

# Journal of Materials Chemistry C

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## Beyond efficiency: scalability of molecular donor materials for organic photovoltaics

Riccardo Po\*

*Istituto Donegani, Renewable Energies and Environmental R&D, Eni S.p.A., via G. Fauser 4, 28100 Novara, Italy.*

Jean Roncali\*

*Group Linear Conjugated Systems, CNRS Moltech-Anjou, University of Angers, 2Bd Lavoisier 49045 Angers, France. E-mail jeanroncali@gmail.com*

### Abstract

The preparation of various molecules taken as representative examples of some of the main classes of molecular donors for organic solar cells has been analyzed in order to assess the complexity and possibilities of scaling-up of their synthesis. Several parameters are taken into account to evaluate the synthetic complexity index (SC) namely the number of synthetic steps, the reciprocal yield of each step, the number of operations (in particular column chromatographies) required for the purification and the safety characteristics of the used chemicals. As could be intuitively understood, large complex molecular structures that have led to the highest conversion efficiencies reported so far require more complex lengthy syntheses than smaller systems. These data underline the necessity to define working molecular structures that represent an acceptable trade-off between conversion efficiency, scalability and cost in order to design active photovoltaic molecular materials for possible large scale production.

### Introduction

The lightness, plasticity, resistance against corrosion and low cost of organic materials has led for many industrial products to the progressive replacement of traditional materials such as stone, wood, metal or textiles by synthetic materials based on carbon chemistry. In this context, electronics and optoelectronics represent a noticeable exception. Although this situation can be explained by the relative youth of the electronic industry, one must admit that the performances of organic semi-conductors (OSCs) are still largely inferior to those of their inorganic counterparts and in particular silicon. Nevertheless, the processability, plasticity and almost endless possibilities of tuning of the properties of OSCs can provide opportunities to develop original applications for which parameters such as high frequency response are not

crucial. Organic light-emitting diodes (OLEDs) that have now entered the state of commercialization provide a particularly demonstrative illustration of such possibilities.

Triggered by the discovery of conducting polymers at the end of the seventies, OSCs have been subject to a continuous effort of both basic and applied research for almost four decades.<sup>1,2</sup> Over such a long period, the vision of these materials has undergone a strong evolution driven by both the progress of basic science and by the external economic and society context. Thus, the turn of the nineties has witnessed a progressive decline of research on the bulk applications of conducting polymers, with the parallel emergence of research based on the electronic properties of the semiconducting form of  $\pi$ -conjugated systems such as OLEDs<sup>3</sup> or field-effect transistors (OFETs).<sup>4,5</sup> A few years later, the convergence of energy problems and environmental concerns have progressively pushed organic photovoltaics (OPV) on the forefront of research on OSCs.<sup>6,7</sup> During the past fifteen years, an intensive multi-disciplinary research effort has generated impressive progress leading to a *ca* tenfold increase of the power conversion efficiency (*PCE*) of OPV cells which now reaches values around 10.0% for single junction devices.<sup>8,9</sup>

OPV cells are basically developed along two main approaches. In 1986, Tang described the first example of planar heterojunction (PHJ) produced by contacting an electron donor material (D) with an electron acceptor (A).<sup>10</sup> This device architecture is still widely investigated today. The concept of bulk heterojunction (BHJ) was proposed in the mid-nineties.<sup>11,12</sup> In these devices, phase-segregated interpenetrated networks of D and A materials are distributed in the whole volume of the active layer. This results in a huge extension of the D/A contacting area and hence of the number of excitons dissociated.<sup>13,14</sup>

Whereas the active materials used in vacuum-deposited PHJ cells are essentially based on small molecules,<sup>7,10</sup> soluble conjugated polymers have represented the major class of donor materials for the fabrication of solution-processed BHJ cells.<sup>11-16</sup> In fact, advanced conjugated polymers with reduced band gap combine good mechanical properties with high hole-mobility and photovoltaic conversion efficiency. However, the inherent polydispersity of polymers can pose problems regarding the reproducibility of the synthesis, purification composition and electronic properties of the material. Crude polymers contain conjugated chains of different lengths and generally require fractioning with various solvents in order to reduce polydispersity, whereas the presence of remnant terminal groups on the polymer chains can be also be a source of problems.<sup>17-20</sup> On the other hand, the presence of traces of metals from organometallic reagents or catalysts used for polymerization can have deleterious effects on the electronic properties of OSCs.<sup>21,22</sup> These purification processes that generate substantial amounts of

chemical wastes also contribute to increase the cost and environmental impact of the synthesis of the material.<sup>23-25</sup>

A possible alternative approach proposed ten years ago consists in replacing polymers by soluble molecular materials. In addition to more reproducible synthesis and purification, molecular donors allow the analysis of structure-properties relationships that remain one of the major tool for chemists to design new molecular structures. Triggered by seminal work in 2005-2006,<sup>26,27</sup> this research area has rapidly expanded and led to the synthesis of a huge number of new molecular donors.<sup>28-33</sup> Intensive parallel research efforts in device optimization and design of new molecular materials has led in less than ten years to performances now equaling those of the best polymer-based devices with *PCE* of ~10.0% for single junction cells.<sup>34</sup>

However, examination of the chemical structure of the molecules implemented in the most efficient OPV cells reveals a trend towards the design of more complex molecular architectures that require an increasing number of synthetic and purification steps. This orientation of chemistry of active OPV materials has several undesired consequences such as lower overall yields of the synthesis, larger consumption of raw materials, energy and time, bigger amounts of chemical wastes and hence higher cost of the final product. This complexification of the structure of active materials results in a paradoxical situation in which the quest for record *PCE* often claimed as a necessity for commercialization could lead in fact to the opposite result since the limited possibilities of scaling-up and prohibitive cost of active materials may contribute to confine OPV in a restricted circle of purely academic interest.

Besides possible development of niche applications resorting to the plasticity and tunability of organic materials, the major motivation to develop research on OPV remains a decisive economic and environmental advantage over existing photovoltaic technologies. In this regard the tendencial decrease of the price of silicon solar cells in recent years makes this objective even more challenging. The overall cost of an OPV module involves different contributions, *i.e.* materials (ITO glass, metal electrodes, buffer layers, encapsulation), capital costs, labour etc.<sup>23-25,35</sup> Since the cost of the active material represents a significant part of the total, the possibility to produce active materials at hundred of kilograms scale with acceptable cost and environmental impact can clearly contribute to the possible industrial future of OPV.

This paper aims at discussing the possibilities of scaling up the synthesis of some representative examples of molecular donor materials for OPV. Beyond high conversion efficiency, the aim is to draw the attention on the potential cost and scalability of donor material in order that these factors can be taken into consideration already at the stage of molecular design.

## Method of analysis

The cost of an active material is, with good approximation, proportional to its synthetic complexity (SC), which in turn can be estimated considering five parameters: the number of synthetic steps (*NSS*), the reciprocal yields of the building blocks (*RY*), the number of unit operations required for the isolation/purification of the intermediate compounds (*NUO*) (in particular the number of column chromatographic purifications (*NCC*) and the number of hazardous chemicals used for their preparation (*NHC*). SC is defined with the following equation and has been used recently to assess the accessibility of a series of highly efficient low gap polymers used in polymer solar cells.<sup>25</sup> According to this definition, SC values range from 0 to 100.

$$SC = 35 * NSS/NSS_{\max} + 25 * \log RY/\log RY_{\max} + 15 * NUO/NUO_{\max} + 15 * NCC/NCC_{\max} + 10 * NHC/NHC_{\max}$$

The chemistry of molecular donors has led to the synthesis of hundreds of molecules that have been discussed in several reviews articles.<sup>28-33</sup> The aim of this short survey is to analyze the potentialities of scaling-up the synthesis of various classes of molecules considered as representative of some important classes of molecular donors (oligothiophenes, squaraines, triphenylamine derivatives etc.). Whereas some of these materials have been implemented in OPV cells with the highest *PCE* values reported so far, some other compounds represent examples of materials with the smallest SC index and hence the highest possibility of scaling-up at low cost. While the chemistry of active materials clearly plays a major role in the progress of OPV it is very difficult to quantify its specific contribution. The efficiency of an OPV cell depends on many experimental variables *e.g.* device architecture PHJ or BHJ,<sup>14,31</sup> processing method (thermal evaporation under vacuum, spin-casting, doctor blade)<sup>36,37</sup> geometry and active area of the cell,<sup>38-41</sup> nature and concentration of the acceptor,<sup>42-44</sup> insertion of hole and/or electron transporting buffer layer,<sup>45-47</sup> additives,<sup>48</sup> thermal and/or solvent annealing,<sup>13,49</sup> nature of the metal electrode with eventual introduction of electropositive metals.<sup>43,50</sup> In this context, comparing the relative efficiency of molecules that have not been evaluated in strictly identical conditions does not make great sense. Such comparisons can lead to an overestimation of the actual contribution of molecular design and/or to erroneous conclusions regarding the relative performances of different active molecules. For these reasons, the various donors discussed

here have considered essentially on the basis of their SC index. In each case the performances of the resulting OPV cells are briefly commented on the basis of the highest reported *PCE* values even if it is clear that these results can be subject to significant statistical variations.

The starting compounds for the preparation of the molecular donors have been considered to be chemicals that can be found on the market in quantities sufficient to produce hundreds of kilograms of materials (which would correspond to tens of MW of generated electricity). When the starting compounds reported in the original references were too much complex, and presumably available only in small quantities from laboratory chemicals suppliers, preparation pathways from simpler - and cheaper - chemical precursors (Table 1) were thoroughly searched in the literature.

## Discussion

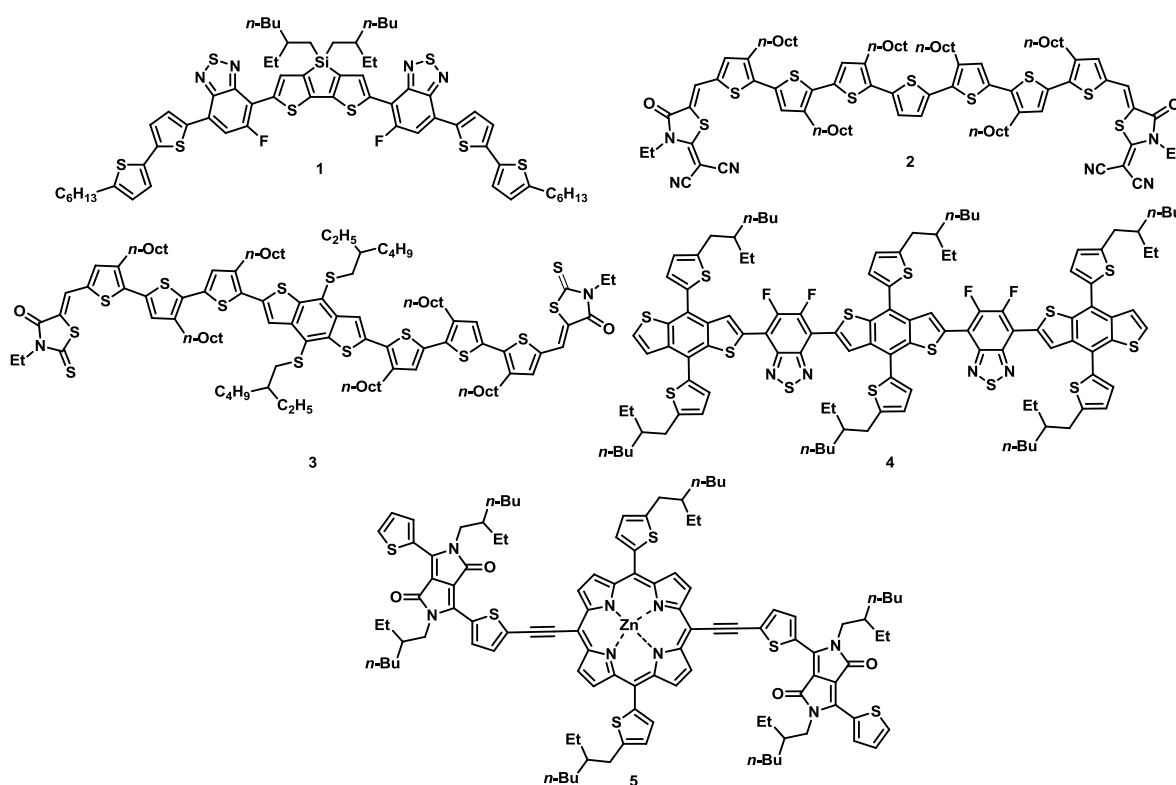
Until now, single junction OPV cells with the highest *PCE* are solution-processed BHJ cells combining PC<sub>71</sub>BM as the acceptor and donors of relatively complex molecular structure. One of the first examples of this class of efficient donors was reported by Bazan and coworkers who developed hybrid conjugated systems combining thiophene and benzothiadiazole derivatives around a dithienylsilole median block.<sup>51</sup> Thus a 12.4 mm<sup>2</sup> cell based on a donor containing a thiadiazolopyridine block gave a *PCE* of 4.52 % with PC<sub>71</sub>BM as the acceptor. The addition of 0.25% of diiodooctane (DIO) in the processing solution increased *PCE* up to 6.70%.<sup>52</sup> More recently, a *PCE* of 7.80 % was reported for a 5 mm<sup>2</sup> inverted cell based on the difluoro substituted compound **1** combined with PC<sub>71</sub>BM and DIO,<sup>53</sup> while a *PCE* of 8.57% was reported for a direct cell of 4.5 mm<sup>2</sup> with barium as additional cathode layer.<sup>50</sup> As shown in Table 1. The preparation of compound **1** requires nine synthetic steps leading to a SC index of 57. However, the large scale synthesis of **1** produces a side product that cannot be separated from compound **1** and that seriously reduces the performance of the material. Compound **1**, when prepared in a large batch synthesis, gives much lower *PCE* than material prepared in small batches. This problem will significantly increase the cost of mass producing this material.<sup>54</sup>

Solution-processed BHJ cells showing high *PCE* values have been described by Chen and coworkers who synthesized various series of symmetrical hybrid thiophene-based oligomers end-capped with electron acceptor groups.<sup>55</sup> Thus, a *PCE* of 9.30 % has been reported for a 4 mm<sup>2</sup> cell based on compound **2** with PC<sub>71</sub>BM as the acceptor (*vs* 7.55% with PC<sub>61</sub>BM).<sup>56</sup> More recently, a *PCE* close to 10 % (9.95%) was reported for a cell based on donor

**3** and PC<sub>71</sub>BM after both thermal and solvent annealing.<sup>34</sup> As appears in Table 1, these donors require multiple synthesis and purification steps which lead to the highest SC values among the donors considered in this survey namely 71 and 89 for compounds **2** and **3** respectively.

The analysis of the relationships between the electronic properties of low band gap conjugated polymers and those of the corresponding oligomers is of particular interest in the context of the design of donor materials for OPV.<sup>57</sup> Yuan *et al* have synthesized compound **4** and they have shown that this oligomeric donor leads to a better *PCE* than the corresponding polymer (8.10% vs 7.41%). In both cases a dramatic effect of DIO was observed boosting *PCE* from 6.0 to 8.0 % for the oligomer and from 2.40 to 7.40 % for the polymer.<sup>58</sup> However, the SC index of the oligomer remains high (70).

Molecular donors combining porphyrins with diketopyrrolopyrrole blocks have been recently introduced by the Cao's group.<sup>59,60</sup> A *PCE* of 5.80% was reported for a BHJ cell with PC<sub>61</sub>BM as the acceptor, this value was increased to 7.20% using 0.40% of DIO as additive.<sup>59</sup> More recently a *PCE* of 5.53 % was reported for a 16 mm<sup>2</sup> cell based on compound **5**, increasing to 8.00 % with pyridine as additive and after thermal annealing.<sup>60</sup> It is worth noting that these results have been obtained with PC<sub>61</sub>BM which is much less expensive than PC<sub>71</sub>BM. However, the number of synthesis and purification steps remain high and the SC index as high as 72.



**Table 1.** Starting materials, number of synthetic steps (*NSS*), reciprocal yield (*RY*), number of operation units for the isolation/purification (*NUO*), number of column chromatographies for the isolation/purification (*NCC*), number of hazardous chemicals (*NHC*) and synthetic complexity index (*SC*) for compounds **1-17**.

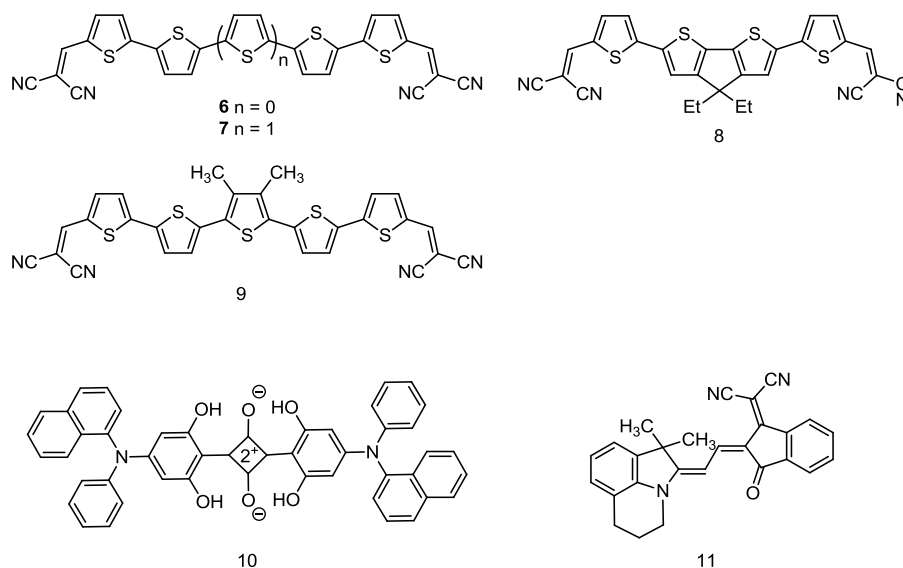
Compd	Key starting materials (yield of final product)	Additional relevant starting materials	<i>NSS</i>	<i>RY</i> <sup>a</sup>	<i>NUO</i>	<i>NCC</i>	<i>NHC</i> <sub>b</sub>	<i>SC</i> <sup>c</sup>
<b>1</b>	5-hexyl-2,2'-bithiophene (21.5%), 1,2-diamino-4-fluorobenzene (14.3%), 2-ethylhexylmagnesium bromide (17.7%)	3,3'-dibromo-2,2'-bithiophene	9	5.61	17	4	43	57
<b>2</b>	3-bromothiophene (18.0%)	2,5-dibromothiophene, Ethyl isothiocyanate, Ethyl-2-bromoacetate	11	5.56	25	7	50	71
<b>3</b>	3-bromothiophene (14.4%), Thiophene-3-carboxylic acid (13.9%)	2,5-dibromothiophene, rhodanine	18	7.04	28	6	69	89
<b>4</b>	Thiophene-3-carboxylic acid (21.6%), Thiophene (18.0%) 4,5-difluoro-2-nitroaniline (4.6%)	-	12	6.79	23	5	50	70
<b>5</b>	2-cyanothiophene (17.1%), Thiophene (32.6%), Pyrrole (30.8%)	dimethylsuccinate	12	3.73	28	9	40	72
<b>8</b>	2,3-dibromothiophene (34%)	5-bromothiophene-2-carboxaldehyde	6	2.94	10	5	28	40
<b>9</b>	3,4-dibromothiophene (24.8%), 5-bromothiophene-2-carboxaldehyde (38.3%)	2-(tributylstannyl)thiophene	7	3.16	10	1	27	36
<b>10</b>	1-bromo-3,5-dimethoxybenzene (43.9%)	<i>N</i> -Phenyl-1-naphthylamine, squaric acid	3	2.28	5	1	11	20
<b>11</b>	1,2,3,4-Tetrahydroquinoline (7.0%), Indane-1,3-dione (54.0%)	-	4	3.28	5	1	6	25
<b>12</b>	5-bromo-2,2'-bithiophene (7.9%)	Tris( <i>p</i> -bromophenyl)amine	6	12.7	9	3	19	49
<b>13</b>	2,3-diaminotoluene (28.3%), 4-bromoaniline (54.9%)	4-iodotoluene	8	2.40	12	4	28	41
<b>14</b>	<i>N</i> -(4-bromophenyl)- <i>N,N</i> -diphenylamine (28.9%)	2-(tributylstannyl)thiophene	3	3.46	5	2	13	26
<b>15</b>	2,2'-bithiophene (14.9%)	<i>N,N</i> -diphenylhydrazine chlorhydrate	3	6.71	6	2	16	33
<b>16</b>	diphenylamine (65.5%)	2-bromothiophene	3	1.53	7	3	18	21
<b>17</b>	2-iodothiophene (37.4%)	4-(diethylamino)benzaldehyde	2	2.67	4	2	6	20

a) Reciprocal Yields (*RY*) have been calculated as the reciprocal of the average of the yields of the final products from the key starting materials multiplied by 100. b) The relevant H-risk phrases (according to CLP Regulation 1272/2008/EC) considered for the computation of *NHC* are H200, H201, H202, H203, H204, H205, H220, H222, H224, H240, H241, H250, H260, H261, H271, H290, H300, H304, H310, H314, H318, H330, H340, H341, H350, H351, H360, H361, H370, H372, H400, H410, H411; a compound is counted as many times as the respective H phrases; chemicals used in the isolation/purification treatments have not been considered. c) The normalization of the synthetic parameters has been made using the following maximum values:  $NSS_{max}=18$ ;  $RY_{max}=12.7$ ;  $NUO_{max}=28$ ;  $NCC_{max}=9$ ;  $NHC_{max}=69$



Oligothiophenes (nTs) form an important class of organic semiconductors that have been widely investigated for almost three decades.<sup>61,62</sup> Sakai *et al.* have reported a *PCE* of 1.50% for a 4 mm<sup>2</sup> multi-layer device based on sexithiophene and C<sub>60</sub> with an exciton blocking layer.<sup>63</sup> Bäuerle *et al.* have extensively investigated the structure-properties relationships on various series of nTs end-capped by dicyanovinyl (DCV) electron-withdrawing groups.<sup>31,64,65</sup> Detailed crystallographic studies have been used to investigate the effects of the length of the conjugated system and of the number and position of alkyl substituents on the nT chain on the molecular packing of the material and on the performances of the resulting OPV cells. These materials have been implemented in rather complex multi-layer devices involving several interfacial layers that renders difficult a direct correlation between the chemical structure of the donor and *PCE*. For example the DCV end-capped quinquethiophene **7** gives a *PCE* of 2.60 % in a five-layer cell of 3 mm<sup>2</sup> active area and a value of 5.20 % for a seven-layer device.<sup>64</sup> Until now, the highest *PCE* reported for an oligothiophene donor (6.90%) has been obtained with a seven-layer cell of 6.6 mm<sup>2</sup> based on the dimethyl quinquethiophene **9** and C<sub>60</sub> as the acceptor material.<sup>65</sup> Compound **9** presents a SC index of 36, much lower than the large molecules **1-5**.

A *PCE* of 1.20% has been reported for a 3 mm<sup>2</sup> multi-layer cell based on the DCV end-capped quaterthiophene **6**.<sup>64</sup> However, a simple bilayer cell of 28 mm<sup>2</sup> with C<sub>60</sub> as the acceptor gave a *PCE* of only 0.50%.<sup>66</sup> Under the same conditions the bridged parent system **8** gives a *PCE* of 2.50 % which can be further improved to 4.30% for a cell of same dimensions with an intermediate co-evaporated layer of **8** and C<sub>60</sub>.<sup>66</sup> The bridging of the median bithiophene group is thus very effective for optimizing the efficiency of the material. However, this approach has a cost in terms of synthetic complexity with SC increasing from 36 for the dimethyl compound **9** to 40 for the bridged system **8**. However, it should be underlined that donor **9** was purified by gradient zone sublimation,<sup>65</sup> which of course can significantly impact the effective cost of the material.

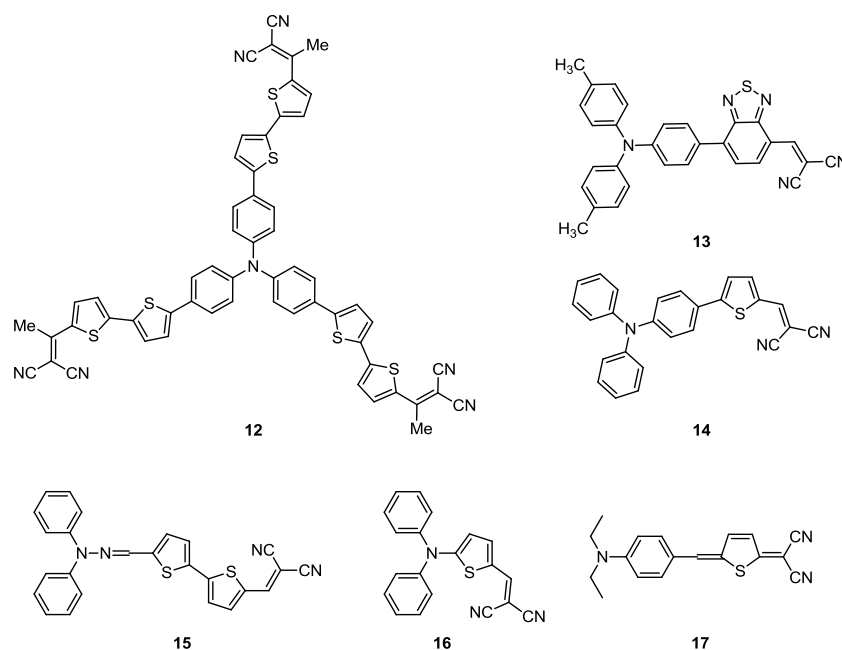


Squaraine dyes are synthesized by connecting two electron-donating groups to the strong electron acceptor squaric unit to produce D-A-D architectures with significant internal charge transfer.<sup>67</sup> Squaraines generally absorb in the visible or NIR region with very high molar extinction coefficients and excellent photo-stability. Already used in early work on OPV cells,<sup>68</sup> squaraines have recently received a renewed interest as donor materials for both vacuum-deposited and solution-processed OPV cells.<sup>69-72</sup> The highest *PCE* of 5.70 % has been reported for a 0.79 mm<sup>2</sup> cell involving vacuum deposited 2,4-bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl]squaraine (**10**), C<sub>60</sub> as the acceptor and a BCP buffer layer.<sup>72</sup> Although until now cells based on squaraine donors have led to moderate *PCE*, the relative simplicity of the synthesis represents a major advantage. Thus compound **10** is obtained in only three steps and requires only one column chromatography leading to a low SC index value of 20.

Merocyanines also belong to the first generation of active OPV materials.<sup>68</sup> These compounds have been recently revisited by Würthner, Meerholz *et al* who developed several series of these dyes.<sup>73,74</sup> Until now the best results have been obtained with a 8 mm<sup>2</sup> cell based on a co-evaporated active layer of compound **11** and C<sub>60</sub> on an ITO electrode modified by MoO<sub>3</sub> and an exciton blocking layer of BPhen. The best device gave a *J<sub>sc</sub>* of 12.40 mA cm<sup>-2</sup>, a *V<sub>oc</sub>* of 0.962 V and a *PCE* of 6.10%.<sup>74</sup> This compound thus provides another example of interesting trade-off between *PCE* and synthetic accessibility with a SC index of 25.

Materials based on triphenylamine (TPA) form an important class of OPV donors.<sup>27-33,75-79</sup> These compounds can be roughly divided into two main categories namely star-shaped molecules and push-pull systems. Star-shaped molecules based on triphenylamine were first proposed as molecular donors for solution-processed OPV cells ten years ago.<sup>27</sup> This seminal

paper has been followed by extensive synthetic work focused on the modulation of the size and composition of the conjugated branches.<sup>28-32,75-79</sup> Compound **12** taken as a representative example of this class of molecule has been used as donor in BHJ cells with a *PCE* close to 4.80 % with PC<sub>71</sub>M as the acceptor.<sup>79</sup> This compound presents a SC index of 49, intermediate between the extended systems **1-5** and the smaller molecules discussed below.



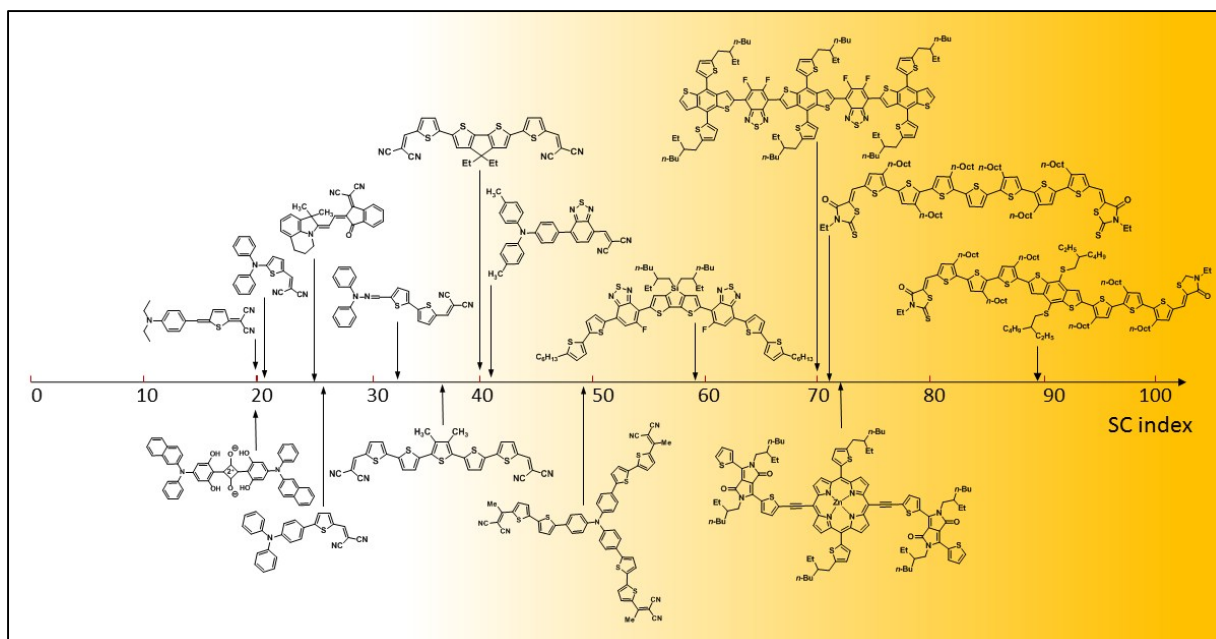
A more recent approach consists in the synthesis of smaller push-pull compounds in which a triarylamine donor block is connected to an electron acceptor group through a short conjugating spacer.<sup>33,80-84</sup> Wong *et al.* have synthesized D-A-A donors by connecting a triarylamine donor block to benzothiadiazole and DCV acceptor (**13**). A *PCE* of 6.80 % has been reported for a 2.5 mm<sup>2</sup> co-evaporated single junction cell with C<sub>70</sub> as the acceptor and MoO<sub>3</sub> and BCP as hole and electron transporting layers respectively.<sup>80</sup> With a SC index of 41, this compound also represents an interesting trade-off between efficiency and synthetic accessibility. Reducing the size of compound **13** to the shorter system **14** results in a decrease of SC to 26. Compound **14** gives a *PCE* of 2.53 % in a simple bi-layer cell with C<sub>60</sub> as the acceptor while a value of 4.00 % was obtained with a 0.28 cm<sup>2</sup> cell with a co-evaporated layer of donor and C<sub>60</sub>.<sup>81,82</sup> Compound **15** and the parent systems were synthesized in order to combine structural simplicity and clean chemistry.<sup>37</sup> In fact, the synthesis of these compounds obtained by basic condensation of aromatic dialdehydes with diphenylhydrazine generates only water as by-product. A *PCE* of 3.30% was obtained with a bilayer cell with C<sub>60</sub> as the acceptor. Based on the large increase of *PCE* obtained by optimization of the cells based on compound

**14**, this first result suggests that there is still much room for progression. However, in spite of cleaner chemistry the passage from **14** to **15** leads to an increase of the SC index from 26 to 33. Compound **16** and other ultra-small analogues based on a simple triarylamine donor block and a dicyanovinyl acceptor group have been synthesized in order to explore the limit of size reduction still compatible with the production of significant photovoltaic performances.<sup>83</sup>

This type of molecule presents a SC index as low as 21, however, the short conjugation length limits the absorption range to relatively short wavelengths ( $\lambda_{\max} = 475$  nm). Nevertheless, a PHJ cell of 28 mm<sup>2</sup> involving a spin-cast film of donor **16** and vacuum deposited C<sub>60</sub> gives a  $J_{sc}$  of 5.40 mA cm<sup>-2</sup> and a *PCE* close to 2.00 %.<sup>83</sup> Very recently Su *et al* reported that the small thienoquinoidal dye **17** leads to a *PCE* of 5.12% in a 6 mm<sup>2</sup> BHJ cell with PC<sub>71</sub>BM as the electron acceptor and a Ca/Al cathode.<sup>84</sup> This molecule combines the smallest molecular weight and the lowest SC index of all compounds discussed in this article thus underlining the interesting synthetic perspectives still opened in the search of simplified molecular OPV donors.

Fig. 1 summarize the SC index of the various compounds discussed in this article. As could be intuitively anticipated, there is a clear correlation between the size of the donor molecule and the SC index. Molecules on the left side present the best possibilities of scaling up whereas those of the right side would appear difficult to scale up at reasonable cost. On the other hand the highest reported *PCE* are mostly obtained with these more complex molecules. Although the difference of *PCE* should be relativised and considered at the light of the various relevant factors (size, acceptor, metal cathode etc.) the general trend is obvious. This clearly underlines the need to operate choices and define trade-off between optimal efficiency and SC index.

A direct comparison of the synthetic complexity of the dyes discussed in this short survey with low band gap polymers,<sup>25</sup> is not possible because the set of normalization parameters used in the calculations is different (see Table 1, note c). However, by applying the normalization parameters of ref. 20 to the present analysis, the SC values would be 20-30% lower. The corrected values demonstrate that, on average, small molecules have potentially a lower cost than polymers which brings further support for the choice of molecular donors.



**Fig. 1.** Synthetic complexity index of some representative examples of molecular donors for OPV cells

However it should be clear that this choice only suggests a general direction for further molecular engineering. In spite of their potential advantages, these smaller and simpler systems still pose several problems that will need an intensification of research effort. For example the hole-mobility is in general low and must be improved in order to increase both the short-circuit current density and fill factor of the OPV cells. On the other hand, further structural manipulation of the open-circuit voltage are still possible and desirable. Before all, some of these possible working structures present insufficient photothermal stability which will also represent a major criterion of selection. In fact a complete analysis of the cost of active materials should also include an index related to the photothermal stability of the materials. Unfortunately such stability data recorded in standard conditions are not available so far.

### Conclusions and perspectives

Despite several obvious major potential advantages in terms of cost, weight, plasticity, tunability, and environmental impact, OPV cells have not reached the stage of industrial production yet. Intense research effort focused on the optimization of device technology and on design of new active materials has led to efficiencies which now surpass that of amorphous silicon, at least on cells of very small active area. However, excessively optimistic communication, exclusive focus on *PCE* and insufficient consideration of critical issues such as cost, stability, scalability, processability over large areas or environmental impact has generated some doubt about the possible industrial future of OPV.

Nevertheless, the potential of OPV for large scale production in areas such as printed electronics or packaging is still there while competition with silicon remains an exciting long term objective which can be the source of important progress in the field of organic electronics in general. Although the replacement of polymers by molecules has represented a first step towards simplification and reduction of the cost of OPV materials, further effort in this direction is needed. In this context the molecular engineering of donor materials, non-fullerene acceptors,<sup>85,86</sup> or D-A systems for single-material OPV<sup>87</sup> that combine decent conversion efficiency, stability, scalability and acceptable cost appears as priority challenges for organic chemists interested in the design of OPV materials and more generally of organic semiconductors. As shown by some of the above discussed examples some materials that represent an interesting trade-off between efficiency and synthetic accessibility have already been reported and it is hoped that this short survey can contribute to stimulate an intensification of research effort in these directions.

## References

1. C.K. Chiang, Y.W. Park, A.J. Heeger, H. Shirakawa, E. Louis, A. G. Mc Diarmid, *Phys. Rev. Lett.* **1977**, 39, 1098.
2. *Handbook of Conductive Polymers*, 1<sup>st</sup> Edition, Ed. T. Skotheim, Marcel Dekker, 1986; 2<sup>nd</sup> Edition, Ed. J. Reynolds, T. Skotheim, R. Elsenbaumer, Marcel Dekker, 1997; Inc.; 3<sup>rd</sup> Ed, T. Skotheim, J. Reynolds, CRC Press 2007.
3. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, R.H. Friend, P.L. Burns, A.B. Holmes, *Nature*, **1990**, 347, 539.
4. F. Garnier, *Acc. Chem. Res.* **1999**, 32, 209.
5. C.D. Dimitrakopoulos, P. Malenfant, *Adv. Mater.* **2002**, 14, 99.
6. C. J. Brabec, N. S. Sariciftci and J. C. Hummelen, *Adv. Funct. Mater.* **2001**, 11, 15.
7. P. Peumans, A. Yakimov, S.R. Forrest, *J. Appl. Phys.* **2003**, 93, 3693.
8. Z. He, B. Xiao, F. Liu, Ho. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell, Y. Cao, *Nature Photonics* **2015**, 174.
9. H. Hu, K. Jiang, G. Yang, J. Liu, Z. Li, H. Lin, Y. Liu, J. Zhao, J. Zhang, F. Huang, Y. Qu, W. Ma, H. Yan, *J. Am. Chem. Soc.* **2015**, 137, 14149.
10. C.W. Tang, *Appl. Phys. Lett.* **1986**, 48, 183.
11. G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science*, **1995**, 270, 1789.

12. J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, *Nature*, **1995**, 376, 498.
13. S. Günes, H. Neugebauer, N.S. Sariciftci, *Chem. Rev.* **2007**, 107, 1324.
14. C.J. Brabec, U. Scherf, V. Dyakonov, *Organic Photovoltaics*. John Wiley & Sons, 2014.
15. Y.-J. Cheng, S.H. Yang, C.-S. Hsu, *Chem. Rev.* **2009**, 109, 5868.
16. Y. Liang, L. Yu, *Acc. Chem. Res.* **2010**, 43, 1227.
17. M. Jayakannan, J.L.J. van Dongen, R.A.J. Janssen, *Macromolecules*, **2001**, 34, 5386.
18. R. Yang, R. Tian, J. Yan, Y. Zhang, J. Yang, Q. Hou, W. Yang, C. Zhang, Y. Cao, *Macromolecules* **2005**, 38, 244.
19. N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.* **2008**, 130, 732.
20. Q. Wang, B. Zhang, L. Liu, Y. Chen, Y. Qu, X. Zhang, J. Yang, Z. Xie, Y. Geng, L. Wang, F. Wang, *J. Phys. Chem. C.* **2012**, 116, 21727.
21. O. Usler, M. Abbas, G. Wantz, L. Vignau, L. Hirsh, E. Grana, C. Brochon, E. Cloutet, G. Hadziioannou, *ACS Macro Lett.* **2014**, 3, 1134.
22. C. Bracher, H. Yi, N.W. Scarratt, R. Masters, A. J. Pearson, C. Rodenburg, A. Iraqi, D. G. Lidzey, *Organic Electronics*, **2015**, 27, 266.
23. D.J. Burke, D.J. Lipomi, *Energy Environ. Sci.* **2013**, 6, 2053.
24. T.P. Osedach, T.L. Andrew, V. Bulovic, *Energy Environ. Sci.* **2013**, 6, 711.
25. R. Po, G. Bianchi, C. Carbonera, A. Pellegrino, *Macromolecules*, **2015**, 48, 453.
26. S. Roquet, R. Bettignies, P. Leriche, J. Roncali, *J. Mater. Chem.* **2006**, 16, 3040.
27. S. Roquet, A. Cravino, P. Leriche, A. Alévêque, P. Frère, J. Roncali, *J. Am. Chem. Soc.* **2006**, 128, 3459.
28. J. Roncali, *Acc. Chem. Res.* **2009**, 42, 1719.
29. Y. Li, Q. Guo, Z. Li, J. Pei, W. Tian, *Energy & Environmental Science*, **2010**, 3, 1427.
30. B. Walker, C. Kim, T.-Q. Nguyen, *Chem. Mater.* **2011**, 23, 470.
31. A. Mishra, P. Bäuerle, *Angew. Chem. Int. Ed.* **2012**, 51, 2020.
32. Y. Lin, Y. Li, X. Zhan, *Chem. Soc Rev.* **2012**, 41, 4245.
33. J. Roncali, P. Leriche, P. Blanchard, *Adv. Mater.* **2014**, 26, 3821.
34. B. Kan, Q. Zhang, M. Li, X. Wan, W. Ni, G. Long, Y. Wang, X. Yang, H. Feng and Y. Chen, *J. Am. Chem. Soc.* **2014**, 136, 15529.
35. F. Krebs, M. Jørgensen, *Solar Energy Mater. & Solar Cells* **2013**, 119, 73.

36. P.-T. Tsai, C.-Y. Tsai, C.-M. Wang, Y.-F. Chang, H.-F. Meng, Z.-K. Chen, H.-W. Lin, H.-W. Zan, S.-F. Horng, Y.-C. Lai, P. Yu, *Organic Electronics* **2014**, 15, 893.
37. A. Diac, D. Demeter, M. Allain, I. Grosu, J. Roncali, *Chem. Eur. J.* **2015**, 21, 1598.
38. A. Cravino, P. Schilinsky, C.J. Brabec, *Adv. Funct. Mater.* **2007**, 17, 3906.
39. A.K. Pandey, J.M. Nunzi, B. Ratier, A. Moliton, *Physics Lett A*, **2008**, 372, 1333.
40. W.-I. Jeong, J. Lee, S.-Y. Park, J.-W. Kang, J.-J. Kim, *Adv. Funct. Mater.* **2011**, 21, 343.
41. D. Gao, D. S. Seferos, *Solar Energy Materials & Solar Cells* **2011**, 95, 3516.
42. Y. He, G. Zhao, B. Peng, Y. Li, *Adv. Funct. Mater.* **2010**, 20, 3383.
43. X. Fan, C. Cui, G. Fang, J. Wang, S. Li, F. Cheng, H. Long, Y. Li, *Adv. Funct. Mater.* **2012**, 22, 585.
44. M. Zhang, H. Wang, H. Tian, Y. Geng, C. Tang, *Adv. Mater.* **2011**, 23, 4960.
45. R. Steim, F.R. Kogler, C.J. Brabec, *J. Mater. Chem.* **2010**, 20, 2499.
46. F. Huang, H.B. Wu, Y. Cao, *Chem. Soc. Rev.* **2010**, 39, 2500.
47. C.K. Song, A.C. White, L.Zeng, B.J. Leever, M.D. Clark, J. D. Emery, S.J. Lou, A. Timalina, L.X. Chen, M. Bedzyk, T.J. Marks, *ACS Appl. Mater. Interfaces* **2013**, 5, 9224.
48. J.K. Lee, W.L. Ma, C.J. Brabec, J. Yuen, J.S. Moon, K. Lee, G.C. Bazan, A.J. Heeger, *J. Am. Chem. Soc.* **2008**, 130, 3619.
49. N. Camaioni, G. Ridolfi, G. Casalbore-Miceli, M. Maggini, *Adv. Mater.* **2002**, 14, 1735.
50. V. Gupta, A. K. K. Kyaw, D. H. Wang, S. Chand, G. C. Bazan and A. J. Heeger, *Sci. Rep.*, **2013**, 3, 1965.
51. J.E. Coughlin, Z.B. Henson, G.C. Welch, G. Bazan, *Acc. Chem. Res.* **2014**, 47, 257.
52. Y. Sun, G.C. Welch, W.L. Leong, C.J. Takacs, G. Bazan, A.J. Heeger, *Nature Mater.* **2012**, 11, 44.
53. A. K. K. Kyaw, D. H. Wang, V. Gupta, J. Zhang, S. Chand, G.C. Bazan, A.J. Heeger, *Adv. Mater.* **2013**, 25, 2397.
54. W.L. Leong, G.C. Welch, L. Kaake, C.J. Takacs, Y. Sun, G.C. Bazan, A.J. Heeger, *Chemical Science*, **2012**, 3, 2103.
55. Y. Chen, X. Wan, G. Long, *Acc. Chem. Res.* **2013**, 46, 2645.
56. Q. Zhang, B. Kan, F. Liu, G. Long, X. Wan, X. Chen, Y. Zuo, W. Ni, H. Zhang, M. Li, Z. Hu, F. Huang, Y. Cao, Z. Liang, M. Zhang, T.P. Russel, Y. Chen, *Nature Photonics*, **2015**, 9, 35.



57. C. Zhou, Y. Liang, F. Liu, C. Sun, X. Huang, Z. Xie, F. Huang, J. Roncali, T. Russell, Y. Cao. *Adv. Funct. Mater.* **2014**, 24, 7538.
58. L. Yuan, Y. Zhao, J. Zhang, Y. Zhang, L. Zhu, L. Lu, W. Yan, Z. Wei, *Adv. Mater.* **2015**, 27, 4229.
59. H. Qin, L. Li, F. Guo, S. Su, J. Peng, Y. Cao, X. Peng, *Energy Environ. Sci.* **2014**, 7, 1397.
60. K. Gao, L. Li, T. Lai, L. Xiao, Y. Huang, F. Huang, J. Peng, Y. Cao, F. Liu, T.P. Russel, R.A.J. Janssen, X. Peng. *J. Am. Chem. Soc.* **2015**, 137, 7282.
61. J. Roncali, *Chem. Rev.* **1992**, 92, 711.
62. A. Mishra, C.-Q. Ma, P. Bäuerle, *Chem. Rev.* **2009**, 109, 1141.
63. J. Sakai, T. Taima, K. Saito, *Organic electronics*, **2008**, 9, 582.
64. R. Fitzner, E. Reinold, A. Mishra, E. Mena-Osteritz, H. Ziehlke, C. Körner, K. Leo, M. Riede, M. Weil, O. Tsaryova, A. Weiss, C. Urich, M. Pfeiffer, P. Bäuerle, *Adv. Funct. Mater.* **2011**, 21, 897.
65. R. Fitzner, E. Mena-Osteritz, A. Mishra, G. Schulz, E. Reinold, M. Weil, C. Körner, H. Ziehlke, C. Elschner, K. Leo, M. Riede, M. Pfeiffer, C. Ulrich, P. Bäuerle, *J. Am. Chem. Soc.* **2012**, 134, 11064.
66. F. Baert, C. Cabanetos, A. Leliège, E. Kirchner, O. Segut, O. Alévêque, M. Allain, G. Seo, S. Jung, D. Tondelier, B. Geffroy, J. Roncali, P. Leriche, P. Blanchard, *J. Mater. Chem. C.* **2015**, 3, 390.
67. S. Sreejith, P. Carol, P. Chithra, A.J. Ajayaghosh, *J. Mater. Chem.* **2008**, 18, 264.
68. G.A. Chamberlain, *Solar Cells*, **1983**, 8, 47.
69. U. Mayerhöffer, K. Deing, K. Gruss, H. Branschweig, K. Meerholz, F. Würthner, *Angew. Chem. Int. Ed.* **2009**, 48, 8776.
70. G. Wei, S. Wang, K. Sun, M.E. Thompson, S.R. Forrest, *Adv. Energy Mater.* **2011**, 1, 184.
71. L. Beverina, M. Dress, A. Fchetti, M. Salamone, R. Ruffo, G.A. Pagani, *Eur. J. Org. Chem.* **2011**, 5555.
72. G. Wei, X. Xiao, J.D. Zimmerman, K. Sun, V.V. Diev, M.E. Thompson, S.R. Forrest, *Nano Lett.* **2011**, 11, 4261.
73. H. Bürckstümmer, E.V. Tulyakova, M. Deppish, M.R. Lenze, N.M. Kronenberg, M. Gsänger, M. Stolte, K. Meerholz, F. Würthner. *Angew. Chem. Int. Ed.* **2011**, 50, 11628.
74. V. Steinmann, N.M. Kronenberg, M.R. Lenze, S.M. Graf, D. Hertel, K. Meerholz, H. Bürckstümmer, E.V. Tulyakova, F. Würthner. *Adv. Energy Mater.* **2011**, 1, 888.

75. J. Zhang, D. Deng, C. He, Y. He, M. Zhang, Z.-G. Zhang, Z. Zhang, Y. Li, *Chem. Mater.* **2011**, 23, 817.
76. E. Ripaud, T. Rousseau, P. Leriche, J. Roncali, *Adv. Energy Mater.* **2011**, 1, 540.
77. Y. N. Luponosov, A. N. Solodukhin and S. A. Ponomarenko, *Polym. Sci., Ser. C*, **2014**, 56, 104.
78. V. Malytskyi, J.-J. Simon, L. Patrone, J.-M. Raimundo, *RSC Advances*, **2015**, 5, 354.
79. J. Min , Y. N. Luponosov , A. Gerl , M. S. Polinskaya ,S. M. Peregudova , P. V. Dmitryakov, A. V. Bakirov, M. A. Shcherbina, S. N. Chvalun, S. Grigorian, N. Kaush-Busies, S.A. Ponomarenko,T. Ameri, C. J. Brabec , *Adv. Energy Mater.* **2014**, 4, 1301234.
80. Y.-H. Chen, L.-Y. Lin, C.-W. Lu, F. Lin, Z.-Y. Huang, H.-W. Lin, P.-H. Wang, Y.-H. Liu, K.-T. Wong, J. Wen, D. J. Miller, S. B. Darling, *J. Am. Chem. Soc.* **2012**, 134, 13616.
81. A. Leliège, C-H. Le Régent, M. Allain, P. Blanchard, J. Roncali, *Chem Commun.* **2012**, 48, 8907.
82. J.W Choi C.H. Kim, J. Pison, A. Oyedele, H. Derbal-Habak, D. Tondelier, A. Leliège, E. Kirchner, P. Blanchard, J. Roncali, B. Geffroy, *RSC Advances*, **2014**, 4, 5236.
83. V. Jeux, D. Demeter, P. Leriche, J. Roncali, *RSC. Adv.* **2013**, 3, 5811.
84. M.-J. Su, J.-H. Huang, L.-P. Zhang, Q.-Q. Zhang, C.-L. Zhan, X.-Q. Zhou, L.-M. Yang, Y. Song, K.-J. Jiang, *RSC Adv.* **2015**, 5, 76666.
85. A. Eftaiha, J.-P. Sun, I.G. Hill, G.C. Welch, *J. Mater. Chem. A* **2014**, 2, 1201.
86. Y.L. Lin, X. Zhan, *Materials Horizons* **2014**, 1, 470.
87. J. Roncali, *Adv. Energy Mater.* **2011**, 1, 147.



The preparation of various molecules taken as representative examples of some of the main classes of molecular donors for organic solar cells is discussed in order to assess the complexity and possibilities of scaling-up of their synthesis.

