

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/271726115>

“All That Glisters Is Not Gold”: An Analysis of the Synthetic Complexity of Efficient Polymer Donors for Polymer Solar Cells

ARTICLE in MACROMOLECULES · JANUARY 2015

Impact Factor: 5.8 · DOI: 10.1021/ma501894w

CITATIONS

9

READS

57

4 AUTHORS:



Riccardo Po

Research Center for Renewable Energies & En...

113 PUBLICATIONS 1,648 CITATIONS

[SEE PROFILE](#)



Gabriele Bianchi

Research Center for Non Conventional Energy

27 PUBLICATIONS 703 CITATIONS

[SEE PROFILE](#)



Chiara Carbonera

eni - Renewable Energy & Environmental R&D

60 PUBLICATIONS 1,356 CITATIONS

[SEE PROFILE](#)



Andrea Pellegrino

Research Center for Non Conventional Energy

14 PUBLICATIONS 145 CITATIONS

[SEE PROFILE](#)

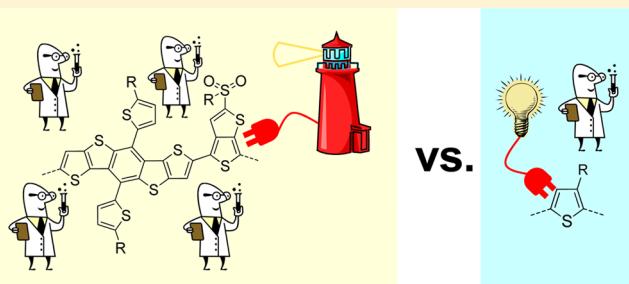
"All That Glisters Is Not Gold": An Analysis of the Synthetic Complexity of Efficient Polymer Donors for Polymer Solar Cells

Riccardo Po,* Gabriele Bianchi, Chiara Carbonera, and Andrea Pellegrino

Research Center for Renewable Energies and Environment, Istituto Donegani, Eni Spa, Via Fauser 4, 28100 Novara, Italy

S Supporting Information

ABSTRACT: Although organic photovoltaic technology offers many advantages, no consolidated commercial applications have been achieved after more than a decade of intensive research. Several challenges have yet to be overcome, including the scalability of the active material production, which is usually complex even at the laboratory scale. In this Perspective, this fundamental challenge is addressed by surveying and analyzing the synthetic complexity (SC) of active-layer donor polymers used in single-junction polymer solar cells published through 2013 with power conversion efficiencies (PCEs) over 6%. Five parameters are taken into account to evaluate the SC: (i) the number of synthetic steps, (ii) the yields of the monomers, (iii) the number of unit operations (in particular, (iv) of the column chromatographies) required for the purification of the monomers, and (v) the safety characteristics of the chemicals used for their preparation. Finally, the polymers are ranked according to a figure of merit based on SC and PCE, and some guidelines for the design of the materials and for the synthesis are given.



INTRODUCTION

Organic photovoltaic (OPV) technology offers unique opportunities for flexible, lightweight solar panels that are aesthetically pleasant (e.g., multicolored and/or semitransparent). Moreover, OPVs can potentially be easily manufactured in a variety of shapes with high throughput¹ in relatively small production facilities. Research on organic and polymer solar cells (PSC) dates back to the 1990s,² and since then impressive progresses in power conversion efficiencies (PCEs) of lab-scale devices have been achieved,³ with certified records of over 10%.² This value is generally deemed the entry point for commercial applications,⁴ even when accounting for efficiency losses between lab-scale cells and large-area modules.⁵

Despite this progress, the widespread commercial application of PSCs has yet to become a reality, and until now only prototypes and demo products have been presented to the public,^{4,6} mainly because the PCE of large-area prototypes, manufactured with roll-to-roll (R2R) printing techniques, are only around 2–3%.⁷ Several factors still hamper the development of OPV,^{8–10} related to both fabrication technology and materials characteristics. Among the materials composing a polymer solar cells (active and buffer materials, electrodes, barrier films for encapsulation), the donor and the acceptor are undoubtedly the most relevant elements because they most directly influence the device efficiency and also contribute significantly to its final cost.¹¹ Furthermore, the polymer's synthesis must be scalable to hundreds of kilograms or tons to be acceptable for industrial scale production of OPV modules.

In this Perspective, the highly efficient single-junction polymer solar cells (PCE > 6%) published through 2013 are surveyed, and

the synthetic complexity of the donor polymers used for their fabrication is assessed. The materials offering the best combination of synthetic accessibility and efficiency are identified, and guidelines for the future research on OPV polymers are presented.

DISCUSSION

Four aspects are important for an OPV polymeric material (Figure 1).¹² The first two requirements are *high efficiency and sufficient stability*^{13,14} of the resulting device. The literature on polymer donors is extensive,¹⁵ and several rules of design for highly efficient materials have been developed;^{16–18} in comparison, acceptors have been much less studied,^{19–21} and fullerene derivatives still represent the most performing alternative.

The third requirement is the *printability of the active layer blend*. This characteristic is determined by the ink properties (viscosity, solid content, and thixotropy), which in turn are affected by the polymer solubility and molecular weight. There are few systematic studies on printability in the literature,^{22–24} but none with highly efficient polymers. In the long term "green" solvents^{25–27} should also be considered for ink formulations, to limit the environmental impact of the fabrication process.

The final requirement, which is the subject of discussion of this paper, is that materials for large-scale production of OPV modules must be as inexpensive as possible, which means

Received: September 12, 2014

Revised: January 2, 2015

Published: January 12, 2015

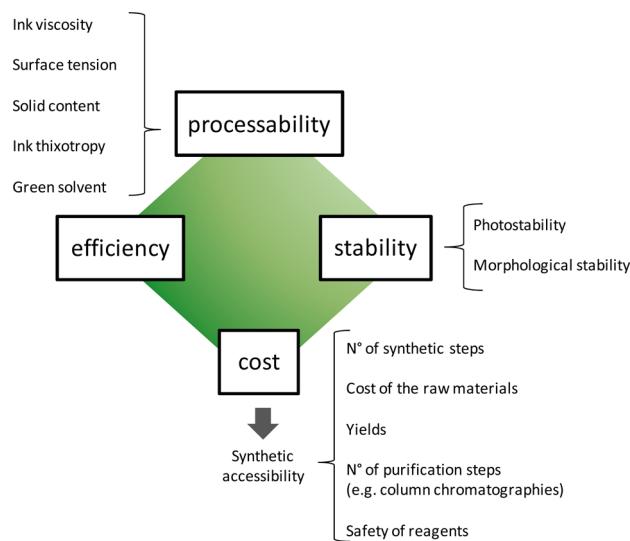


Figure 1. Schematic of areas of improvement on OPV polymers.

accessible from widely available raw materials, with a synthesis that involves few steps and scalable purification processes.²⁸ An acceptable cost, which leads to commercially viable modules, is around 10 €/g.¹¹ The expected industrial cost of a new chemical compound, however, is not easily estimated, especially starting from unoptimized recipes of lab-scale preparations. In such preparations, the minimization of synthetic steps and reactants consumption is not typically a key focus, and expensive column chromatography is routinely used for products purification. In fact, the main goal of the synthetic chemist during the first attempt to produce a new polymer is typically only to obtain a few hundred milligrams of polymer, regardless of its synthetic complexity. Furthermore, the market prices of raw materials and fine chemicals used for the preparation of such polymers are often not available in the literature. Using prices of chemicals taken from lab-scale supplier's catalogues and unoptimized synthesis, unrealistically high prices for conjugated polymer are obtained.²⁹ Nevertheless, a preliminary indirect estimation of the cost of a polymer can be accomplished by considering its synthetic accessibility (Figure 1),³⁰ assessed through five parameters: (1) the number of synthetic steps (NSS), (2) the reciprocal yields of the monomers (RY), (3) the number of unit operations required for the isolation/purification of the monomers (NUO), (4) the number of column chromatographic purifications required by the monomers (NCC), and (5) the number of hazardous chemicals used for their preparation (NHC).

The single-junction PSCs exhibiting PCE above 6% published through 2013 are listed in the Supporting Information, Table S1 and Chart S1. For each polymer, different PCE values are often found in the literature (in fact, some materials have been widely studied by multiple research groups) due to the type of alkyl chains, the extent of the optimization of the active and buffer layers, the solvents and additives, thermal treatments, etc. In the present analysis, for a given macromolecular backbone only the best reported efficiency (to our knowledge) is considered. If multiple PCE values are reported for a given polymer backbone with different alkyl substituents, only the highest value is reported here. For instance, the PCE of poly(benzodithiophene-thienopyrroloidine) (PBDTTPD) with heptyl chains on TPD (**P4**) is 8.5%;³¹ thus, devices containing PBDTTPD bearing octyl chains are not included in this analysis. Ninety-two polymers

(**P1–P92**) are defined according to this criterion, which are shown in Table S1: 84 are combined with PC₇₁BM acceptor, seven (**P36, P42, P53, P57, P68, P69**, and **P81**) are combined with PCBM, and one (**P61**) is combined with ICBA. Non-fullerene acceptors, which would be very attractive for their potential simplicity, have not achieved satisfactory performances to date.^{32–34} As for polymeric acceptors, although all-polymer solar cells have recently broken the 6% barrier,^{35,36} they have not been included in this survey due to lack of detailed information available in the literature.

Because PC₇₁BM is significantly more expensive than PCBM, a separate analysis has been carried out on active blends based on PCBM, in this case considering devices with PCE > 5%. The 26 polymers that have been found (**PA–PZ**) are reported in Table S2. Polymers **P1–P92** and **PA–PZ** arise from the combination of 128 monomers (**M1–M128**), shown in Chart 1, based on 85 different π -conjugated cores, which can be splitted into 14 families (Figure S3): **D1** = naphtho/benzodithiophenes (S → Se); **D2** = fluorenes/cbazoles (C, N → Si); **D3** = dithienocyclopentadienes (C → Si, Ge); **D4** = dithienoindacenes (C → Ge; S → Se); **D5** = phenylenes; **T** = thiophenes; **A1** = thieno[3,4-*b*]thiophenes (S → Se); **A2** = thienopyrrolediones; **A3** = dithienoquinones; **A4** = naphtho/benzothiadiazoles (S → O, N); **A5** = diketopyrrolopyrroles; **A6** = quinoxalines; **A7** = isoindigos; **A8** = thiazolothiazoles.

Chart 2 summarizes the compositions of the polymers. The synthesis of monomers **M1–M128** is described in the Supporting Information (Scheme S1). The starting compounds for the preparation of **M1–M128** were considered to be chemicals that could be found on the market in quantities sufficient to produce hundreds of kilograms of polymers (which correspond to tens of MW of generated electricity). When the starting compounds reported in the original sources were too complex, and presumably available only in small quantities from lab-chemicals suppliers, the preparation pathways have been extended to simpler chemical precursors. For each monomer the number of synthetic steps and yields are summarized in Table S3, along with the type and number of purification steps and the type and number of hazardous chemicals used in the synthesis. In a few cases, the monomer unit present in a polymer does not exactly match the structure of the monomer whose preparation is described in the experimental section of the references (the differences reside in the alkyl chains). Details about how each of these cases have been managed are reported in the Supporting Information. Tables S4 and S5 list the parameters defining the synthetic complexity (SC) of the monomers and the polymers, respectively. SC summarizes the five parameters (NSS, RY, NUO, NCC, and NHC) according to the following equation:

$$\begin{aligned} \text{SC} = & 35\text{NSS}/\text{NSS}_{\max} + 25 \log \text{RY}/\log \text{RY}_{\max} \\ & + 15\text{NUO}/\text{NUO}_{\max} + 15\text{NCC}/\text{NCC}_{\max} \\ & + 10\text{NHC}/\text{NHC}_{\max} \end{aligned}$$

An empiric coefficient is assigned to each parameter, which accounts for the relative importance. The number of synthetic steps is considered the most relevant (weight = 35) because it affects labor costs, capital costs, utilities, and maintainance. The yield is second in importance (weight = 25) because it affects the raw material costs as well as capital, labor, and waste treatments costs (the lower the yield, the higher the costs). Each unit operation (weight = 15), and in particular column chromatographies (additional weight = 15) which are burdensome in an

Chart 1. Monomers Structures (Blue: Electron-Rich Monomers; Red: Electron-Poor Monomers)

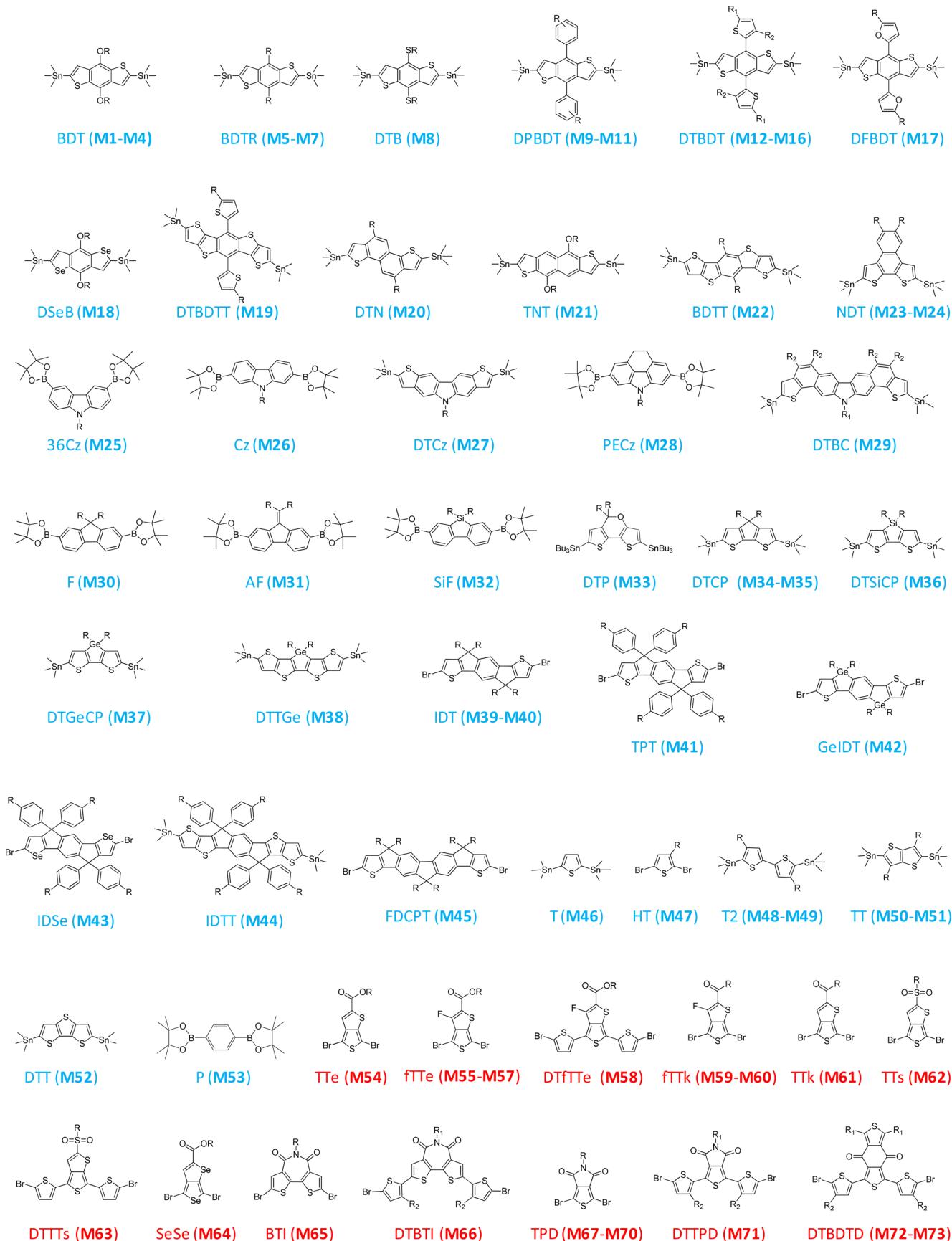
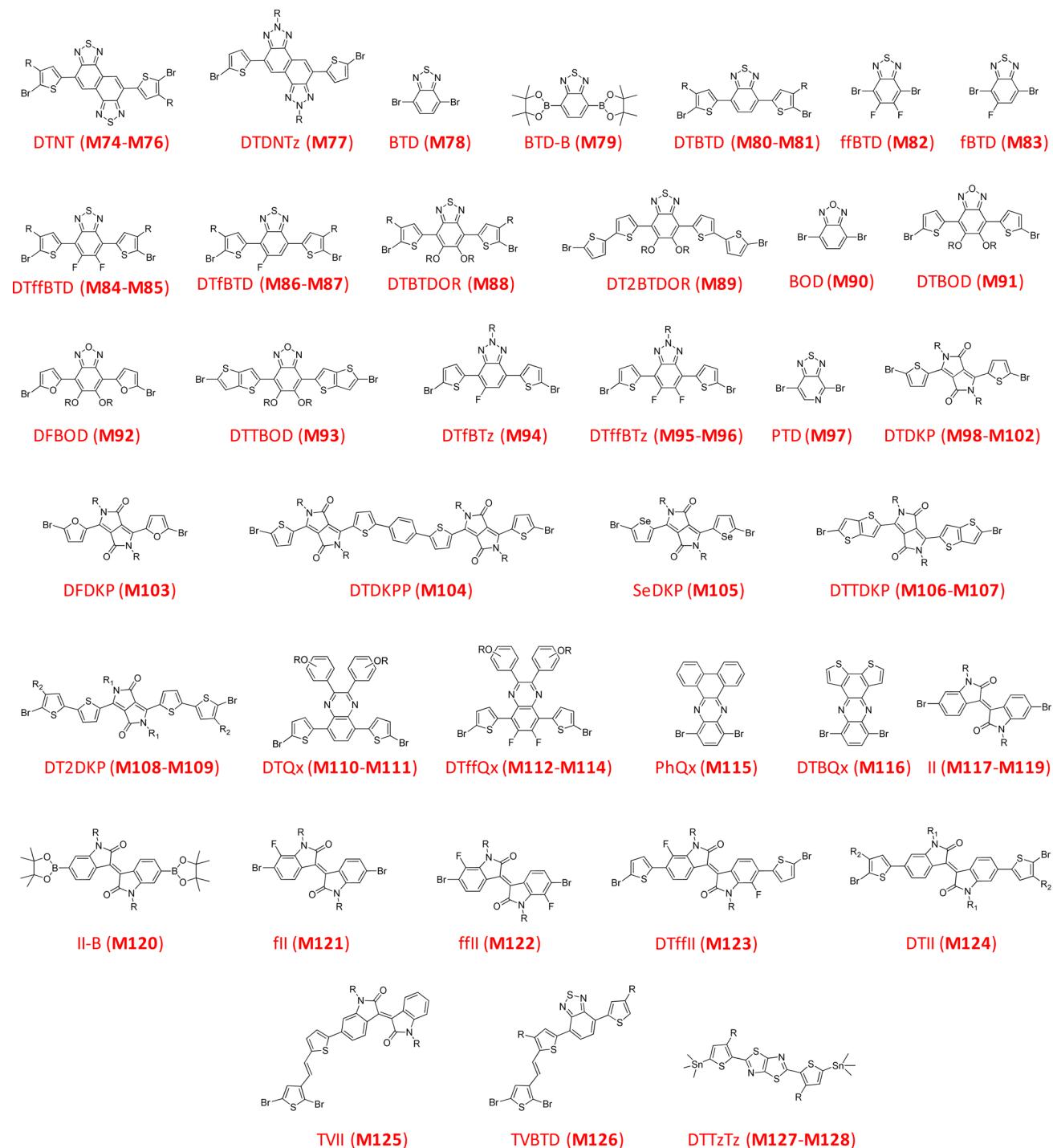


Chart 1. continued



industrial environment, requires in many cases additional and special equipment, thus affecting capital, labor, and utilities costs. Finally, the hazardous chemicals used in the process have impact on safety aspects (including wastes treatment) and lead to a comparably small, but non-negligible, contribution to costs (weight = 10).

The SC can be considered a rough, but reasonable, tool to sort polymers according to their probable cost. From SC and PCE a figure of merit ($FOM = SC/PCE$) was also calculated which best represents the cost-efficiency balance of a given donor material.

Figure 2 shows a plot of the PCE of polymers **P1-P93** vs their synthetic complexity. In particular, regions with the same color

correspond to constant values of FOM; for instance, the green area corresponds to polymers with relatively high efficiency and fair accessibility. Poly(3-hexylthiophene) (**P3HT, P61**) offers the best trade-off, mostly due to its simple preparation, but the PCE is not remarkable. It is worth noting that the P3HT PCE of 6.48% is obtained for the blend with ICBA;³⁶ blends of this polymer with other fullerenes have much lower PCEs. Straddling the green and yellow areas, two groups of polymers are found. The first one includes **P11, P27, P34, P35, and P60**, having SC lower than 32 and PCEs in the range 6.5–8.0%; these polymers contain diketopyrrolopyrrole (DKP) derivatives as electron-poor monomer units and thiophene or phenylene derivatives as

Chart 2. Polymers Composition^a

P1	M12+M55	P23	M26+M80	P45	M50+M102	P67	M12+M68+M99	P89	M32+M88
P2	M1+M55	P24, PF	M127+M128	P46	M48+M73	P68, PI	M113+M120	P90	M41+M82
P3	M46+M66	P25	M11+M58	P47	M18+M64	P69, PJ	M48+M76	P91	M108
P4	M1+M67	P26	M1+M81	P48, PX	M12+M91+M98	P70	M12+M59	P92	M14+M95
P5	M37+M68	P27	M53+M100	P49	M43+M82	P71	M8+M96	PB	M1+M68
P6	M3+M84	P28	M17+M91	P50	M1+M70	P72	M41+M115	PC	M6+M85
P7, PA	M20+M75	P29	M49+M69	P51	M25+M26+M80	P73	M13+M87	PL	M1+M56
P8	M27+M118	P30	M46+M107	P52	M41+M97	P74	M29+M80	PM	M2+M90
P9	M33+M82	P31	M12+M105	P53, PG	M12+M72	P75	M10+M91	PN	M1+M91
P10	M9+M81	P32	M38+M68	P54	M35+M83	P76	M9+M99	PO	M24+M85
P11	M46+M104	P33	M16+M77	P55	M12+M99	P77	M12+M85	PQ	M32+M80
P12	M1+M112	P34	M46+M100	P56	M1+M61	P78	M31+M88	PR	M1+M126
P13	M46+M71	P35	M48+M102	P57, PH	M1+M125	P79	M30+M89	PU	M51+M91
P14	M27+M121	P36, PD	M6+M96	P58	M39+M78	P80	M12+M106	PV	M46+M109
P15	M12+M63	P37	M4+M93	P59	M42+M78	P81, PK	M12+M68	PW	M6+M86
P16	M36+M68	P38	M15+M123	P60	M46+M103	P82	M40+M80	PY	M23+M81
P17	M19+M62	P39	M44+M82	P61	M47	P83, PS	M16+M74	PZ	M111+M117
P18	M9+M94	P40	M45+M79	P62, PP	M34+M68	P84	M18+M54		
P19	M1+M60	P41	M17+M92	P63	M41+M78	P85	M7+M114		
P20, PT	M22+M57	P42, PE	M48+M118+M119	P64	M36+M65	P86	M28+M110		
P21	M27+M122	P43	M46+M124	P65	M1+M62	P87	M41+M116		
P22	M12+M61	P44	M5+M102	P66	M21+M100	P88	M52+M101		

^aFull chemical structures are reported in Supporting Information, Chart S1).

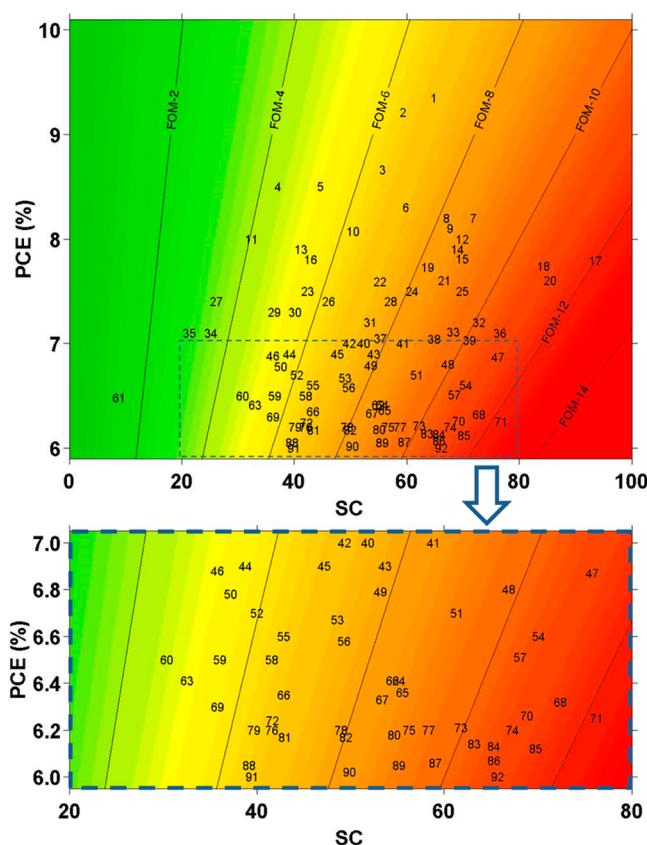


Figure 2. PCE of highly efficient solar cells vs synthetic complexity of donor polymers (“P” is omitted from the polymer codes for clarity). Raw data are reported in the Supporting Information, Table S1 (PCE) and Table S4 (SC).

electron-rich monomers. The second one includes P4, P5, P13, P16, and P29, which are polymers based on thienopyrroledione (TPD) and combine a slightly higher synthetic complexity with higher PCEs (7.2–8.5%). Thieno[3,4-*b*]thiophenes polymers

(P1 and P2) have the highest PCE (>9%), but their SCs exceed 60; other thieno[3,4-*b*]thiophenes-based polymers (e.g., P15, P17, P19, P20, P22, and P25) are even more complex, although their PCEs around 7.8% make them appealing.

Figure 3 shows polymers P1–P92 sorted by increasing FOM values. The red points correspond to (i) some widely studied

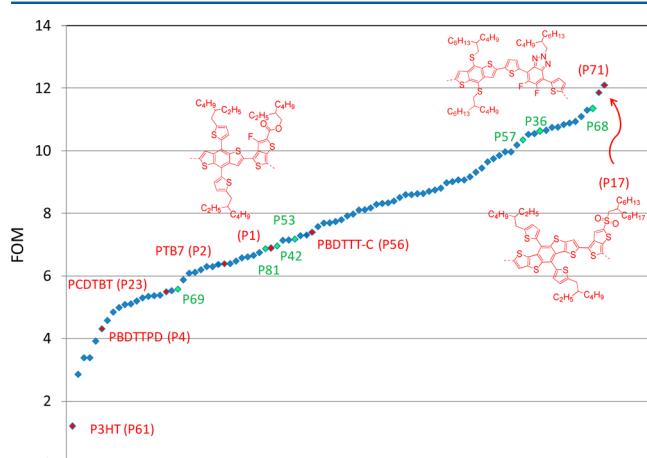


Figure 3. Figure of merit of polymers P1–P92.

polymers (P3HT,³⁷ PBDTTPD,³¹ PCDTBT,³⁸ PTB7,³⁹ and PBDTTT-C⁴⁰), (ii) the most efficient (P1), (iii) the most complex (P17), and (iv) the highest FOM (P71). In Figure 4, polymers P1–P92 are again sorted by increasing FOM and are split into subgroups according to their chemical families (sketched in Figure S3).

From the plot it is evident how benzo/naphthodithiophene derivatives (D1) are the most used electron-rich units, and benzothiadiazole derivatives (A4) are the most used electron-poor units. On average, thiophene units (used either as electron-rich or electron-poor components) afford the lowest FOMs; among the electron-poor units, DKK and TPD derivatives prove to be the most advantageous, as discussed above. It is worth

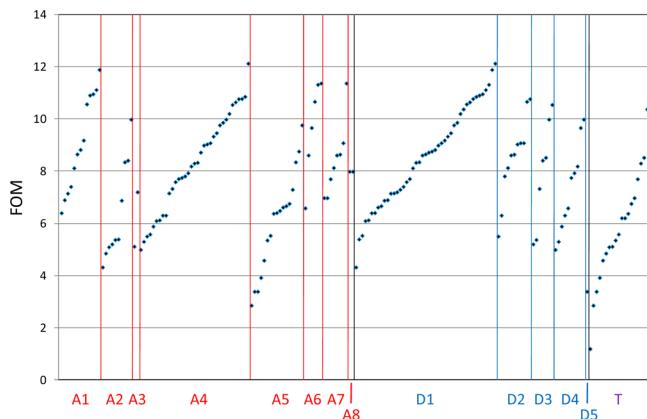


Figure 4. Figure of merit of polymers P1–P92 split according to the chemical families of the monomers.

noting that the values of the FOM of any family are affected by the FOM of the counterpart monomer. However, by considering a FOM_M calculated from the parameters of “isolated” monomer units (Supporting Information, Figure S27), the trends are confirmed (and actually are even more pronounced). Polymers containing fluorinated monomers are intriguing from the point of view of the efficiency, with 11 out of 25 polymers exhibiting a $PCE > 7.5\%$. However, fluorination increases the material complexity significantly with nearly all these polymers on the right section of Figure 2 ($SC > 49.5$). Fluorinated starting materials are also generally very expensive because the fluorination requires reactors made of special materials. The green points in Figure 3 are related to the seven polymers used in combination with PCBM. Several other polymers in Table S1 (P7, P20, P24, P48, P62, P83, and variants of P4 and P2 bearing different alkyl chains), while giving their best in combination with PC71BM, exhibit fair PCEs also with PCBM (Supporting Information, Table S2) compared to PC71BM-based cells. Since PCBM is currently much cheaper than PC₇₁BM, large-scale production of OPV modules will be likely based on the former. Thus, as mentioned above, an analysis of polymer:PCBM solar cells ($PCE > 5\%$) was also performed (Figure 5). In this set, there

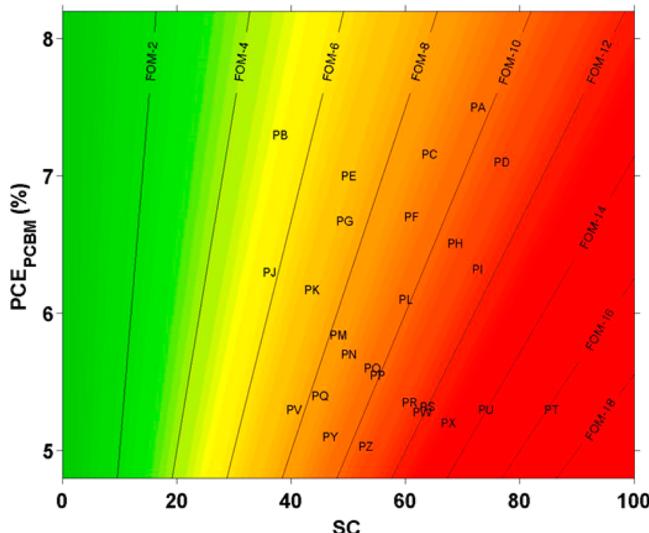


Figure 5. PCE of polymer solar cells based on PCBM acceptor vs synthetic complexity of donor polymers.

are 26 polymers above the PCE threshold, based on fewer monomers, with the overwhelming majority of the polymers (even more than in the P1–P92 set) based on D1 and A4 derivatives (Figure S28).

PBDTTTPD (PB, that is the same as P4, except for the octyl chain on the TPD unit in place of heptyl chains) is clearly the more promising material because it exhibits a high efficiency (7.3%)⁴¹ with an excellent accessibility. The main shortcoming of PBDTTTPD appears to be the electron-rich monomer (BDT), whose preparation is not as simple as it would be desirable. On the other hand, optimizing the synthesis of TPD⁴² has likely made this monomer the most suitable unit for highly efficient and scalable OPV. PJ (P69 in Figures 2 and 3), a tetrathiophene–naphthobisthiadiazole copolymer,⁴³ is also relatively simple especially thanks to the simplicity of the electron-rich component, and its PCE is 6.3%. This polymer is also a good example of a promising material whose unoptimized synthesis (Supporting Information, Scheme S1) would need to be improved to make the DTNT monomer accessible at large scale. The presently applied preparation method involves the use of N₄S₄, a highly explosive reagent, which can only be handled on the laboratory scale in very small quantities. Remarkably, DTNT is also employed for the preparation of PA, the most efficient polymer to date (PCE = 7.5%) used in combination with PCBM.⁴⁴

In this context, polymers employed as cathode buffer layers in some devices are worth mentioning. Although they are not active materials, nevertheless in many cases their use demonstrated to be fundamental to obtain optimized devices with high PCEs.^{39,45,46} The structure and preparation of these polyfluorenes bearing amino or ammonium moieties in the side chains are shown in Scheme S2, and their SC is reported in the Supporting Information, Table S6. They are relatively simple materials (compared to active polymers), with SC values ranging between 20 and 40.

CONCLUSION

Despite being aware that there might be a certain degree of discretion in some assumptions and that the evaluations are based on nonoptimized synthesis and on devices (often having different areas) fabricated in different laboratories, nevertheless the presented survey is, to the best of our knowledge, the first attempt to compare a large number of efficient OPV polymers, to assess their synthetic accessibility and, hence, their scalability and presumable costs. It should be noted that the SC parameter is just a preliminary approximation, and only the real costs can reliably assess the scalability of a given material. Hopefully, this analysis motivates attention to finding alternative synthetic pathways for the preparation of unoptimized efficient donor polymers to make them transferable from the laboratory research to the industrial context. Improvement of purification techniques, focusing on environmentally friendly and easy-to-dispose chemicals, and reduction in the number of synthetic steps are some of the approaches that can be followed to achieve this goal. For instance, direct heteroarylation polymerization (DArP), which has gained increased recent interest,^{47–50} would avoid the use of toxic organotin derivatives and pyrophoric lithium alkyls and would save one reaction step (the functionalization of one of the comonomers). In fact, with the exception of P3HT and a couple of polymers obtained through Suzuki cross-coupling polymerization, all the polymers considered in this analysis are prepared through Stille polymerization.

In addition to simplifying the preparation of already proven efficient materials, developing radically new, but simple, polymers is another strategy. These could be either combinations of simple previously reported monomers or polymers based on new monomers. After more than a decade of research on OPV, the latter possibility is the most challenging; for the former, although many combinations in alternating polymers have been already studied, there is probably still space for additional research. Figure 6 gives a glance at the reported combinations of

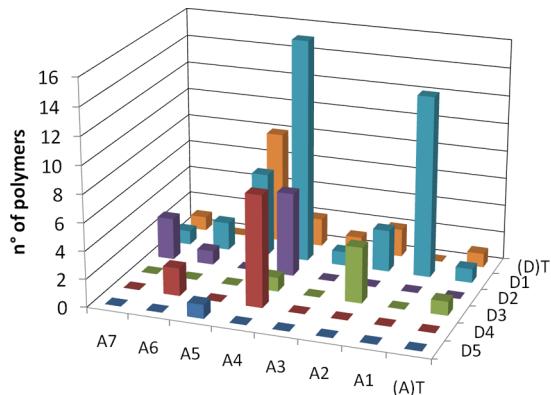


Figure 6. Electron-rich/electron-poor monomer combinations for polymers P1–P92, according to the families they belong to. Only binary “donor–acceptor” polymers are considered. “T” monomers can be either electron-rich [(D)T] or electron-poor [(A)T], depending on the structure.

electron-rich/electron-poor monomers (leading to PCEs > 6%). There are several families of monomers—including dithienoquinones, quinoxalines, thiazolothiazoles, and dithienocyclopadienes—that are relatively unexplored and might produce polymers with interesting characteristics.

As an additional possibility, random copolymers^{51–53} might be a field worth of deeper investigations. Moreover, although “simple” polymers might not have outstanding performances when used in single-junction cells (the architecture this analysis has been restricted to), it is possible that tandem devices could be a route to higher efficiencies with these materials. The costs must be carefully considered in this case, since more than one active material is involved.

Among the most synthetically accessible electron-poor monomers, thienopyrrolodione and diketopyrrolopyrrole derivatives appear to be the most prominent; thiophene derivatives stand out both as electron-rich and electron-poor monomers. Benzodithiophene derivatives are the most used electron-rich monomers because they provide polymers with the highest PCEs; however, their preparations are rather complicated, and a better replacement should be found.

As a final comment, it can be said that sophisticated polymers are pursued to break the current efficiency record, but complex materials are doomed to remain confined to the world of research. To successfully transfer the research results from the laboratory to the industrial context, inexpensive and accessible polymers are essential and, to date, the winning OPV materials are yet to be found.

■ ASSOCIATED CONTENT

S Supporting Information

Reaction schemes and monomer families, summary of synthetic parameters used for SC and FOM calculations, additional

correlations and histograms with monomers and polymer statistics, full list of references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel +39-0321-447541; Fax +39-0321-447241; e-mail riccardo.po@eni.com (R.P.).

Notes

During 2014 several other highly efficient polymers have been disclosed in the open literature. In particular, while revising our manuscript, this paper—reporting PCEs over 10%—was published: Liu et al. *Nat. Commun.* **2014**, *5*, 5293. Highly efficient solar cells based on non-fullerene acceptors have also been published: Lin et al. *Energy Environ. Sci.* **2015**, doi: 10.1039/c4ee03424d. Zhao et al. *Energy Environ. Sci.* **2015**, doi: 10.1039/c4ee02990a. “All that glitters is not gold” is a quotation from William Shakespeare’s *The Merchant of Venice* (II, vii). The authors declare no competing financial interest.

Biographies



Riccardo Po studied Industrial Chemistry at the University of Pisa, where he received the MSc (Laurea) in 1988. Subsequently, he moved to the Enichem Research Center in Novara, where he joined the Materials Department, working on polymer synthesis and modification. In 1999 he became Manager of the Polymer Chemistry and Physics Department. In 2007 the Research Center was incorporated by Eni SpA, and he was appointed Manager of the Solar Energy Department and put in charge of the research activities on polymer solar cells.



Gabriele Bianchi received his Ph.D. in Environmental Chemistry in 2006 at the University of L’Aquila, Italy, where he developed with Prof. A. Arcadi unconventional, green approach to the synthesis of heterocyclic compounds. From 2006 to 2010, he was a postdoctoral fellow at the University of L’Aquila, where his research focused on green electro-

chemical synthesis. He joined Eni SpA-Research Center for Renewable Energies & Environment in 2010. His current research interests are organic synthesis and organometallic chemistry, in particular, development of novel synthetic strategies for organic electronics.



Chiara Carbonera received her MSc in Industrial Chemistry with focus on chemical physics at the University of Milan. She then earned her PhD in chemistry at the University of Florence in 2003. From 2003 to 2008, she was a postdoctoral fellow first at the Institute for Solid State Chemistry (Bordeaux, France) and then at the Institute of Materials Science of Aragón (Saragossa, Spain), before she joined Po's research group at the "Research Center for Renewable Energies and Environment - Eni Donegani Institute", where her research is directed mainly toward the improvement of polymer solar cell devices features through their fabrication and characterization.



Andrea Pellegrino received his MSc in Organic Chemistry at the University of Milan in 2007. He joined Eni SpA at the "Research Center for Renewable Energies and Environment" in 2008. He is involved in the design and synthesis of novel photoactive materials and macromolecular characterization.

ACKNOWLEDGMENTS

The authors thank José F. Rodriguez Matas for help with data elaboration and eni SpA for the permission to publish this work.

REFERENCES

- (1) Søndergaard, R.; Hösel, M.; Angmo, D.; Larsen-Olsen, T. T.; Krebs, F. C. *Mater. Today* **2012**, *15*, 36–49.
- (2) www.nrel.gov/ncpv/images/efficiency_chart.jpg, accessed Dec 2014.
- (3) Krebs, F. C.; Fyenbo, J.; Tanenbaum, D. M.; Gevorgyan, S. A.; Andriessen, R.; van Remoortere, B.; Galagan, Y.; Jørgensen, M. *Energy Environ. Sci.* **2011**, *4*, 4116–4123.
- (4) Brabec, C. J.; Gowrisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S.; Williams, S. P. *Adv. Mater.* **2010**, *22*, 3839–3856.
- (5) Dongaonkar, S.; Loser, S.; Sheets, E. J.; Zaunbrecher, K.; Agrawal, R.; Marks, T. J.; Alam, M. A. *Energy Environ. Sci.* **2013**, *6*, 782–787.
- (6) Krebs, F. C.; Nielsen, T. D.; Fyenbo, J.; Wadström, M.; Pedersen, M. S. *Energy Environ. Sci.* **2010**, *3*, 512–525.
- (7) Carlé, J. E.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2013**, *119*, 309–310.
- (8) Po, R.; Bernardi, A.; Calabrese, A.; Carbonera, C.; Corso, G.; Pellegrino, A. *Energy Environ. Sci.* **2014**, *7*, 925–943.
- (9) Darling, S. B.; You, F. *RSC Adv.* **2013**, *3*, 17633–17648.
- (10) Krebs, F. C.; Jørgensen, M. *Sol. Energy Mater. Sol. Cells* **2013**, *119*, 73–76.
- (11) Machui, F.; Hösel, M.; Li, N.; Spyropoulos, G. D.; Ameri, T.; Søndergaard, R. R.; Jørgensen, M.; Scheel, A.; Gaiser, D.; Kreul, K.; Lenssen, D.; Legros, M.; Lemaitre, N.; Vilkman, M.; Välimäki, M.; Nordman, S.; Brabec, C. J.; Krebs, F. C. *Energy Environ. Sci.* **2014**, *7*, 2792–2802.
- (12) Jørgensen, M.; Norrman, K.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 686–714.
- (13) Jørgensen, M.; Norrman, K.; Gevorgyan, S. A.; Tromholt, T.; Andreassen, B.; Krebs, F. C. *Adv. Mater.* **2012**, *24*, 580–612.
- (14) Yan, F.; Noble, J.; Peltola, J.; Wicks, S.; Balasubramanian, S. *Sol. Energy Mater. Sol. Cells* **2013**, *114*, 214–218.
- (15) Jørgensen, M.; Carlé, J. E.; Søndergaard, R. R.; Lauritzen, M.; Dagnæs-Hansen, N. A.; Byskov, S. L.; Andersen, T. R.; Larsen-Olsen, T. T.; Böttiger, A. P. L.; Andreassen, B.; Fu, L.; Zuo, L.; Liu, Y.; Bundgaard, E.; Zhan, X.; Chen, H.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2013**, *119*, 84–93.
- (16) Xu, T.; Yu, L. *Mater. Today* **2014**, *17*, 11–15.
- (17) Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607–632.
- (18) Li, Y. *Acc. Chem. Res.* **2012**, *45*, 723–733.
- (19) Delgado, J. L.; Bouit, P. A.; Filippone, S.; Herranz, M. A.; Martin, N. *Chem. Commun.* **2010**, *46*, 4853–4865.
- (20) He, Y.; Li, Y. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1970–1983.
- (21) Hudhomme, P. *EPJ Photovoltaics* **2013**, *4*, 40401.
- (22) Jakubka, F.; Heyder, M.; Machui, F.; Kaschta, J.; Eggerath, D.; Lövenich, W.; Krebs, F. C.; Brabec, C. J. *Sol. Energy Mater. Sol. Cells* **2013**, *109*, 120–125.
- (23) Machui, F.; Langner, S.; Zhu, X.; Abbott, S.; Brabec, C. J. *Sol. Energy Mater. Sol. Cells* **2012**, *100*, 38–146.
- (24) Burgués-Ceballos, I.; Stella, M.; Lacharmoise, P.; Martínez-Ferrero, E. *J. Mater. Chem. A* **2014**, *2*, 17711–17722.
- (25) Larsen-Olsen, T. T.; Andersen, T. R.; Andreassen, B.; Böttiger, A. P. L.; Bundgaard, E.; Norrman, K.; Andreassen, J. W.; Jørgensen, M.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2012**, *97*, 43–49.
- (26) Duan, C.; Cai, W.; Hsu, B. B. Y.; Zhong, C.; Zhang, K.; Liu, C.; Hu, Z.; Huang, F.; Bazan, G. C.; Heeger, A. J.; Cao, Y. *Energy Environ. Sci.* **2013**, *6*, 3022–3034.
- (27) Chueh, C.-C.; Yao, K.; Yip, H.-L.; Chang, C.-Y.; Xu, Y.-X.; Chen, K.-S.; Li, C.-Z.; Liu, P.; Huang, F.; Chen, Y.; Chen, W.-C.; Jen, A.K.-J. *Energy Environ. Sci.* **2013**, *6*, 3241–3248.
- (28) Roncali, J.; Leriche, P.; Blanchard, P. *Adv. Mater.* **2014**, *26*, 3821–3838.
- (29) Osedach, T. P.; Andrew, T. L.; Bulovic, V. *Energy Environ. Sci.* **2013**, *6*, 711–718.
- (30) Marzano, G.; Ciasca, C. V.; Babudri, F.; Bianchi, G.; Pellegrino, A.; Po, R.; Farinola, G. M. *Eur. J. Org. Chem.* **2014**, *30*, 6583–6614.
- (31) Cabanetos, C.; El Labban, A.; Bartelt, J. A.; Douglas, J. D.; Mateker, W. R.; Fréchet, J. M. J.; McGehee, M. D.; Beaujuge, P. M. *J. Am. Chem. Soc.* **2013**, *135*, 4656–4659.
- (32) Anthony, J. E. *Chem. Mater.* **2011**, *23*, 583–590.
- (33) Sonar, P.; Lima, J. P. F.; Chan, K. L. *Energy Environ. Sci.* **2011**, *4*, 1558–1574.
- (34) Eftaiha, A. F.; Sun, J.-P.; Hill, I. G.; Welch, G. C. *J. Mater. Chem. A* **2014**, *2*, 1201–1213.
- (35) Facchetti, A. *Mater. Today* **2014**, *16*, 123–132.
- (36) Lin, Y.; Zhan, X. *Mater. Horiz.* **2014**, *1*, 470–488.
- (37) Zhao, G.; He, Y.; Li, Y. *Adv. Mater.* **2010**, *22*, 4355–4358.

- (38) Wang, D. H.; Kim, J. K.; Seo, J. H.; Park, I.; Hong, B. H.; Park, J. H.; Heeger, A. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 2874–2880.
- (39) He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. *Nat. Photonics* **2012**, *6*, 591–595.
- (40) Chen, H.-Y.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L.; Wu, Y.; Li, G. *Nat. Photonics* **2009**, *3*, 649–653.
- (41) Hoke, E. T.; Vandewal, K.; Bartelt, J. A.; Mateker, W. R.; Douglas, J. D.; Noriega, R.; Graham, K. R.; Fréchet, J. M. J.; Salleo, A.; McGehee, M. D. *Adv. Energy Mater.* **2013**, *3*, 220–230.
- (42) Berrouard, P.; Dufresne, S.; Pron, A.; Veilleux, J.; Leclerc, M. J. *Org. Chem.* **2012**, *77*, 8167–8173.
- (43) Osaka, I.; Shimawaki, M.; Mori, H.; Doi, I.; Miyazaki, E.; Koganezawa, T.; Takimiya, K. *J. Am. Chem. Soc.* **2012**, *134*, 3498–3507.
- (44) Osaka, I.; Kakara, T.; Takemura, N.; Koganezawa, T.; Takimiya, K. *J. Am. Chem. Soc.* **2013**, *135*, 8834–8837.
- (45) Su, M.-S.; Kuo, C.-Y.; Yuan, M.-C.; Jeng, U. S.; Su, C.-J.; Wei, K.-H. *Adv. Mater.* **2011**, *23*, 3315–3319.
- (46) Dong, Y.; Hu, X.; Duan, C.; Liu, P.; Liu, S.; Lan, L.; Chen, D.; Ying, L.; Su, S.; Gong, X.; Huang, F.; Cao, Y. *Adv. Mater.* **2013**, *25*, 3683–3688.
- (47) Burke, D. J.; Lipomi, D. J. *Energy Environ. Sci.* **2013**, *6*, 2053–2066.
- (48) Berrouard, P.; Najari, A.; Pron, A.; Gendron, D.; Morin, P.-O.; Pouliot, J.-R.; Veilleux, J.; Leclerc, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2068–2071.
- (49) Facchetti, A.; Vaccaro, L.; Marrocchi, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 3520–3523.
- (50) Mercier, L. G.; Leclerc, M. *Acc. Chem. Res.* **2013**, *46*, 1597–1605.
- (51) Khlyabich, P. P.; Burkhardt, B.; Rudenko, A. E.; Thompson, B. C. *Polymer* **2013**, *54*, 5267–5298.
- (52) Kotowski, D.; Luzzati, S.; Bianchi, G.; Calabrese, A.; Pellegrino, A.; Po, R.; Schimperna, G.; Tacca, A. *J. Mater. Chem. A* **2013**, *1*, 10736–10744.
- (53) Kang, T. E.; Kim, K.-H.; Kim, B. J. *J. Mater. Chem. A* **2014**, *2*, 15252–15267.