Identifying potential candidates for donor–acceptor copolymers on a series of 4H-1,2,6-thiadiazines: An electrochemical approach

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ARTICLE INFO

ABSTRACT

A series of synthesized small organic molecules based on the 4H-1,2,6-thiadiazine moiety are studied using electrochemistry, to probe their potential as comonomer building blocks for solar-absorbing polymers for organic solar cells. This is the first instance of an electrochemical report for this family of heterocycles. Structure–physical property relationships are identified that can guide future synthetic efforts. Parameters that can influence the properties of the final copolymer such as the choice of electron donor comonomer and the energy level of the fullerene adduct acceptor are factored-in and discussed and the thiadiazines that can meet the requirements are singled-out.

1. Introduction

Material science, although a fairly new standalone branch, encompasses many traits from parent scientific fields such as chemistry, physics, mechanical engineering and electrical engineering. The quest for novel materials is more intense than ever before as the ideas for practical applications and devices require an increasing pool of readily available materials and substances. Apart from novel materials with interesting properties, that are being discovered from time to time, such as carbon nanostructures [1–4] and boron-nitride tubes [5] the bulk of the scientific effort for new materials stems from chemical tailoring and the modification of existing properties. It has been shown that such chemical tailoring can be very efficient and there are examples where relatively small chemical variations result in new or largely modified material properties [6,7].

The area of organic electronics and polymer:fullerene photovoltaic cells, in particular, is a field with rapid advancements during the last decade. Along with considerable progress in the device design, geometry and fabrication i.e., the demonstration of state-of-the-art inverted [8–10] and tandem [11–13] solar cells and advances in the understanding of fundamental properties of existing reference systems [14], new materials are being synthesized at an unprecedented rate. To effectively guide the synthetic efforts for novel polymers as light absorbers, several publications have emerged qualitatively laying down some fundamental rules for the design and synthesis of new copolymers [15–17]. The state of the art today in light harvesting p-type polymers is dominated by copolymers based on the donor–acceptor "push–pull" synthetic approach. The bulk of the copolymers synthesized, are predominantly based on such moieties as cyclopentadithiophene [18], and its Si [19] or Ge [20,21] derivatives, fluorene [22,23], carbazole [24,25], and benzodithiophene [9,26–32]. These moieties are not only suitable for donor-type comonomers but are also common building blocks for highly efficient soluble small-molecule based photovoltaic devices [33,34].

Compounds based on the 1,2,6-thiadiazine moiety have been employed in medicinal [35], material [36] and agrochemical [37] science. Polymers incorporating the moiety remain largely unexplored although possibilities of interesting properties stemming from such an approach were hinted by Woodward [38].

Due to its electron withdrawing character the 1,2,6-thiadiazine moiety is more suitable as a "pull-molecule" in low-bandgap copolymers. As such, this study focuses on the structural–physical property relationships of the thiadiazines examined using electrochemistry, with a view of identifying prime candidate materials for copolymerization with the various "push-molecules" currently used by synthetic chemists. Moreover the role of alkyl chains on enhancing the molecules solubility is discussed as they affect

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critically the blending of the materials, with established electron donors and acceptors. Several papers exist in the literature dealing with the fine-tuning of the side chains in polymers influencing processing conditions (mixed solvents), optoelectronic properties and ultimately improved morphology and power conversion efficiencies in the resulting solar cells [30,39,40]. Side chains can be fine-tuned either on the donor comonomer or on the acceptor. Although not of extreme importance when studying the bulk physicochemical properties of these materials, these considerations should be taken into account when solidifying the selection of the materials either as standalone soluble small molecules or building blocks for copolymers.

2. Experimental

2.1. Instrumentation

Electrochemical studies were performed using a standard three-electrode cell under argon atmosphere. All measurements were performed with Ar bubbling into the electrochemical cell for 5 min and 10 s prior to measurements; the Ar was turned to "blanket-mode". Platinum wire (99.99%) was used as working electrode and platinum gauze (55 mesh, 99.9%) as counter electrode. Silver/silver chloride was used as a reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$, 98%) was used as supporting electrolyte. Measurements were recorded using an EG&G Princeton Applied Research potensiostat/galvanostat Model Verstastat 4 connected to a personal computer running VersaStudio software. In all the measurements, either during cyclic voltammetry or in differential pulse voltammetry, the variation of the scan rate did not yield any appreciable shifting of the peak potentials that would affect our results. All samples were studied in dichloromethane (DCM) solution and the results were calibrated using ferrocene as internal standard. To calculate the higher occupied molecular orbital (HOMO) and lower unoccupied molecular orbital (LUMO) levels,

using the onsets of the peak potentials obtained, the following equations [41] were used.

$$E_{HOMO} = -\left(Eox\left[vs\frac{Fc}{Fc^+} \right] + 5.1 \right) (eV)$$

$$E_{LUMO} = -\left(Ered\left[vs\frac{Fc}{Fc^+} \right] + 5.1 \right) (eV)$$
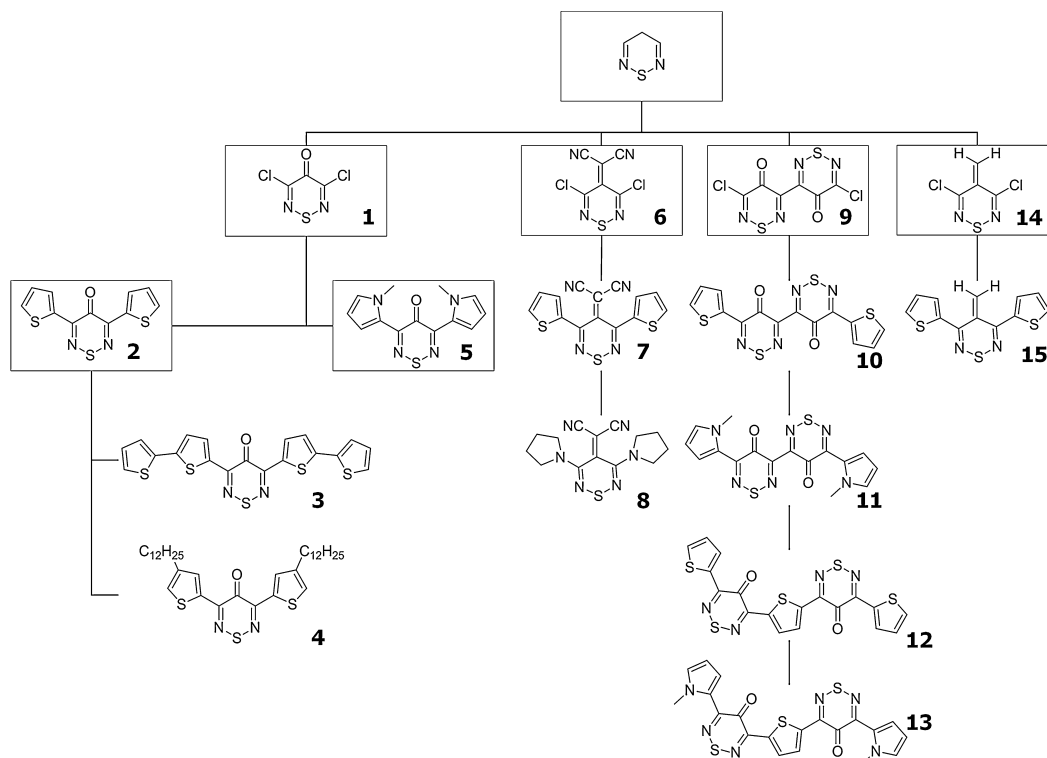
2.2. Materials

All the reagents were purchased from Aldrich SA. CH$_2$Cl$_2$ was dried before electrochemistry measurements, ferrocene was purified through sublimation and the supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was recrystallized from acetone 3 times and dried in vacuum at 100 °C before each experiment.

All the thiadiazine compounds discussed in this publication have been synthesized according to literature procedures [42–50] and characterized using ^{1}H and ^{13}C NMR, to ascertain the purity of the synthesized materials.

3. Results and discussion

3.1. Electrochemistry

The thiadiazines examined are summarized in Scheme 1, their optical and electrochemical data are depicted in Table 1 and all the voltammograms of the materials studied, obtained either through cyclic voltammetry or differential pulse voltammetry are included as Supporting Information. All the thiadiazines were studied in dichloromethane solution (0.1 M TBAPF$_6$ as supporting electrolyte). To the best of our knowledge this family of molecules has never been probed using electrochemistry.

Scheme 1. Structures of the studied thiadiazine-based compounds.

Table 1
Optical and electrochemical characteristics of the studied thiadiazines in solution. Where available, the $E_{1/2}$ redox potentials of the compounds are mentioned. If not, the peak maxima are mentioned. Values with a * denote that the energy levels have been obtained by adding the LUMO level from the optical bandgap.

Thiadiazine compounds	λ_{max}^{sol} (nm)	E_g^{opt} (eV)	E^{ox} (V)	E_{HOMO} (eV)	E^{red} (V)	E_{LUMO} (eV)	$E_g^{echem.}$ (eV)
1	325	3.57	1.30	6.22	−1.52	3.66	2.56
2	261, 403, 431	2.75	1.11	6.11	−1.76	3.42	2.69
3	292, 479	2.30	0.61	5.76	−1.64	3.53	2.23
4	265, 415, 440	2.69	0.97, 1.25	6.02	−1.78	3.38	2.64
5	261, 376, 436	2.62	0.58	5.70	−1.89	3.25	2.45
6	232, 381, 412	2.81	–	7.19*	−0.78	4.38	–
7	281, 426, 475	2.32	1.23	6.24	−1.14	4.01	2.23
8	231, 321, 592	1.84	0.29	5.29	−1.31	3.89	1.40
9	320	3.31	–	7.27*	−1.24	3.96	–
10	271, 381	2.70	–	6.49*	−1.41	3.79	–
11	281, 380, 400	2.54	0.74	5.95	−1.70	3.40	2.55
12	268, 385, 475, 504	2.29	–	6.02*	−1.41	3.73	–
13	270, 412, 492, 518	2.24	0.74	5.79	−1.61	3.66	2.13
14	230, 308	3.79	1.37	6.32	−2.17	3.07	3.25
15	277, 354, 431	2.47	0.76, 1.56	5.80	−2.11	3.11	2.69

For ease of reading, the thiadiazines examined can be categorized into four families according to the substituents of the thiadiazine ring and the number of thiadiazine rings in the small molecule. The single-ring carbonyl substituted ones (thiadiazinones **1**–**5**), the dicyanomethylene-substituted ones (ylidenemalononitriles **6**–**8**), the ones incorporating two thiadiazinone rings (**9**–**13**), and finally, the methylene substituted thiadiazines (**14** and **15**).

Before continuing with the examination of these compounds the optical characteristics of these molecules are a useful aid that will allow potential matching of the optical and electrochemical bandgap of the molecules thus, providing additional confirmation on the accuracy of our measurements. The optical data, along with all the electrochemical data are summarized in Table 1. As a general remark, the electrochemical studies performed show excellent matching of the electrochemical and optical bandgaps, with very few exceptions.

Starting from the thiadiazinone **1** voltammogram (Scheme 1) we can clearly see a reversible reduction at −1.52 V and a non-reversible oxidation signal at 1.30 V. Upon examination of this "parent" molecule, the characteristic reversible reduction should provide a signature-type signal that will facilitate direct comparison with the other thiadiazine compounds.

Sandwiching the thiadiazinone moiety between two thiophenes affords thiadiazinone **2**. The substitution of chlorine by thiophene is expected to influence the oxidation of the molecule. A cathodic shift of almost 200 mV is observed for the oxidation along with an, approximately 240 mV, cathodic shift of the reversible reduction. Besides the shift, it is observed that, while in the parent thiadiazinone **1** there is a large discrepancy between the electrochemical and the optical energy bandgap values (the largest in this study), with the addition of the thiophene moiety, the two calculated bandgap values coincide rather well. Concerning the former we are unsure on the origin of the discrepancy between the optical and electrochemical bandgap for parent molecule **1**. In our case, a critical factor would be the method of pinpointing the optical bandgap which can be estimated through photoelectrochemical spectra, whereas our estimation of the optical bandgap was based on the UV–vis absorption spectra. Given that the scope of this manuscript is not only to study this thiadiazine family from a strictly electrochemical standpoint but to extract trends useful for material scientists involved in polymer optoelectronics it is worth noting that the discrepancies between optically and electrochemically pinpointed energy bandgaps are still a matter of debate among the community [51]. In our case, the estimated optical bandgap of the aforementioned material **1**, is so large (<3.5 eV) that if this value is closer to the truth, the window within which we can confidently

run electrochemistry is exceeded, as one can easily deduce that with a reduction signal situated at −1.52 V a possible matching of the two bangap values, would place the oxidation of the monomer at around +2 V.

Adding a second thiophene moiety along the backbone of the small molecule, further increases the thiophene character of compound **3**. As expected, there is now a clear reversible oxidation at 0.61 V as well as the reversible reduction attributed to the thiadiazine moiety at −1.64 V.

Finally, the incorporation of the dodecyl substituted thiophenes, shifts the reversible reduction of the thiadiazine moiety towards more negative potentials, at −1.78 V, while two distinct oxidation peaks are observed at 0.97 and 1.25 V. While not directly comparable to standard alkyl substituted oligothiophenes, this multitude of oxidation peaks can be partly explained by the formation of multiple cations on the thiophene moiety [52,53]. However, the same behaviour is observed in non-substituted oligothiophene analogues [54]. In Fig. 1 the voltammograms of the 4 thiadiazines are presented for ease of comparison. It is worth outlining the comparison of the thiadiazines **2** and **4** where the presence of a flexible alkyl side chain (even in solution) on the thiophene moiety, causes significant alterations to the oxidation of the molecule facilitating the formation of the thiophene cation.

When replacing the thiophene moiety with *N*-methylpyrrole to give the thiadiazinone **5** (Figure S5), the reduction of the thiadiazine is cathodically shifted to −1.89 V while in the positive potential region, a reversible oxidation attributed to the pyrrole moiety is clearly evident at 0.58 V. These values provide an excellent agreement between the electrochemical and optical bandgap of compound **5**.

Moving on to the ylidenemalononitrile **6** (Figure S6) where the carboxyl substituent is replaced by the dicyanomethylene group, a profound shift of the reversible reduction is observed owed, presumably, to the introduction of the electronegative C≡N groups. The reversible reduction is anodically shifted by more than 700 mV, compared to the thiadiazinone **1**. We can calculate the LUMO of the ylidenemalononitrile **6** at 4.38 eV making it a highly electronegative molecule. When the chlorine substituents are replaced by thiophenes to give the ylidenemalononitrile **7** a sharp oxidation peak is present at 1.23 V (Figure S7) attributed to the thiophenes, since no signal is seen in this region on the parent ylidenemalononitrile **6**. The reversible reduction compared to the thiadiazinone **2**, again shows a profound shift of 620 mV towards positive potentials (−1.14 V for **7** *vs* −1.76 V) for thiadiazinone **2**. Finally, the introduction of pyrrolidine rings to the ylidenemalononitrile affords compound **8** with the lowest energy bandgap of this group. A reversible oxidation at 0.29 V and a reversible reduction at −1.31 V
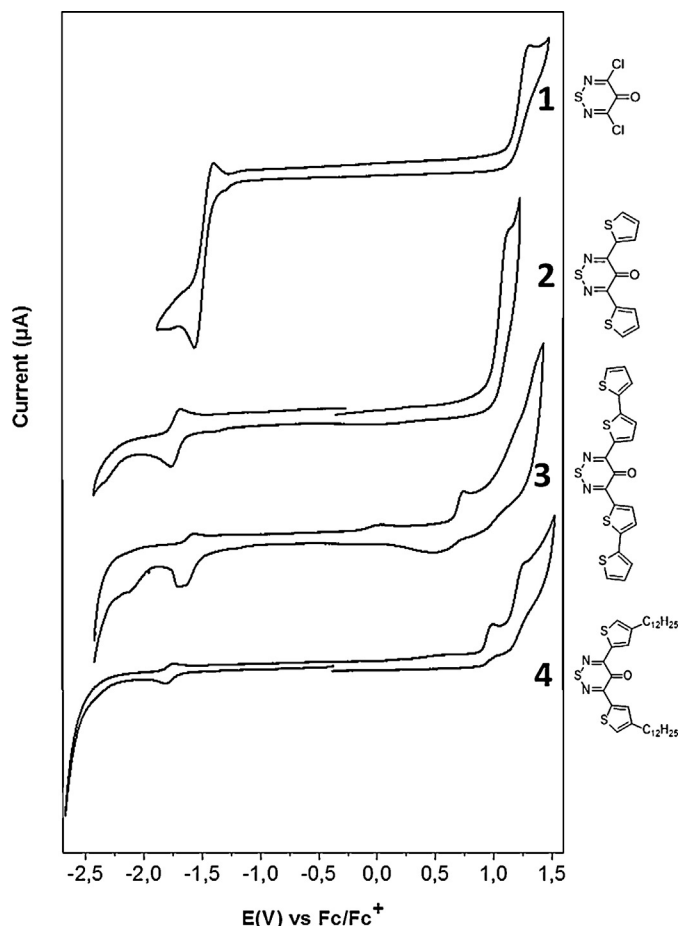
Fig. 1. Cyclic voltammograms of thiadiazine compounds **1**–**4**. The chemical structure of each one is shown on the right for ease of reference. All voltammograms were run in CH_2Cl_2 solution using 0.1 M TBAPF$_6$ as supporting electrolyte. Scan rate: 50 mV/s.

Fig. 2. Schematic representation of the evolution of the energy levels (HOMO/LUMO) of the thiadiazines with different substituents.

(Figure S8) yield an electrochemical bandgap of 1.40 eV. In a preliminary attempt to extract a structure–property relationship, it is clear that the pyrrole ring has a lower oxidation potential than thiophene. Even in small organic molecules it is possible to control the energy levels of the resulting system by combining a moiety with a low oxidation potential with a moiety with a low reduction potential, yielding a compound with strong absorption in the visible spectrum.

When examining systems with two thiadiazinone rings the expectation from the optical data is that the conjugation of the compound will increase but not considerably. The differential pulse voltammetry (DPV) data of **9** (Figure S9) show a reversible reduction at −1.24 V, while no oxidation process is observed. As is the case with previous thiadiazines, the fairly large optical bandgap (Table 1) of 3.31 eV for this molecule places the expected oxidation process at potentials of over +2 V, beyond the measuring window of our experimental process. The addition of a second thiadiazine ring yields an anodic shift of ∼300 mV compared to thiadiazinone **1** denoting that extending the thiadiazinone conjugation length facilitates reduction strengthening the electron accepting character of the produced material. Further addition of two thiophene rings, similar to **2**, causes a shift of the reversible reduction by more than 300 mV (Figure S10) compared to the compound with one thiadiazine ring. The pyrrole ring (**11**) causes a reversible oxidation to appear at 0.74 V but the reduction is shifted to more negative potentials at −1.70 V (Figure S11). Comparing the compounds **1**, **2**, and **5** to their double thiadiazine analogues **9**, **10** and **11**, respectively, we
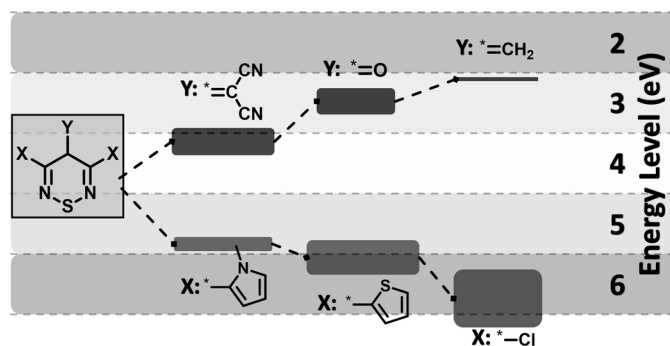
can see that there is a direct trend: In all the cases incorporation of an electron rich moiety such as thiophene or pyrrole, shifts the reduction by ∼200–350 mV to more negative potentials (*i.e.*, the compound becomes more difficult to reduce).

As we move to the more complex structure **12** where a thiophene is used as a "spacer" between the two thiadiazinones we see that the reversible reduction (Figure S12) is virtually unaffected compared to compound **10** which bears the closest resemblance. Roughly the same trend is followed when we compare compounds **11** and **13**, as the oxidation attributed to the pyrrole remains at 0.74 V (Figure S13) but much less pronounced and the reduction is observed slightly shifted, by ∼90 mV at −1.61 V, compared to **11**.

Finally the methylene substituted thiadiazines **14** (Figure S14) and **15** (Figure S15) show, in both instances, a considerably cathodically shifted reduction at −2.17 and −2.11 V, respectively. This represents a ∼700 mV cathodic shift of compound **14** compared to the thiadiazinone **1** and an almost 400 mV shift for **15** compared to compound **2**.

In Fig. 2, all the major trends, shifts and evolutions, discussed previously, for the HOMO and LUMO levels of the thiadiazine compounds, depending on the substituent, are schematically presented.

3.2. Energy levels of the compounds and their potential as building blocks

When discussing the option of utilizing these compounds either as standalone moieties or in conjunction with another comonomer for polymerization it is useful to point out the most prominent materials for these purposes. The bulk of the copolymers used for optoelectronics comprise of fluorene, carbazole, cyclopentadithiophene and benzodithiophene. There are a few prerequisites that lead to a high efficiency copolymer. The resulting polymer, must possess a broad absorption, ideally, covering most of the visible spectrum and extending to the near-IR [55], sufficiently high hole mobilities for efficient charge transport and appropriate levelling of energy states of donor, acceptor and electrode materials allowing for efficient charge separation and collection. According to the "push–pull" synthetic approach the orbital interaction between donor and acceptor units lowers the band gap of conjugated polymers by the creation of an intramolecular charge transfer state (ICT) [56,57]. The fluorene [58] and carbazole [59] moieties have relatively high optical bandgaps and HOMO/LUMO levels around the areas of 6.0 and 2.4 eV, respectively. Owing to this fact, they tend to produce low bandgap copolymers with low-lying HOMO levels. Cyclopentadithiophene [60] and benzodithiophene [61] moieties, generally tend to produce copolymers with slightly elevated ionization potentials, in the area of 5.0–5.5 eV.

Therefore when trying to screen for suitable comonomers for low bandgap polymers the LUMO levels of choice should be around

3–5 eV, while the HOMO levels should be located, depending on the chosen "donor comonomer" below 5.5 or, ideally, 6.0 eV.

All of the studied thiadiazines, match well with the "LUMO-limitation" of below 3.0 eV, but only a handful of compounds have sufficiently low HOMO levels to allow for a D–A copolymerization approach.

Specifically compounds **1**, **2**, **4**, **6**, **7**, **9**, **10**, **12** and **14** have reported HOMO levels below 6.0 eV. Compound **14**, however has a relatively high LUMO, so it may not be suitable as a potential candidate for copolymerization. Of the remaining six compounds, thiadiazines **6**, **7** and possibly **10** and **12**, have a relatively low LUMO level around 4 ± 0.3 eV, so assuming that the D–A approach is successful, the resulting copolymer is expected to have an electron affinity of the same order. In light of this, when we take into account exciton binding energy phenomena [62,63], this would, potentially, hinder efficient charge separation to the electron acceptor (assuming the well-established phenyl butyric acid methyl ester fullerene adducts $PC_{60}BM$ [6,64] or $PC_{70}BM$ [65] are used) since they exhibit LUMO levels ranging from 3.7 to 4.3 eV. Of the three remaining thiadiazines, thiadiazinone **1** has the lowest LUMO, which means that it would, theoretically, yield the copolymer with the lowest energy bandgap and therefore the better solar absorption. At this point we have to point out that this simple comparison does not factor in the other parameters affecting the energy bandgap of the copolymer such as planarity and solubilizing chains. The latter, depending on the comonomer used, could favour the use of thiadiazine **4** due to the added dodecyl chains. As for the planarity, compound **6**, for example, has been shown to have a non-planar shallow boat confirmation [45]. Similar advantages and disadvantages may promote the uses of other thiadiazines.

4. Conclusions

A series of fifteen thiadiazine compounds has been studied using cyclic voltammetry and differential pulse voltammetry to determine their ionization potential and electron affinity. Of the studied compounds, several trends emerge, as the decoration of the thiadiazine core on the 3, 5 position with thiophenes or pyrrole and pyrrolidine rings raises the HOMO level and reduces the energy bandgap. Similarly, alteration of the carboxyl moiety in the 4-position with dicyanomethylene, significantly lowers the LUMO level. Taking the electrochemical data into account, the most promising thiadiazine compound to be used for copolymerization with various prominent comonomers to produce solar harvesting polymers, is dichlorothiadiazinone **1**. From the library of examined compounds, thiadiazines **6** and **8**, both with dicyanomethylene substitution, exhibited the lowest LUMO level and the lowest energy bandgap, respectively. It should be noted that when decorated with alkyl chains to enhance solubility and promote thin film processability, they can act as basic building blocks for stand-alone electron donating or electron accepting small organic molecules.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2013.06.038.

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