a function of time at AM1.5 (1000 W m⁻²).^[94] The stability was found to be highest for polymers with the benzothiadiazole-like acceptor unit (A1, A2, A5, A7, A12, A13, and A14) and the donor unit thiophene (D5 and D8), dithienosilole (D1), and a combination of thiophene and benzene (D3 and D7). This is in good agreement with the literature, where the benzothiadiazole, dithienosilole, and thiophene units are reported to be among the most photochemically stable monomer units.^[95]

2.9. Roll-Coated Polymer Solar Cells (Entry 5)

The polymers were employed in fully roll-coated and printed PSC devices using Flextrade substrate^[96,97] on a mini roll

coater as described earlier.^[9,98,99] Several parameters can be studied during such a screening, e.g., solvent, annealing, ratio between polymer and [60]PCBM, film thickness, and coating temperature. All these parameters influence the photovoltaic response of the PSC. However, evaluating all parameters would be impossible within a reasonable timescale, and it would certainly not be possible to do it in this study which included 104 polymers. Consequently, we chose to vary only a subset of the parameters during the screening. The parameters we chose to study included: (1) the ratio between the polymer and [60]PCBM (1:1 or 1:2), (2) the solvent from which the polymer/[60]PCBM mixture is coated (chloroform or o-dichlorobenzene), and (3) the thickness of the coated active layer (thin, medium, and thick, which corresponds to a wet thickness of around 10, 12, and 15 μm , and a dry thickness of around 315, 400, and 475 nm, respectively). The active layer was thick compared to spin coated films (100 nm) to avoid electrical shorts from the less smooth films.^[100] The coating temperature was kept constant at 70 °C, which may have affected the morphology of the active layer. However, the choice of a high and low boiling solvent will also affect the different morphologies which can be obtained from a given polymer. The photovoltaic responses are presented as the average efficiency plus/minus the standard deviation together with the maximum recorded PCE and V_{OC} . Many of the polymers failed to generate working devices despite the variations tested. This was due to coating defects such as dewetting, insufficient solubility, destruction of the devices during switching,^[97] and electrical shorts due to defects.

2.10. PCE Values from the Literature (Entry 6)

All monomers and some of the polymer materials have been reported in the literature. The values from these studies are listed for reference in Table 1. The PCE values are reported for small spin coated devices with a normal geometry, prepared with an ITO electrode and thermally evaporated electrodes under vacuum, rather than for roll coated devices with a larger area. Also, the devices made for this study were not optimized

Table 3. The maximum PCE for roll-coated devices relative to the PCE of P3HT/PCBM roll-coated devices. The colors indicate: bold: polymer performs better than P3HT, grey: roughly the same performance as P3HT, and plain text: poorer performance than P3HT. NA indicates a failure (please refer to Table S2, Supporting Information, for the specific type of failure).

	D1	D2	D3	D5	D6	D7	D8	D9
A1	0.9	0.3	NA	NA	NA	1.4	NA	NA
A2	0.3	0.8	0.4	0.3	NA	0.9	NA	NA
A3	0.2	NA	0.4	0.4	0.1	0.3	0.2	0.2
A4	NA	0.1	NA	0.4	NA	NA	NA	NA
A5	0.2	0.9	0.7	0.1	0.1	0.4	0.1	NA
A6	0.7	0.7	0.5	NA	NA	0.2	NA	0.6
A7	NA	NA	NA	NA	NA	NA	NA	NA
A8	0.2	0.4	0.1	0.1	NA	NA	NA	NA
A9	0.2	0.5	0.4	NA	NA	NA	NA	NA
A10	NA	NA	NA	NA	NA	NA	NA	NA
A12	0.8	0.1	NA	NA	NA	0.6	NA	0.2
A13	0.4	NA	NA	NA	NA	NA	NA	NA
A14	0.2	0.3	NA	NA	NA	0.1	NA	NA

for maximum performance, but rather prepared using the exact same procedures to make comparison possible.

2.11. Comparison of the Polymers

The PCE of the polymers relative to P3HT:PCBM (Table 3) shows that only one polymer (A1D7) generates devices with a better PCE. Only 8 polymers performed similarly to P3HT:PCBM and the rest much more poorly, which is indicated by the low value, or simply by NA in the table. Failure could have occurred for the following reasons: (1) problems in the synthesis, (2) insolubility, (3) dewetting of the active layer on the Flextrode substrate or dewetting of the PEDOT:PSS layer on top of the active layer, (4) no switching of the device, or (5) a shunted device, which is described in more details below. This result indicates the significant challenge in finding polymers that are suitable for R2R-fabricated PSC devices. As seen in Table 1, many of the polymers that failed have been shown to perform excellently in spin-coated devices, however, as described above it is not possible to compare these results with the results of this screening. The 9 polymers that performed on par or better than P3HT:PCBM, based on the PCE alone, are considered promising candidates for further optimization. These are based on the donors D1, D2, D7 and the acceptors A1, A2, A5, A6, and A12.

Although most reports in the literature focus on the PCE, other parameters are also important. We have combined all these factors in a merit factor (χ) defined as

$$\chi = \frac{\text{PCE} \times \text{stability} \times V_{\text{OC}} \times \text{band gap}}{\text{number of synthetic steps}} \quad (1)$$

$$\chi_{\text{rel}} = \chi / \chi_{\text{P3HT:PCBM}} \quad (2)$$

The photochemical stability of polymers used in PSCs varies greatly as shown in previous studies^[95] and must be taken into consideration in the selection of an active material. In the

merit factor, it is the degradation rate of the polymer normalized to the degradation rate of P3HT at equal absorption value (see the Supporting Information). It is desirable to have a high V_{OC} , and it is therefore incorporated into the merit factor. The band gap (in nm) of the polymer determines how much of the solar spectrum is utilized and gives a theoretical upper limit for the current output of the device. The voltage and band gap are included in order to identify the polymers which could give high PCE, i.e., a high voltage and/or an absorption to longer wavelengths theoretically gives a higher PCE. Finally, we also consider the number of synthetic steps needed to prepare the polymer, since this obviously has a great impact on the embedded energy and therefore also on the cost. Instead of looking at the merit factor for each polymer we introduce the relative merit factor. The relative merit factor (χ_{rel}) of the polymers is a simplified measure of an overall score against the standard P3HT:PCBM active layer combination and is seen in Table 4. This ranks 13 out of the 104 polymers as better or equal to the standard, which makes them candidates for future development. This demonstrates that the success rate is quite low and that the requirements for roll and R2R fabrication seems to be much higher than for spin coating (which cannot be scaled to industrial applications).

Figure 2 provides an overview of the V_{OC} , the HOMO energy levels, and the optical band gap (E_g). It is clear that when preparing 104 different polymer materials, smooth and continuous variation in the different properties can be achieved. This highlights the strength of the synthetic organic chemistry approach to materials, since almost any number can be matched within a large range through the synthetic approach. We observed V_{OC} values within the range of 0.4 to 0.8 V, HOMO energy level within the range of -4.9 to -5.8 eV, and the band gap within the range of 2.1 to 1.3 eV. The relation between the HOMO and V_{OC} is known to be $V_{\text{OC}} = \text{HOMO}_{\text{polymer}} - \text{LUMO}_{\text{acceptor}} - 0.3 \text{ V}^{[101]}$ and we found that to some extent the polymers in this screening follow this trend though with a little higher loss in the device of 0.6 V (see Figure S1, the Supporting Information).

Table 4. The relative merit factor χ_{rel} . The colors indicate: bold: polymer performs better than P3HT, grey: roughly the same performance as P3HT, and plain text: poorer performance than P3HT. A minimum 70% yield for each step is assumed. Thus, the yield is not taken into account for the synthetic steps. NA indicates a failure (please refer to Table S2, Supporting Information, for the specific type of failure).

	D1	D2	D3	D5	D6	D7	D8	D9
A1	1.4	3.0	NA	NA	NA	2.7	NA	NA
A2	NA	3.1	0.6	1.0	NA	1.2	NA	NA
A3	NA	NA	0.2	NA	NA	0.1	NA	NA
A4	NA	NA	NA	1.0	NA	NA	NA	NA
A5	NA	2.9	0.4	0.2	NA	0.7	NA	NA
A6	0.2	0.8	0.5	NA	NA	0.1	NA	0.4
A7	0.1	NA	NA	NA	NA	0.1	NA	NA
A8	0.1	0.5	0.2	NA	NA	NA	NA	NA
A9	NA	1.9	0.9	NA	NA	NA	NA	NA
A10	NA	NA	NA	NA	NA	NA	NA	NA
A12	1.8	2.6	NA	NA	NA	2.7	NA	NA
A13	0.2	NA	NA	NA	NA	NA	NA	NA
A14	0.3	1.6	NA	0.1	NA	0.1	NA	NA

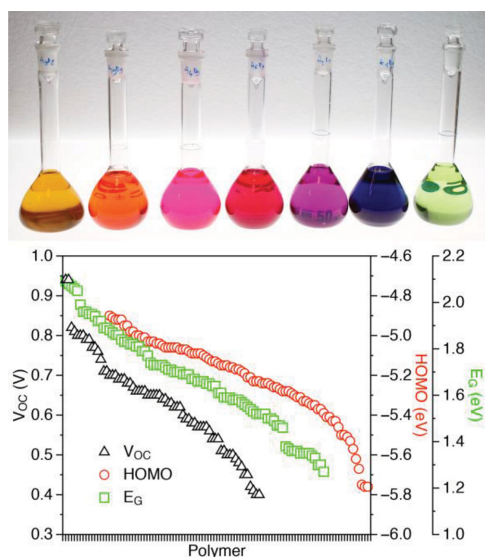


Figure 2. Top: Illustration of the different polymer solutions with the different color/absorbance achieved by coupling the different donor and acceptors in the screening. Bottom: Illustration of the accessible ranges for V_{OC} , E_g , and HOMO levels as a function of polymer number arranged according to the numerical data value (which is different for each property) to show the smooth variation that can be attained. For a complete list of polymers with numerical data, see Table S1, Supporting Information.

The enormous spans of V_{OC} , HOMO, and band gap can be efficiently explored in final devices where overall performance for instance depends on band gaps being of a particular value (i.e., in tandem devices), or where energy levels need a certain value (i.e., with specific electrode materials).

3. Future and Outlook

It is clear from this study that a large research effort is required for the successful development of a material that meets all the requirements of roll coating/printing besides reaching the customary high efficiency target. The method presented here shows the magnitude of the task, but also how to rationally address the challenge and as such represent the first stage of the search. As we have demonstrated, there are a number of steps in the highly linear approach from synthesis through materials characterisation, processing and devices studies. As illustrated in **Figure 3**, the outcome for any of the materials may stop at any of these stations along the path. The entries in **Figure 3** represent the following steps where failure may occur: 1) design, 2) synthesis, 3) characterization, 4) ink, 5) coating, 6) device, 7) PCE, and 8) PCE better than P3HT. As can be seen, failure at steps 1 to 4 account for 28 of the polymers. These failed mainly due to steric hindrance, low molecular weight, or insolubility. A solution could be to re-synthesize them with other side chains to enhance solubility, lower steric hindrance, and increase the molecular weight. Failure at step 5 accounts for 20 of the polymers. Failure mainly occurred due to dewetting of the active layer, which could be solved by using a different device structure, e.g., using a different substrate, or by

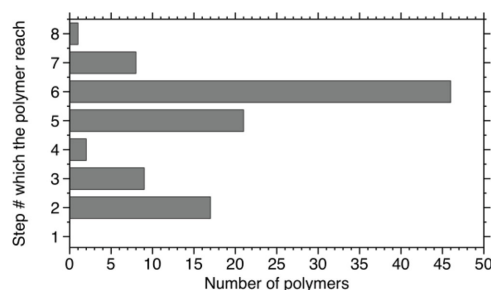


Figure 3. Illustration of the number of polymers that failed at a given step in the serial value chain for the process that comprises steps: 1 = design, 2 = synthesis, 3 = characterization, 4 = ink, 5 = coating, 6 = device, 7 = performance (PCE), 8 = PCE better than P3HT.

enhancing the adhesion of the polymer to the Flextrode substrate. Failure at step 6 accounts for almost half of the polymers. In some instances, it represents mechanisms, such as electronic shorts in the device during switching, which can be solved by increasing the thickness of the active layer, or insufficient switching, which can be solved by using a different device structure which does not need switching. However, in most cases (see Table 3), it represents a very low PCE. There are several possibilities to overcome this. For example, if the V_{OC} is low, another acceptor than [60]PCBM can be used. Similarly, if the I_{SC} is low, the ratio of the polymer and [60]PCBM can be optimized. For some materials, the hurdles may be overcome and the potential realized through suitable modification, but it is clear that the earlier in the process a material fails, the greater the effort needed to overcome the problem.

To progress from the results of this work, the most suitable candidates (see **Figure 4**) should be further explored through side chain engineering, processing optimisation, and device architecture studies. Of course, it is not impossible that this approach will miss the ultimate material for PSCs, but it is highly unlikely. The majority of materials that have been successful in the past already shows potential in an unrefined form, and this potential has been further explored in subsequent studies. This study should thus be seen as a mining effort for raw candidate materials that, when further refined, can be expected to deliver with respect to performance at all levels (efficiency, physical properties, operational stability, cost, and processability).

4. Conclusion

This screening of 104 light-absorbing polymers for PSCs has illustrated the massive challenge of discovering materials which can offer high efficiency, high stability, and compatibility with large-scale R2R processing. The challenge for the polymer materials has been shown to lie not only in the polymer backbone, but also in the side chains, more specifically where the side chains are attached, and in the size and nature of the side chain. The donor-acceptor approach has pointed out a number of units worthy of further study. A further study will include side chain variations, the morphology of the active layer, the stability of the device, new device structures like tandem architectures, where polymer materials with high

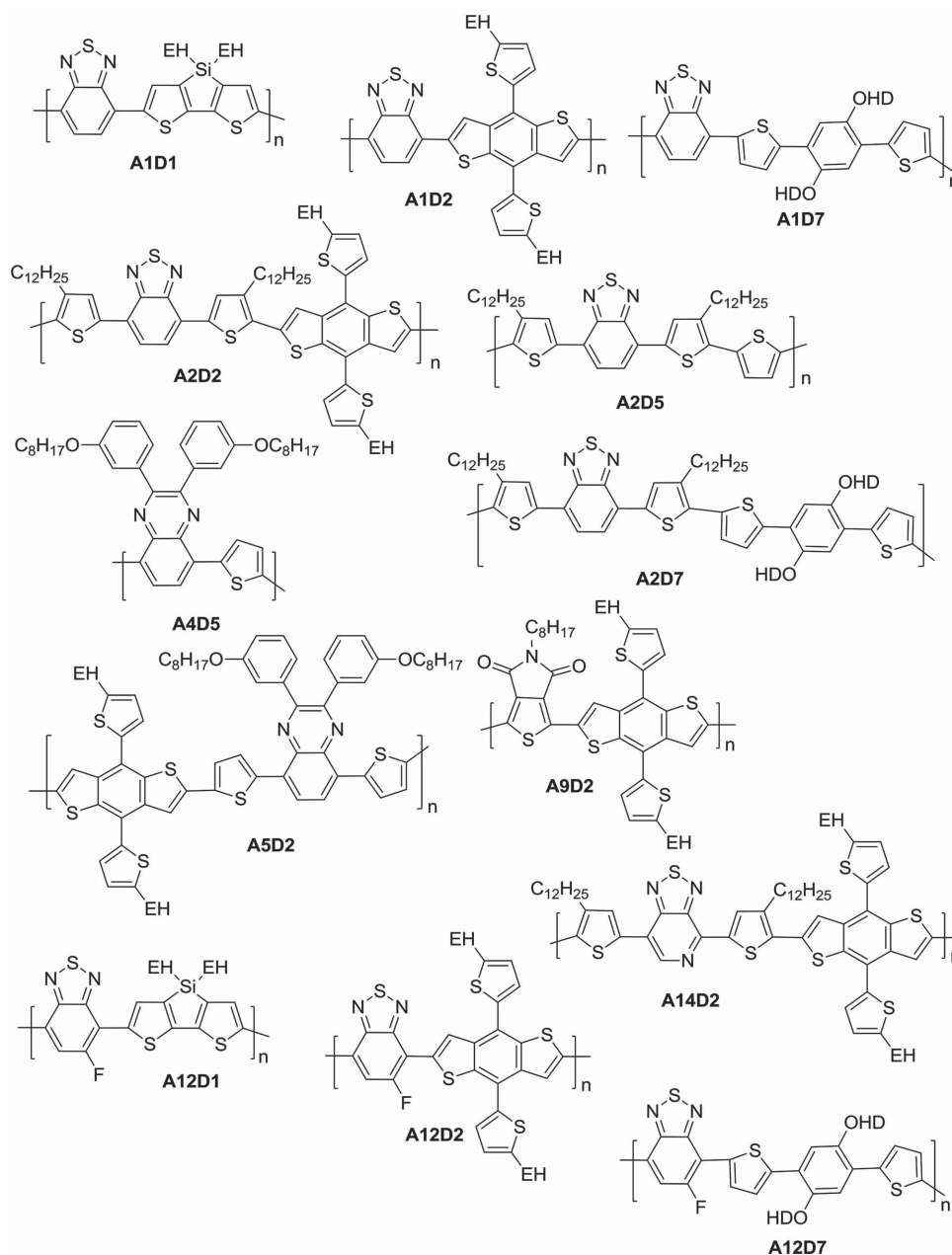


Figure 4. The 13 polymer backbones which were found to be suited for roll-coated PSCs in this screening. Side chains' length and position will be studied in future experiments.

V_{OC} are of great interest, and finally devices optimized through the use of other PEDOT:PSS types. The present study has shown that 13 polymers out of 104 (corresponding to 12.5% of the polymers) are performing better than the prototypical reference material P3HT and are therefore suitable for further development.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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