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Push-pull molecules bearing a hydrazonocyclopentadiene acceptor moiety: from the synthesis to organic photovoltaic applications

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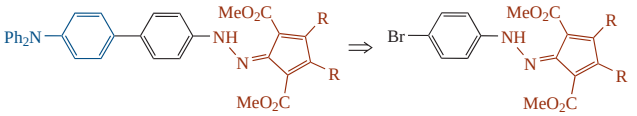
First representatives of a novel class of compounds containing an electron-accepting hydrazonocyclopentadiene moiety, π-conjugated phenylene spacer, and electron-donating triphenylamine moiety have been synthesized. Investigation of their optical, electrochemical and photovoltaic properties revealed a high potential of the hydrazonocyclopentadiene acceptor moiety in the design of donor–acceptor compounds for organic photovoltaics.



R = CO_2Me or Ph

Solar energy is believed to be among the most promising alternative energy sources.[1] The interest in organic solar cells (OSC) with bulk heterojunction based on small conjugated molecules, which act as both donors and acceptors in an OSC photovoltaic layer, grew considerably in the past few years.[2,3] In comparison with polymeric analogues, low-molecular donor molecules possess a number of advantages, such as monodispersity, controlled purity, and batch-to-batch reproducibility of characteristics.[4] Subsequently, low-molecular acceptors exceed fullerenes in the efficient charge separation upon small driving energies and in the easy control of the layer morphology.[3]

The majority of low-molecular donors and acceptors are conjugated molecules of donor–acceptor (D–A) type and have diverse structures and architecture. The molecular designs employed most frequently are linear symmetric (A–D–A)[5] and nonsymmetric (D–A)[6] ones, where D is an electron-enriched and A is an electron-deficient moieties. Such molecular structures enable independent and efficient tuning of levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and ensure an efficient intramolecular charge transfer, shifting the absorption spectrum considerably towards the longer wavelengths, *i.e.*, to the region of the highest sunlight intensity on the Earth surface.

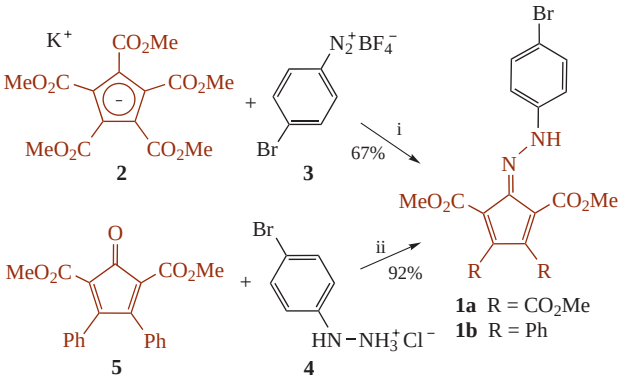
Within the design of D–A molecules for OSC, the main attention of scientists was focused on variations in the donor moieties and π-conjugated spacers, while the A groups deserved less attention. In the majority of structures, the A moieties are represented by dicyanovinyl groups, rhodanine, or indanone derivatives.[7,8] The configuration of the energy levels of organic semiconductive materials is an important factor in the development of organic electronic and photonic devices, wherein the A moieties make the major contribution into the LUMO energy level.[10,11] At this end, expanding the diversity of electron-withdrawing groups presents an urgent challenge.

We have recently suggested to introduce a hydrazonocyclopentadiene moiety containing electron-withdrawing ester substituents as the terminal A-group and developed two synthetic approaches to such chromophores.[12,13] Electron-deficient hydrazonocyclopentadiene acceptors ensure a high degree of molecule polarization, which consequently gives rise to the absorption in the long wavelength region (450–500 nm) with high molar extinction coefficients (25000–30000 $dm^3\ mol^{-1}\ cm^{-1}$) even if the conjugation chain is quite small. These developed approaches had certain limitations and could not afford compounds bearing more complex and stronger D moieties *via* a direct synthetic procedure.[13]

In this work, we have elaborated a new synthetic approach allowing one to increase the conjugated chain in molecules containing the hydrazonocyclopentadiene groups *via* addition of various D-blocks to simpler dyes bearing D moieties that can be functionalized. Moreover, the first photovoltaic performance data for this class of compounds have been obtained.

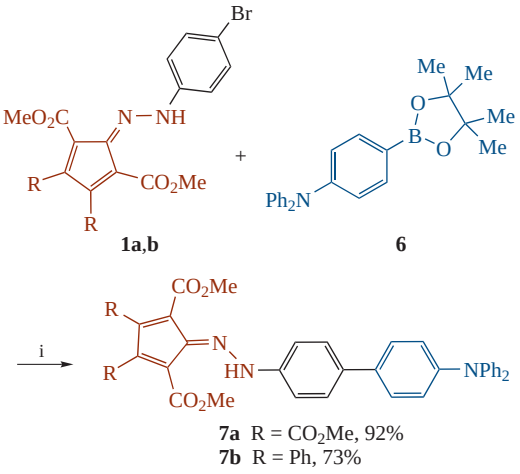
At the first step, the developed approaches were used to access precursor molecules **1a**,**b** containing a 4-bromophenyl group as a donor and two different hydrazonocyclopentadiene moieties as an acceptor (Scheme 1). Compound **1a** was prepared *via* the known decarboxylative azo coupling reaction of potassium penta(methoxycarbonyl)cyclopentadienide **2**[14,15] with 4-bromophenyldiazonium borofluoride **3**. Compound **1b** was synthesized *via* the condensation of 4-bromophenylhydrazine hydrochloride **4** with cyclopentadienone **5**.[13]

The cross-coupling of 4-bromophenylhydrazones **1a**,**b** with triphenylamine organoboron derivative **6** under the Suzuki reaction conditions was employed to insert an electron-donor triphenylamine block (Scheme 2). Both reactions resulted in target compounds **7a**,**b**, which illustrates the important fact that methoxycarbonyl substituted hydrazonocyclopentadiene moieties are preserved under the Suzuki reaction conditions (refluxing in a



Scheme 1 *Reagents and conditions*: i, MeCN, CF_3CO_2H, reflux; ii, MeOH, reflux.

water–acetonitrile medium). Thus, we have synthesized the first two D–A structures bearing different hydrazonocyclopentadiene moieties as the terminal A groups bound to a triphenylamine D-block *via* the phenylene spacer. To identify the effect of the type of substituent at the hydrazonocyclopentadiene moiety and estimate the potential of practical utilization of the developed compounds, their optical, electrochemical and photovoltaic properties were explored.



Scheme 2 *Reagents and conditions*: i, Na_2CO_3, MeCN–H_2O, $Pd(PPh_3)_4$, reflux.

The electrochemical properties of chromophores **7a**,**b** were evaluated by cyclic voltammetry (CV) (Figure S1, Online Supplementary Materials). They were oxidized at the equal potentials, since the identical donor triphenylamine groups underwent the oxidation in these compounds, while the A moiety did not considerably affect this process. Consequently, the calculated HOMO energies possess similar values of –5.31 (**7a**) and –5.33 eV (**7b**), whereas the LUMO energies were significantly different: –3.74 (**7a**) and –3.41 eV (**7b**) (Table 1). This in turn reflects the difference in the potentials of reduction that occurs on the different acceptor hydrazonocyclopentadiene moieties. Thus, the energy gaps (E_g) for chromophores **7a**,**b** are 1.57 and

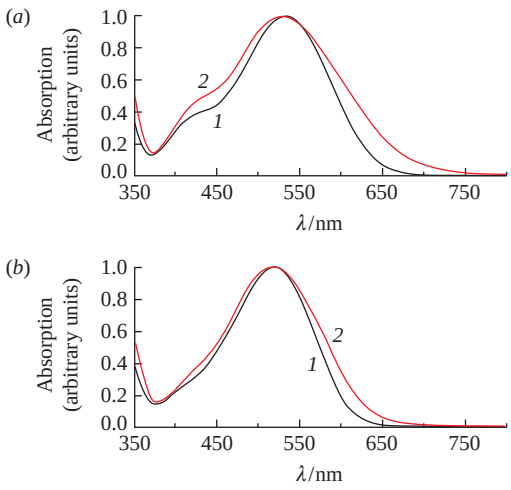


Figure 1 Normalized absorption spectra for compounds (*a*) **7a** and (*b*) **7b** in (*1*) a dilute solution in chloroform and (*2*) a thin film.

1.92 eV, respectively. This difference in E_g values is in good agreement with the acquired optical data.

The optical properties were estimated by UV–VIS spectroscopy, both in solution and in thin films (Figure 1). These data are summarized in Table 1. The obtained compounds **7a**,**b** exhibited an intensive absorption of visible light in the range 450–600 nm. Incorporation of the strong triphenylamine donor into the molecule resulted in a noticeable (~40 nm) bathochromic shift of absorption maxima (λ_{max}) and an increase in the molar extinction coefficient (ε) as compared to similar model dyes **1a**,**b** without the triphenylamine moiety.[13] The absorption maxima of compounds **7a** and **7b** are 536 and 518 nm, respectively, and equal in a solution and in a film, which indicates that there are no pronounced intermolecular interactions. However, the absorption range was somewhat broadened in the case of film, due to which the absorption edge was shifted upon transition from a solution to a film from 640 to 680 nm for **7a** and from 610 to 630 nm for **7b**. The shift of the absorption maximum towards the longer wavelengths and the narrowing of the band gap in the case of **7a** as compared to that of **7b** can be explained by the larger number of electron-withdrawing ester substituents at the cyclopentadiene acceptor moiety, which increases the polarity of the D–A system and ensures a more efficient intramolecular charge transfer.[16] There is only one known example of a compound similar to **7a**,**b** but having other electron-withdrawing moiety. It is compound **8**[17] containing a triphenylamine donor and phenylene π-spacer parts identical to those of **7a**,**b**, but a different dicyanovinyl acceptor. Herein absorption maxima of **7a**,**b** are red-shifted by

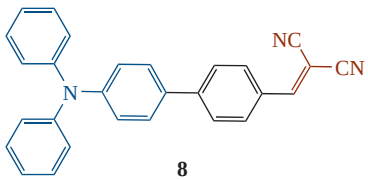


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Table 1 Optical properties and frontier orbital energy data.

Compound	$\lambda_{max}^{solution}$/nm	λ_{max}^{film}/nm	$\lambda_{edge}^{solution}$/nm	λ_{edge}^{film}/nm	ε/dm^3 mol^{-1} cm^{-1}	HOMO/eV	LUMO/eV	E_g/eV
1a	471	–	570	–	24000	–	–	–
1b	468	–	580	–	26000	–	–	–
7a	536	536	640	680	31000	–5.31[a]	–3.74[a]	1.57
7b	518	518	610	630	44600	–5.33[a]	–3.41[a]	1.92
8	461	476	–	–	29894	–5.56[b]	–2.98[b]	2.58

[a] The values were calculated using acquired CV data on the potentials. [b] DFT calculated values.[17]

Table 2 Photovoltaic properties of the best samples of solar cells.

Compound	**7a**,**b**:$PC_{71}BM$ ratio	J_{SC}/ mA cm^{-2}	V_{OC}/V	FF (%)	PCE (%)
7a	1:5	5.75	0.83	29.0	1.37
7a (optimized)	1:5	6.40	0.93	31.0	1.85
7b	1:10	3.07	0.65	25.1	0.50

75 and 57 nm towards that of **8**, the extinction coefficients are higher, and the band gap is narrower (see Table 1).

Thus, the obtained compounds can efficiently absorb the sunlight and possess suitable HOMO levels for a productive dissociation of excitons in a mixture with fullerene acceptors. Therefore, it seemed quite interesting to estimate whether they could be used as the donors in OSC.

The photovoltaic properties were investigated in bulk heterojunction solar cells of the structure glass/ITO/PEDOT:PSS/**7a** or **7b**:$PC_{71}BM$/Ca/Al.† For the sake of optimization, a number of photovoltaic cells with various mass ratios of compounds **7a**,**b** and $PC_{71}BM$ were made (data on the performance of devices are depicted in Figure S4). The main output parameters of the best solar cells based on **7a**,**b** are given in Table 2. For the voltammetric curves and external quantum efficiency spectra, see Figures S2 and S3. The higher value of the short-circuit current (J_{SC}) in devices based on **7a** may be due to its more efficient sunlight absorption in the long wavelength region of spectrum. The smaller open-circuit voltage (V_{OC}) of solar cells based on **7b** may be caused by a non-optimum morphology of the photoactive layer that may give rise to higher recombination losses. To compare the morphologies of **7a**:$PC_{71}BM$ and **7b**:$PC_{71}BM$ films, their surfaces were scanned with an atomic-force microscope (AFM). However, both films demonstrated a similar picture with a smooth surface (Figure S5) and equal roughness (0.40–0.39 nm), which allows one to assume that the differences exist in the morphology of these compounds in the film bulk. Thus, despite the relatively equal filling factors (FF) in photovoltaic materials based on compounds **7a** and **7b**, the power conversion efficiency (PCE) of the former is much higher (1.37 *vs*. 0.50%) due to the higher V_{OC} and J_{SC} values.

In addition, a couple of well-known methods for optimizing active layer morphology have been tested for solar cells based on **7a**, since this material exhibited a more promising performance as compared to **7b**. We managed to increase the PCE of solar cells from 1.37 to 1.85% (see Table 2 and Figure S1) using a combination of solvent vapor annealing in *o*-dichlorobenzene (30 s) and doctor blade deposition for the active layer instead of spin-coating. However, a solvent additive such as 1,8-diiodooctane (0.25–1%) did not result in increased efficiency.

In conclusion, a novel synthetic approach to extend the conjugated chain in chromophores containing hydrazonocyclopentadiene acceptor moieties was developed using the Suzuki cross-coupling reaction. The first representatives of such chromophores bearing a triphenylamine electron-donating moiety were prepared. In comparison with the model compounds **1a**,**b**, the donor-containing molecules **7a**,**b** absorb light in a longer wavelength region of spectrum and possess larger values of the molar extinction coefficients. Hydrazonocyclopentadiene derivatives were for the first time tested in photovoltaic cells as donor components of the OSC photovoltaic layers. The largest performance (up to 1.85%) was achieved in the case of devices based on **7a**. Note that the structure of the linker between the D and A moieties may not seem optimal since the biphenyl fragment does not favor an efficient overlap of π-orbitals due to its nonplanar structure. However, the disclosed efficiencies are comparable to those of nonsymmetric small molecule analogues containing standard acceptor moieties and donor linker blocks with more complex coplanar structures. Though the demonstrated efficiences are far from record ones, this work revealed the principal opportunity to employ hydrazonocyclopentadiene A moieties in the design of polarized chromophores for photovoltaics and discovered rich synthetic prospects for creating new, more complex molecules of this type.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.021.

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† See Online Supplementary Materials for details.

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