New "push-pull" type merocyanine dye for application in bulk-heterojunction organic solar cells

J. Dikova[*], S. Kitova, D. Stoyanova, A.Vasilev[1], T. Deligeorgiev[1] and S. Angelova[2]

Institute for Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences,
"Acad. G. Bonchev" str. Bl. 109, 1113 Sofia, Bulgaria
[1]Sofia University."St. Kliment Ohridski, Faculty of Chemistry and Farmacy,
1 James Bourchier Blvd., 1164 Sofia, Bulgaria
[2]Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,
"Acad. G. Bonchev" str. Bl. 9, 1113 Sofia, Bulgaria

The potentiality of our newly synthesized push-pull type merocyanine dye, labeled BMBII, for using as electron donating component in solution processed bulk heterojunction (BHJ) organic solar cells has been studied. For the purpose, soluble n-type fullerene, (6,6)-phenyl C_{61} butyric acid methyl ester (PCBM), which is without alternative in the near future, is chosen as acceptor. The optical constants (n and k) of thin films obtained by spin coating from solutions in chlorbenzene of BMBII as well as of BMBII/PCBM blend are determined by spectrophotometric measurements. Further, an optical simulation of a standard BHJ cell with active layer from BMBIIdye/PCMB blend has been performed using transfer-matrix formalism. Thus, the optimum thickness of the active layer is calculated to be about 80 nm, which provides an overlapping of the total absorption with solar spectrum in a broad range between 400 and 800 nm. Finally, the maximum current density J_{sc} of 13 mA.cm^{-2} is determined, assuming the internal quantum efficiency, IQE, equals one. By comparing the calculated J_{sc} with data for some advanced small molecular BHJ devices the perspectives for practical applications of the new merocyanine dye are discussed.

Keywords: Bulk heterojunction solar cells, small molecule, push-pull chromophores, merocyanine dyes

INTRODUCTION

During the past years the organic photovoltaics (PV) are subject of continuously growing interest as promising alternative for high cost crystalline silicon cells (c-Si), which still dominate the market. In the most successful devices, a soluble n-type fullerene, (6,6)-phenyl C_{61} butyric acid methyl ester (PCBM) as acceptor, is blended with the donor from conjugated p-type polymers to form bulk-heterojunction (BHJ) cells [1]. An attraction of these devices, which are processed from solution, is the ability to deposit active layer precursors over large areas in a single step, using techniques ranging from inkjet printing to spin-coating. Small molecule donors offer the same facile processing however are easier to synthesize in many variants and purify, are intrinsically monodisperse, and are often photo- and chemically more stable [2]. The disadvantage of lower solubility of this class of organic semiconductors can be overcome by functionalizing of their molecular structure. This approach has been successfully applied to different dyes and very encouraging results about the performance of devices developed on this base have been achieved [3]. However, the power conversion efficiency remains considerably lower than that of the polymeric solar cells [4]. This explains the increased scientific efforts recently for developing new small molecular electron donors for solution processed BHJ solar cells. In this respect the so-called "push-pull" chromophores look very promising [5]. The molecular structure of this unique class of dyes comprises electron-donating, π-conjugated bridging and electron withdrawing moieties. In the exited state a strong intramolecular charge transfer occurs which provides an enlargement of the absorption area of the donor, increasing of the charge mobility and therefore rising of the conversion efficiency [6].

The present work represents a first step in characterization of our newly synthesized push-pull type merocyanine dye (E)-3-((1-benzylquinolin-4(1H)-ylidene)methyl)-7H-benzo[de]benzo[4,5] imidazo-[2,1-a]isoquinolin-7-one, which we labelled as BMBII. The structure and electronic

---

* To whom all correspondence should be sent:
E-mail: julita@iomt.bas.bg

properties of the dye were studied by means of density functional theory (DFT) calculations. We determined also the optical constants (refractive index n and extinctions coefficient k) of spin coated thin BMBII dye and BMBII/PCMB films using previously developed methods, based on spectrophotometric measurements. Based on that, optical simulation was carried out in order to predict and understand photovoltaic performance of a bulk heterojunction cell with active layer from a solid-state blend of BMBII and the fullerene C_{61} derivative PCBM.

EXPERIMENTAL

The new push-pull dye BMBII was synthesized via the reaction between 3-nitro-7H-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (1) and 1-benzyl-4-methyl-quinolinium bromide (2) in metoxyethanol, in the presence of diizopropyl-ethylamine (DIPEA) and pyridine (Scheme 1).
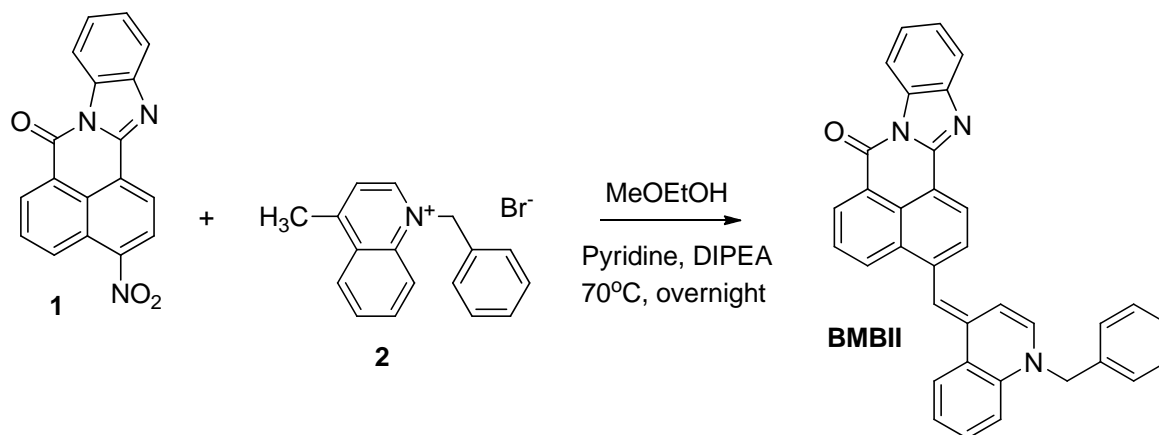
Scheme 1. Synthesis of new type merocyanine dye (E)-3-((1-benzylquinolin-4(1H)-ylidene) methyl)-7H-benzo[de]benzo[4,5]imidazo-[2,1-a]isoquinolin-7-one (BMBII).

The target merocyanine compound (E)-3-((1-benzylquinolin-4(1H)-ylidene)methyl)-7H-benzo[de]benzo[4,5] imidazo-[2,1-a]isoquino-lin-7-one (BMBII) was obtained with excellent yield. Detailed description of the reaction procedure and full characterization data of dye BMBII will be published in a separate paper [7].

The molecular ground-state geometry of BMBII compound was optimized - using Perdew-Burke-Ernzerhof (PBE0) hybrid functional [8] with triple-ζ polarized basis set, 6-311G(d,p). Local minima were verified by establishing that all vibrational frequencies are real. All calculations were performed using Gaussian 09 [9]. Thus, the values of HOMO (the highest occupied molecular orbital), LUMO (the lowest unoccupied molecular orbital) and their energy difference HLG (HOMO-LUMO gap), which are very important for photovoltaic application of the dye, were calculated.

Further, thin dye films were prepared from solution of the compound BMBII in chlorobenzene by spin coating. In the preliminary experiments the concentration of the solution, the spin rate and duration were varied in order to obtain films with thickness, suitable for optical measurements. Thus, 25 nm films were deposited from solution containing 4mg/ml BMBII, coated at 1500 rpm for 120 s. Blended films were prepared also by spin coating from chlorobenzene solutions of 1:1 (by weight) mixture of BMBII and PCBM (PCBM was commercially available). In both cases preliminary carefully cleaned BK7 optical glass plates and Si wafers were used as substrates.

Optical constants of the BMBII dye and blended BMBII/PCMB layers were determined on the basis of three spectrophotometric measurements at normal incidence of light - transmittance T and reflectances R_f and R_m of the both kinds of films, deposited on transparent (BK7) and opaque (Si wafers) substrates, respectively. Spectro-photometric measurements were performed with a spectrophotometer Cary 5E in the spectral region 350 – 800 nm. A value of the dye film thickness derived from the (TR_fR_m) method [10] was used for determining n and k by (TR_m) or (TR_f) methods, using Newton Raphson iterative techniques [11]. The combination of the two methods makes possible the determination of the optical constants

of the dye and blended films with a high accuracy [11].

Optical simulation of a BHJ device stack was carried out using the transfer matrix formalism, based on the Fresnel formulas for the several interfaces occurring in the cell. This approach has been explained in great detail in the literature [12, 13]. In our work a Matlab script developed by Burkhard and Hoke, which treats the case of normal incidence of light, was applied [14]. The absorption distribution for each wavelength over the film thickness has been calculated in the wavelength range 350 – 800 nm. Multiplying with the light of the AM 1.5 sun spectrum and integration over the film thickness results in the total number of photons, absorbed for each wavelength. Lastly, a summation over all wavelength results in the total number of absorbed photons. The possible maximum current density J_{sc} was calculated assuming that each absorbed photons results in a collected electron i.e. the internal quantum efficiency, IQE, equals one [14].

For optical simulation we have chosen a common BHJ device structure consisting of ITO(120nm)/MoO$_3$(5nm)/blendBMBII/PCBM (x nm)/LiF(10nm)/Al(100nm). 5 nm thick MoO$_3$ and 10 nm LiF films were inserted between active layer and the ITO surface and Al surface respectively, to form the ohmic contacts for hole and electron collection. The thickness of the blended layer was changed for numerical simulation in the range 40-320 nm.

The optical constants of ITO, Al and LiF used in simulation were taken from the literature [15]. The optical constants of MoO$_3$ films were determined by us using the same procedure as for BMBII dye and blended films. For the purpose 50 nm thick MoO$_3$ films were thermally evaporated in vacuum (10^{-4} Pa).

RESULTS

Fig. 1 shows molecular structure of dye BMBII (a) and calculated energy levels for dye and experimental energy values [16] for PCBM (b). The data analysis showed that HOMO is mainly located on the electron-donating moiety whereas the LUMO is more spread over the electron-accepting region. The frontier orbital energy difference for BMBII is calculated to be 2.78 eV. The estimated HOMO level of the dye is reasonably low (-5.17 eV) and very close to the desired range (between -5.2 and -5.8 eV). Besides, the difference between the LUMO energy level of PCBM and the dye's

HOMO energy level is 0.87 eV, which is much higher than the required minimum of 0.2-0.3 eV.
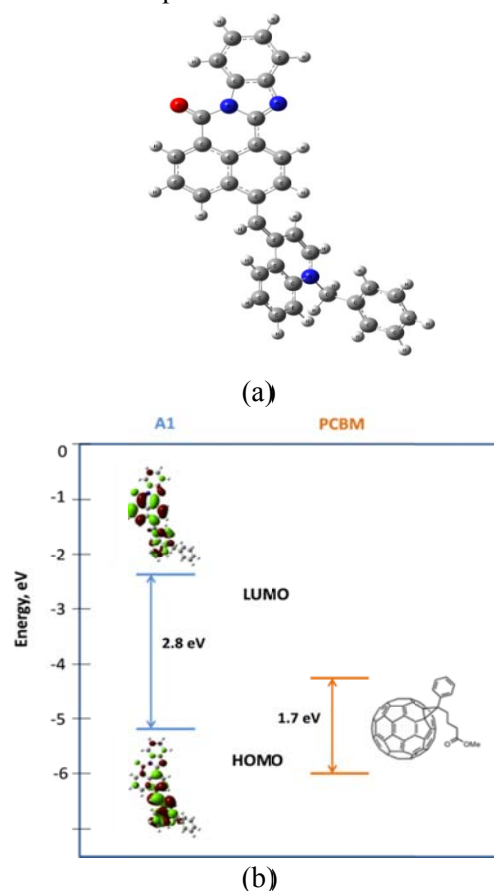

Fig. 1. PBE0/6-311G(d,p) optimized geometry of BMBII (a) and experimental energy levels for PCBM [16] and PBE0/6-311G(d,p) calculated energy levels for dye BMBII.

As known, this difference determines the value of open circuit voltage V_{oc} that is one of the basic characteristics of the cell's performance. From this result, we can roughly guess that the V_{oc} of devices fabricated using BMBII/PCBM BHJ active layer may be about 0.7 V [17], which is comparable with data for some promising new push-pull chromophores, based on squarine dyes [6]. Therefore, it can be concluded that the newly sensitized merocyanine dye has also potential for application as electron donating component in BHJ organic solar cells. This statement is additionally confirmed by the spectral dependence of absorption coefficient α determined for 25 nm thick dye film and presented in Fig. 2. As it is seen, there are two absorption peaks of 7.3 x10^4 cm^{-1} and 5.5 x10^4 cm^{-1} at $\lambda = 598$ and 402 nm, correspondingly. Besides, although the absorption of the film is moderate the
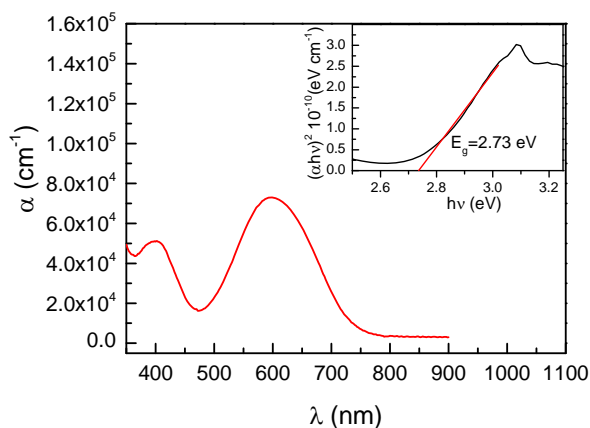
Fig. 2. Absorption coefficient profile ($\alpha=4\pi k/\lambda$) of 25 nm thick BMBII dye film.

absorption area is broad and covers the 400 - 750 nm spectral region, where the solar photon flux is maximum. This as well as the low intrinsic fluorescence of the new push-pull merocyanine dye [7] are an important prerequisite for its photovoltaic application. Simultaneously, it is worth to pointing out the good coincidence between the values of optical energy gap E_g, determined according to the so-called Tauc's law [18] as 2.73 eV (see the inset in Fig. 2), and calculated HLG energy of 2.8 eV. This fact can be regarded as an experimental confirmation of the results obtained from the theoretical analysis performed in the study.

For modeling of light propagation within a solar cell device, the optical constants of all involved layers needed to be known. The refractive index (n) and the extinction coefficient (k) of each layer used in optical simulation are plotted as a function of wavelength in Fig. 3. Optical constants of the blended film were determined for an about 45 nm thick film. As it was mentioned, the optical simulation was performed for a standard BHJ cell structure, where the light enters through the glass substrate, sequentially passing the layers of ITO, MoO_3, BMBII/PCBM blend layer and LiF. Then the light is reflected back from the Al electrode and finally leaves the solar cell partly at the front again.

Figure 4 presents the spectral dependence of total absorption within the BMBII/PCBM active layer for a set of different layer thicknesses. For comparison, the photon flux of a standard AM1.5 solar spectrum is shown as a gray solid line. It is clear that the blue light is mainly absorbed by PCBM and red and near infrared by BMBII dye. Besides, it is seen that the absorption of blended film overlaps the solar spectrum from 400 to 800 nm as required for high efficiency solar energy conversion.
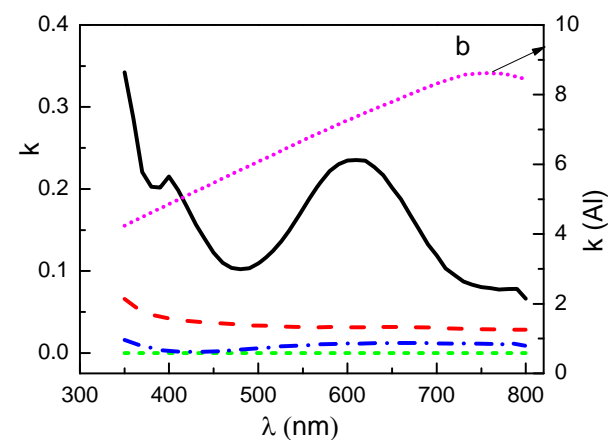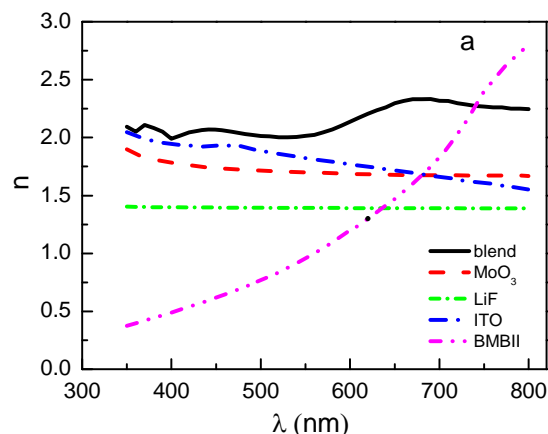

Fig. 3. Optical constants of layers used in simulation: refractive indices n (a) and extinction coefficients k (b).
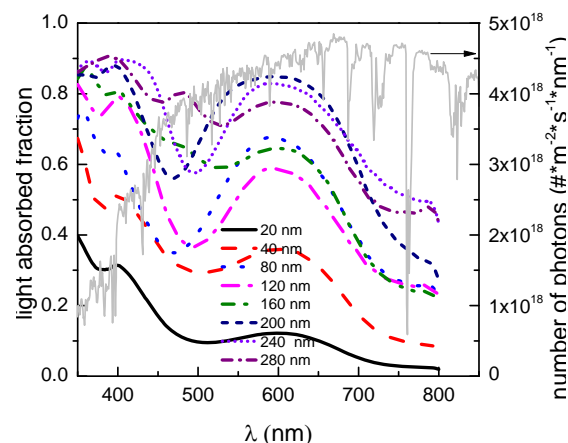

Fig. 4. Fraction of incident light absorbed within the dye-PCBM layer of the solar cell for several layer thickness. For comparison, the photon flux of a standard AM 1.5G solar spectrum is shown as a gray solid line (right axis).

Assuming an IQE=1, the maximum short circuit current density J_{sc} under AM 1.5 illumination for different BMBII/PCBM layer thickness is depicted

in Figure 5. Due to the interference effects in the device structure J_{sc} does not follow a straight line, but shows a local maximum at about 80 and 230 nm. In general, the photocurrent is higher for a larger active layer thickness, but due to the limited exciton diffusion length in the organic layer the real photocurrent decreases with increasing active layer thicknesses. Therefore, we may expect an optimized overlap between the 80 nm active layer absorption and the solar spectrum. Thus, J_{sc} of about 13 mA.cm^{-2} for this thickness is obtained,
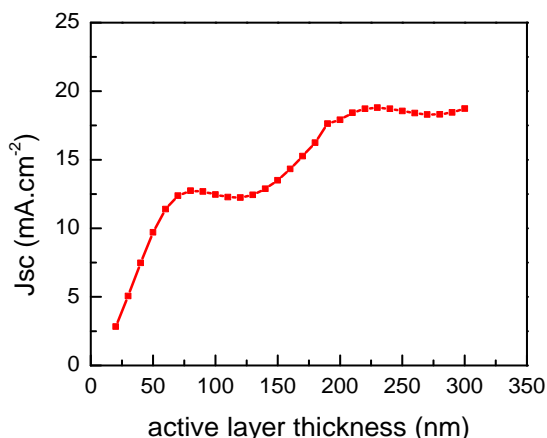

Fig. 5. Calculated short-circuit current density JSC under 100 mW.cm−2 AM 1.5 spectral illumination versus active layer thickness (IQE =1).

which is comparable to the maximum current calculated for example in MDMO-PPV (poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene) and PCBM bulk heterojunction solar cells [19].

Finally, it should be mentioned that experimental studies of a real device are in progress and will be forthcoming in a separate paper.

CONCLUSIONS

The results of the present study show that the newly sensitized merocyanine dye (E)-3-((1-benzylquinolin-4(1H)-ylidene)methyl)-7H-benzo[de]benzo[4,5] imidazo-[2,1-a] isoquino-lin-7-one (BMBII) is characterized by a low HOMO energy level, which presupposes a higher energy difference with the LUMO level of the PCBM acceptor than the required minimum of 0.2 - 0.3 eV. On this basis a roughly estimated value of 0.7 V for V_{oc} of a BHJ cell with BMBII/PCBM blended active layer could be expected. Besides, the total absorption within the layer with thickness of 80 nm overlaps the solar spectrum from 400 to 800 nm, where the solar spectrum flux is maximum.

Therefore, it could be supposed that as an active layer the blended film obtained will provide a good sun light harvesting and thereafter high efficiency of solar energy conversion. This is confirmed by the established comparability between the estimated value of the maximum density of short circuit current J_{sc} under AM 1.5 illumination for optimum thickness of the blended BMBII/PCBM film and literature data for some advanced solar devices. Thus, the results obtained demonstrate that our new merocyanine dye has a real potential for application as electron donor in solution processed BHJ solar cells.

REFERENCES

1. G. Dennler, M. Scharber, C. Brabec, *Adv. Mater.,* **21,** 1323 (2009).
2. B. Walker, C. Kim, T. Nguyen, *Chem. Mater.,* **23,** 470 (2011).
3. X. Xin, G. Wei, S. Wang, G. Zimmerman, C. Renshaw, M. Thompson, S. Forrest, *Adv. Mater.,* **24,** 1956 (2012).
4. H. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L.Yu, Y. Wu, G. Li, *Nat. Phot.,* **3,** 649 (2009).
5. H. Ko, H. Choi, S. Paek, K. Kim, K. Song, J. Lee, J. Ko, *J. Mater. Chem.,* **21,** 7248 (2011).
6. S. So, H. Choi, H. Ko, C. Kim, S. Paek, N. Cho, K. Song, J. Lee, J. Ko, *Sol. Energy Mater. & Sol. Cells,* **98,** 224 (2012).
7. A. Vasilev, T. Deligeorgiev, D. Cheshmedzhieva, S. Ilieva, O. Castaño, S. Angelova, to be published.
8. C. Adamoand V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model," *J. Chem. Phys.*, **110** (1999) 6158-69
9. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V.

Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

10. V. Panayotov, I. Konstantinov, *SPIE Proc*., **2253,** 1070 (1994).

11. I. Konstantinov, Tz. Babeva, S. Kitova. *Appl. Opt.,* **37,** 4260 (1998).

12. L. Pettersson, L. Roman, O. Inganä, *J. Appl. Phys.,* **86,** 487 (1999).

13. P. Peumans, A. Yakimov, R. Forrest, *J. Appl. Phys.,* **9**3, 3693 (2003).

14. G. Burkhard, E. Hoke, M. McGehee, *Adv. Mater.,* **22,** 3293 (2010).

15. D. Smith, E. Shiles, M. Inokuti, in: Handbook of Optical constants of Solids, E.Palik (ed.), New York: Academic, 1985 pp 377-405.

16. N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao, and M. Leclerc, *J. Am. Chem. Soc*., **130** 732 (2008).

17. M. C. Scharber, D. Muhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec, *Adv. Mater.,* **18,** 789 (2006).

18. J. Tauc, in: The Optical Properties of Solids, F. Abeles (ed.), North Holland, Amsterdam, 1970, pp 277–415.

19. H. Hoppe, N. Arnold, N. Sariciftci, D. Meissner, *Sol. Energy Mater. & Sol. Cells,* **80,** 105 (2003).

НОВО „PUSH-PULL" ТИП МЕРОЦИАНИНОВО БАГРИЛО ЗА ПРИЛОЖЕНИЕ В ОРГАНИЧНИ СЛЪНЧЕВИ КЛЕТКИ С ОБЕМЕН ХЕТЕРОПРЕХОД

Ю. Дикова, С. Китова, Д. Стоянова, А. Василев[1], Т. Делигеоргиев[1] и С. Ангелова[2]

Институт по оптически материали и технологии "Акад. Й. Малиновски", Българска Академия на науките, ул. "Акад. Г. Бончев", бл. 109, 1113 София, България
1Софийски Университет "Св. Климент Охридски", Факултет по Химия и фармация, ул. Джеймс Баучер, 1164 София, България
[2]Институт по органична химия с Център по фитохимия, Българска Академия на науките, ул. "Акад. Г. Бончев", бл. 9, 1113 София, България

(Резюме)

Изследвани са възможностите за приложение на синтезирано от нас ново мероцианиново багрило от „push-pull" тип, означено с BMBII, като електронен донор в органични слънчеви клетки с обемен хетеропреход. За целта като акцептор е избран разтворим дериват на фулерена от n-тип (6,6)-phenyl C61 butyric acid methyl ester (PCBM), чието приложение е без алтернатива в близко бъдеще. На базата на резултатите от спектрофотометрични измервания са определени оптичните константи (n и k) на тънки филми, получени чрез нанасяне на центрофуга от разтвор на BMBII, както и на смес BMBII/PCBM в хлорбензол. Проведена оптична симулация на стандартна клетка с обемен хетеропреход и активен слой от BMBII/PCBM, прилагайки формализма на трансферна матрица. По този начин е определена оптимална дебелина на активния слой от 80 нм, която осигурява припокриване на областта на абсорбция със слънчевия спектър в широк интервал - от 400 до 800 нм. Определена е възможната максимална плътност на тока Jsc от около 13 mAcm-2, приемайки че вътрешната квантова ефективност е равна на 1. Чрез сравняване на тази стойност с литературни данни за някои перспективни аналогични устройства са дискутирани перспективите за практическо приложение на новосинтезираното мероцианиново багрило.