

PAPER • OPEN ACCESS

Carbazole-based donor-acceptor small molecules with hexyldicyanovinyl electron-withdrawing groups: synthesis and properties

To cite this article: A N Solodukhin *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **525** 012036

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Carbazole-based donor-acceptor small molecules with hexyldicyanovinyl electron-withdrawing groups: synthesis and properties

A N Solodukhin¹, Yu N Luponosov^{1,2*} and S A Ponomarenko^{1,2}

¹Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Profsoyuznaya st. 70, Moscow 117393, Russia

²Chemistry Department, Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia

E-mail: luponosov@ispm.ru

Abstract. In this work, synthesis of two novel donor-acceptor small molecules based on donor 9-phenyl-9*H*-carbazole and acceptor hexyl-dicyanovinyl units was carried out. A comparative analysis of these molecules differing in the position of bithiophene π -spacer at the carbazole block only showed that changing the position allows to fine-tune absorption spectra, HOMO value, bandgap and phase behaviour of the materials.

1. Introduction

Donor-acceptor (D-A) small molecules are one of the most interesting and promising class of materials among various π -conjugated molecules for application in organic electronics, such as organic solar cells [1] and organic light emitting diodes [2] and organic field effect transistors. Binding of donor and acceptor moieties within one molecular structure allows fine-tuning properties of target materials: absorption and emission spectra and energy value of frontier orbitals - the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [3]. Carbazole is a donor block which combines low redox potential and high chemical stability and uses actively to design functional materials for organic electronics [4-9]. In this work, we designed and synthesized novel D-A molecules by attaching bithiophene arms end-capped with electron-withdrawing hexyl-dicyanovinyl groups to the carbazole block at either 2 and 7 or 3 and 6 positions (Figure 1, molecules I and II, respectively). The optical and electrochemical properties and phase behavior of the obtained materials were studied and compared to each other.



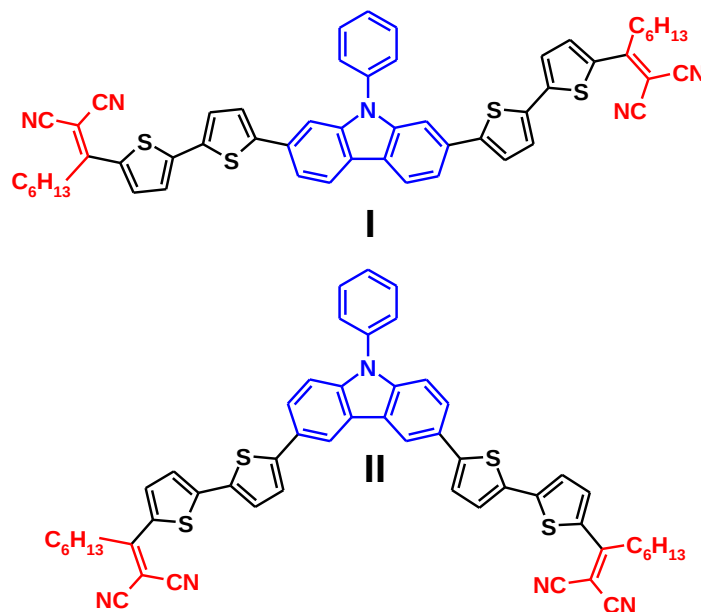


Figure 1. Structural formulas of I and II.

2. Experimental part

2.1. Materials

Malononitrile and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) were purchased from Sigma-Aldrich Co and used as received. THF, toluene, hexane, and pyridine were dried and purified according to known procedures. All reactions, unless otherwise specified, were performed in an argon atmosphere and dry solvents. 2,7-dibromo-9-phenyl-9*H*-carbazole (1) [10], 3,6-dibromo-9-phenyl-9*H*-carbazole (2) [11], 2-[5'-(2-hexyl-1,3-dioxolan-2-yl)-2,2'-bithien-5-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3) [12] and 2-hexyl-5,5-dimethyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-2,2'-bithien-5-yl]-1,3-dioxane (4) [13] were prepared as described earlier.

2.2. Synthesis of molecules

Synthesis of 2,7-bis[5'-(2-hexyl-5,5-dimethyl-1,3-dioxan-2-yl)-2,2'-bithien-5-yl]-9-phenyl-9*H*-carbazole, 5a. In an inert atmosphere, $\text{Pd}(\text{PPh}_3)_4$ (0.08 g, 0.07 mmol) was added to a degassed solution of 2,7-dibromo-9-phenyl-9*H*-carbazole (1) (0.40 g, 1.00 mmol) and 2-hexyl-5,5-dimethyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithien-5-yl]-1,3-dioxane (3) (1.07 g, 2.39 mmol) in a mixture of toluene/ethanol (20/2 mL) and 2 M aqueous solution of sodium carbonate (3.6 mL). The reaction mixture was refluxed for 10 h, cooled to room temperature, and poured into a dropping funnel containing distilled water (100 mL) and toluene (100 mL). The organic phase was separated, washed with water, dried over sodium sulfate, and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel using mixture of toluene–hexane (1 : 1) as the eluent to obtain a pure compound 5a (0.8 g, 90%) as a light brown powder. ^1H NMR (250 MHz, CDCl_3), δ : 0.79–0.93 (overlapping signals, 6H), 1.21–1.45 (overlapping signals, 16H), 1.94–2.05 (overlapping signals, 4H), 3.92–4.09 (overlapping signals, 8H), 6.89 (d, 2H, $J = 3.7$ Hz), 7.03 (d, 2H, $J = 3.7$ Hz), 7.08 (d, 2H, $J = 3.7$ Hz), 7.22 (d, 2H, $J = 3.7$ Hz), 7.50–7.74 (overlapping signals, 9H), 8.07 (d, 2H, $J = 8.9$ Hz). Calculated (%) for $\text{C}_{52}\text{H}_{53}\text{NO}_4\text{S}_4$: C, 70.63; H, 6.04; N, 1.58; S, 14.50. Found: C, 70.74; H, 6.24; N, 1.53; S, 14.39.

Synthesis of 3,6-bis[5'-(2-hexyl-5,5-dimethyl-1,3-dioxan-2-yl)-2,2'-bithien-5-yl]-9-phenyl-9*H*-carbazole, 5b. This compound was obtained according to the procedure described for compound 5a using 3,6-dibromo-9-phenyl-9*H*-carbazole (2) (0.70 g, 1.75 mmol), 2-hexyl-5,5-dimethyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithien-5-yl]-1,3-dioxane (4) (2.06 g, 4.20 mmol), 2 M

sodium carbonate (6.3 mL), toluene/ethanol (40/4 mL), and Pd(PPh₃)₄ (0.15 g, 0.13 mmol). The product was purified by column chromatography on silica gel (eluent - toluene : hexane 1:1) to give a pure compound 5b (1.2 g, 71%) as a light brown powder. ¹H NMR (250 MHz, CDCl₃), δ: 0.66 (s, 6H), 0.80–0.91 (overlapping signals, 6H), 1.24 (s, 18H), 1.35–1.51 (overlapping signals, 4H), 1.79–1.97 (overlapping signals, 4H), 3.41 (d, 4H, *J* = 11.3 Hz), 3.74 (d, 4H, *J* = 11.3 Hz), 6.88 (d, 2H, *J* = 3.7 Hz), 7.08–7.17 (overlapping signals, 4H), 7.28 (d, 2H, *J* = 3.7 Hz), 7.38 (d, 2H, *J* = 8.3 Hz), 7.50–7.71 (overlapping signals, 7H), 8.34–8.42 (overlapping signals, 2H). Calculated (%) for C₅₈H₆₅NO₄S₄: C, 71.94; H, 6.77; N, 1.45; S, 13.24. Found: C, 71.97; H, 6.82; N, 1.44; S, 13.16.

Synthesis of 1,1'-[(9-phenyl-9*H*-carbazole-2,7-diyl)bis(2,2'-bithiene-5',5'-diyl)]diheptan-1-one, 6a. 1M hydrochloric acid (2 mL) was added to a solution of compound 5a (0.65 g, 0.7 mmol) in THF (30 mL) and the reaction mixture was refluxed with stirring for 4 h. Upon completion of the reaction, the product formed as yellow precipitate. The organic phase was separated using diethyl ether, washed with water, and filtered off to give a pure compound 6a (0.58 g, 98%) as yellow powder. ¹H NMR (250 MHz, CDCl₃), δ: 0.84–0.94 (overlapping signals, 6H), 1.27–1.42 (overlapping signals, 12H), 1.67–1.84 (overlapping signals, 4H), 2.85 (t, 3H, *J* = 7.6 Hz), 7.15 (d, 2H, *J* = 4.0 Hz), 7.25–7.31 (overlapping signals, 5H), 7.52–7.64 (overlapping signals, 9H), 7.65–7.72 (overlapping signals, 2H), 8.08 (d, 2H, *J* = 8.9 Hz). Calculated (%) for C₄₈H₄₅NO₂S₄: C, 72.41; H, 5.70; N, 1.76; S, 16.11. Found: C, 72.52; H, 5.79; N, 1.74; S, 15.99.

Synthesis of 1,1'-[(9-phenyl-9*H*-carbazole-3,6-diyl)bis(2,2'-bithiene-5',5'-diyl)]diheptan-1-one, 6b. This compound was obtained according to the procedure described for compound 4a using 1M hydrochloric acid (4 mL), compound 5b (1.18 g, 1.2 mmol), and THF (18 mL), which yielded a pure compound 6b (0.79 g, 80%) as a yellow powder. ¹H NMR (250 MHz, CDCl₃), δ: 0.85–0.94 (overlapping signals, 6H), 1.28–1.43 (overlapping signals, 12H), 1.69–1.82 (overlapping signals, 4H), 2.87 (t, 4H, *J* = 7.3 Hz), 7.08–7.22 (overlapping signals, 2H), 7.29–7.73 (overlapping signals, 15H), 8.86 (s, 2H). Calculated (%) for C₄₈H₄₅NO₂S₄: C, 72.41; H, 5.70; N, 1.76; S, 16.11. Found: C, 72.54; H, 5.81; N, 1.73; S, 15.96.

Synthesis of 2,2'-[(9-phenyl-9*H*-carbazole-2,7-diyl)bis(2,2'-bithiene-5',5'-diyl)hept-1-yl-1-ylidene)]dimalononitrile, I. Compound 6a (0.52 g, 0.7 mmol), malononitrile (0.26 g, 3.9 mmol), and dry pyridine (12 mL) were placed in a reaction vessel and stirred under argon atmosphere for 8 hours at reflux using microwave radiation. Upon completion of the reaction, pyridine was evaporated in vacuum and the residue was dried at 1 Torr. The resulting residue was purified by column chromatography on silica gel using dichloromethane as the eluent. Further purification included the precipitation of the product with hexane from its solution in THF to give pure product as a black solid (0.47 g, 81%). ¹H NMR (250 MHz, CDCl₃), δ: 0.85–0.96 (overlapping signals, 6H), 1.26–1.49 (overlapping signals, 12H), 1.63–1.76 (overlapping signals, 4H), 2.91 (t, 3H, *J* = 7.6 Hz), 7.25–7.35 (overlapping signals, 6H), 7.52–7.62 (overlapping signals, 7H), 7.67–7.75 (overlapping signals, 2H), 7.93 (d, 2H, *J* = 4.3 Hz), 8.09 (d, 2H, *J* = 7.9 Hz). ¹³C NMR (125 MHz, CDCl₃), δ: 13.88, 22.41, 29.19, 30.40, 31.28, 37.56, 76.88, 106.94, 113.79, 114.62, 118.87, 121.00, 123.30, 124.52, 124.82, 127.35, 127.50, 128.32, 130.37, 131.75, 134.30, 134.96, 135.34, 137.06, 142.30, 146.68, 147.65, 166.28. Calculated (%) for C₅₄H₄₅N₅S₄: C, 72.69; H, 5.08; N, 7.85; S, 14.37. Found: C, 72.78; H, 5.13; N, 7.88; S, 14.28.

Synthesis of 2,2'-[(9-phenyl-9*H*-carbazole-3,6-diyl)bis(2,2'-bithiene-5',5'-diyl)hept-1-yl-1-ylidene)]dimalononitrile, II. This compound was obtained according to the procedure described for I using compound 6b (0.73 g, 0.9 mmol), malonitrile (0.36 g, 5.4 mmol), and pyridine (15 mL), which yielded a pure product (0.49 g, 60%) as a black solid. ¹H NMR (250 MHz, CDCl₃), δ: 0.77–0.97 (broad signal, 6H), 1.19–1.53 (overlapping signals, 12H), 1.58–1.79 (broad signal, 4H), 7.24 (d, 2H, *J* = 4.1 Hz), 7.29–7.43 (overlapping signals, 6H), 7.48–7.58 (overlapping signals, 3H), 7.59–7.71 (overlapping signals, 4H), 7.91 (d, 2H, *J* = 4.7 Hz), 8.28–8.38 (overlapping signals, 2H). ¹³C NMR (125 MHz, CDCl₃), δ: 13.98, 22.45, 29.23, 30.49, 31.26, 37.42, 76.03, 110.67, 113.94, 114.78, 117.73, 123.49, 123.64, 124.47, 124.61, 125.97, 126.81, 127.68, 128.10, 130.13, 133.31, 134.81, 135.26, 136.77, 141.28, 147.08, 147.76, 166.21. Calculated (%) for C₅₄H₄₅N₅S₄: C, 72.69; H, 5.08; N, 7.85; S, 14.37. Found: C, 72.75; H, 5.11; N, 7.86; S, 14.31.

2.3. Characterization

^1H NMR spectra were recorded at a “Bruker WP-250 SY” spectrometer, working at a frequency of 250.13 MHz and utilising CDCl_3 signal (7.25 ppm) as the internal standard. ^{13}C NMR spectra were recorded using a “Bruker Avance II 300” spectrometer at 75 MHz. In the case of ^1H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in CDCl_3 . In the case of ^{13}C NMR spectroscopy, the compounds to be analyzed were taken in the form of 5% solutions in CDCl_3 . The spectra were then processed on the computer using the ACD Labs software.

Elemental analysis of C, N and H elements was carried out using CHN automatic analyzer CE 1106 (Italy). The settling titration using BaCl_2 was applied to analyze sulfur. Experimental error for elemental analysis is 0.30-0.50%. The Knövenagel condensation was carried out in the microwave “Discovery”, (CEM corporation, USA), using a standard method with the open vessel option, 50 watts. In the case of column chromatography, silica gel 60 (“Merck”) was taken. Absorption profiles were recorded with a Perkin Elmer Lambda-35 absorption spectrometer from 350 to 1100. All measurements were carried out at room temperature in diluted solutions (10^{-5} M) of THF. Films were cast from THF solutions on quartz substrate.

Cyclic voltammetry measurements were carried out using solid compact layers of the oligomers, which in turn were made by electrostatically rubbing the materials onto a glassy carbon electrode. Measurements were made in $\text{CH}_3\text{CN}:\text{o-C}_6\text{H}_4\text{Cl}_2=1:4$ solution using 0.1 M Bu_4NPF_6 as supporting electrolyte and using IPC-Pro M potentiostat. The scan rate was 200 mVs^{-1} . The glassy carbon electrode was used as a work electrode. Potentials were measured relative to a saturated calomel electrode (SCE). The HOMO and LUMO energy levels were calculated using the first standard formal oxidation and reduction potentials obtained from CV experiments in films according to the following equations: $\text{LUMO}=-e(\varphi_{\text{red}}+4.40)$ (eV) and $\text{HOMO}=-e(\varphi_{\text{ox}}+4.40)$ (eV) [14, 15].

DSC scans were obtained with Mettler Toledo DSC30 system with $20^\circ\text{C}/\text{min}$ heating/cooling rate in temperature range of $+20$ – 290°C for all compounds. N_2 flow of $50 \text{ mL}/\text{min}$ was used.

3. Results and discussion

The molecules I and II were synthesized in three consecutive steps (Fig. 2). At the first step, precursors 5 a,b with protective dioxane groups were obtained by Suzuki cross coupling between branching center either (2,7-dibromo-9-phenyl-9H-carbazole (1) or 3,6-dibromo-9-phenyl-9H-carbazole (2)) and 2-[5'-(2-hexyl-1,3-dioxolan-2-yl)-2,2'-bithien-5-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3) or 2-hexyl-5,5-dimethyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithien-5-yl]-1,3-dioxane (4) in yields of 90% and 71%, respectively. At the second step, the protective group was removed by refluxing of compounds 5a, 5b in THF at the presence of 1M hydrochloric acid as a catalyst. The yields of compounds 6a, 6b with carbonyl groups were 98% and 80%, respectively. At the last step, the Knoevenagel reaction between compounds 6a, 6b and malononitrile in pyridine resulted in the substitution of the carbonyl group for dicyanovinyl one. The crude products were purified by column chromatography to give D-A molecules I and II in yields of 81 and 60%, respectively. The chemical structures and purity of the molecules were determined by a set of modern physicochemical methods, such as ^1H and ^{13}C NMR spectroscopy, in combination with analytical GPC and elemental analysis. The NMR spectra displayed only typical signals for such compounds and the integral intensities of the signals agreed to the calculated ones. The determined contents of elements (C, H, and N) coincided well with the calculated values.

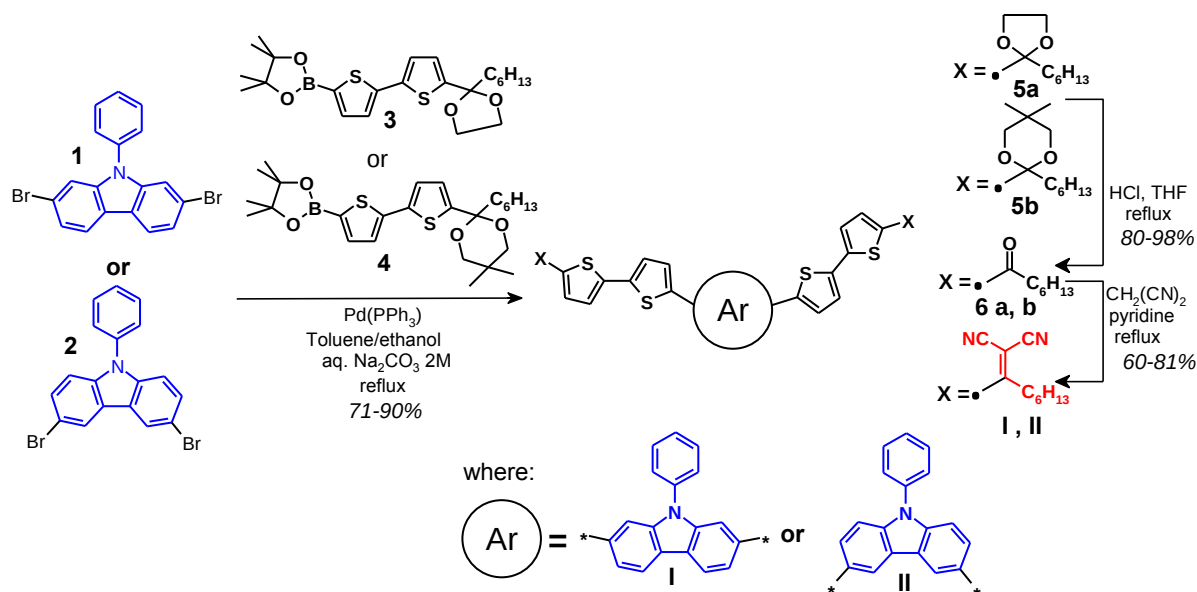


Figure 2. Synthesis of compounds I and II.

The optical properties of the synthesized molecules based on carbazole were studied by absorption spectroscopy in both solutions and thin films. The absorption spectra are shown in Fig. 3a.

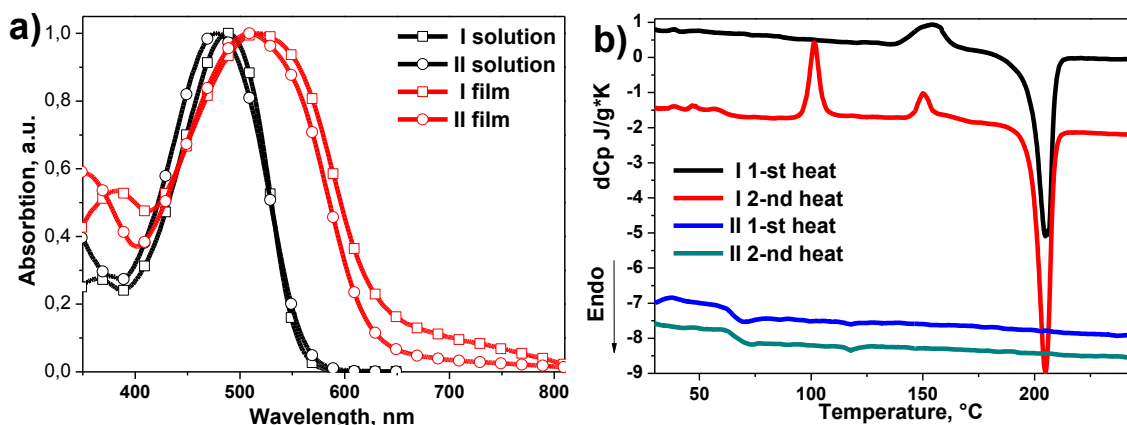


Figure 3. (a) Absorption spectra and (b) DSC scans for I and II.

The compounds efficiently absorb sunlight in the range from 350 nm to 650 nm. The spectra and absorption maxima (λ_{max}) of the molecules in diluted THF solutions have similar shape and peak values (Table 1). The spectra display two absorption bands: the first absorption band in a short-wavelength region is typically assigned to the π - π^* transition and the second more intense band in a long-wavelength region is assigned to the intramolecular charge transfer between electron donating carbazole blocks with bithiophene fragments and electron-withdrawing dicyanovinyl substituents [16]. However, it has been shown that in fact both electronic excitations have a mixed character and the intensity of the high-energy absorption feature is a direct measure of the degree of conformational disorder in the molecule [17]. The absorption spectra in thin films obtained from molecules I and II by the solution method are broadened when compared to solutions and the absorption peaks are red-shifted by 30–34 nm (Table 1). Comparing the λ_{max} of the molecules one can see that the compound I has a bit red-shifted absorption both in solution and films.

Table 1. Optical and electrochemical properties of molecules I and II

Molecule	UV-vis spectroscopy		Cyclic voltammetry		
	Solution ^{a)} $\lambda_{\max}$, nm	Film ^{b)} $\lambda_{\max}$, nm	HOMO, eV	LUMO, eV	E_g , eV
I	488	518	-5.49	-3.30	2.19
II	477	511	-5.34	-3.30	2.04

^a Measured in a THF solution.^b Film cast from THF solution.

Thus, the position of the bithiophene π -spacer relatively to the carbazole influence the $\lambda_{\max}$ of the compounds I and II, which can be explained by the fact that π -conjugation of the arms with carbazole through position 2 and 7 is more efficient as compared to that of through 3 and 6 positions. Therefore absorption spectra of compound I are slightly red-shifted both in solution and in the film as compared to that of compound II.

The electrochemical properties of the molecules were investigated by the cyclic voltammetry (CV). The reduction of the oligomers proceeds at the same values, since in these compounds the electron-withdrawing hexyl-dicyanovinyl group is mainly responsible for the reduction process and the position of the π -bridge should have no effect on that. However, the oxidation potentials were found to be depended significantly on the position of the thiophene π -bridge, since the oxidation occurs mainly through the carbazole-thiophene fragment. A facilitation of the oxidation process was observed when going from compound II to I. The values of HOMO and LUMO energies were calculated using the first standard formal oxidation and reduction potentials (Table 1). Values of the LUMO energy levels for this series of molecules are the same, whereas values of the HOMO energy levels tend to increase from I to II. The latter leads to a corresponding decrease of the electrochemical band gap from 2.19 eV to 2.04 eV.

The phase behavior of synthesized molecules were studied by differential scanning calorimetry (DSC). Figure 3b shows the thermograms for the first and second heats of the samples. It is seen that the compound II does not form a crystalline phase. The sample shows only a glass transition at 63–66 °C region. In contrast, I has a pronounced tendency to crystallization. On the first DSC heating scan it can crystallize in region of 140 – 160 °C followed by melting at 205 °C with enthalpy (ΔH_m) of 46 J/g. However, crystallization from the melt is hindered and on the second heating scan we observe a glass transition (60-65 °C) followed by two cold crystallization processes peaked at 101 °C and 150 °C and then a complete melting at 205 °C ($\Delta H_m = 46$ J/g). Thus, the position of bithiophene arms at the carbazole block results in significant changes in the mechanism of intermolecular interaction and the appearance of an ordered phase.

4. Conclusions

To sum up, two donor–acceptor molecules based on the electron-donating 9-phenyl-9*H*-carbazole derivatives and electron-withdrawing hexyldicyanovinyl groups were designed, synthesized and characterized. The influence of the position of the bithiophene π -spacer at the carbazole block on the properties of donor-acceptor molecules was studied by optical absorption spectroscopy, CV and DSC techniques. It was shown that the attachment of bithiophene π -spacers to the carbazole at positions of 2 and 7 (I) leads to a red shift of the absorption spectra, decrease of HOMO energy values and appearance of the ability to form crystalline phases as compared to compound II, having the bithiophene arms at 3 and 6 positions of carbazole. The both materials have a potential to be used as donor component of active layer in bulk heterojunction organic solar cells.

Acknowledgments

The project has been implemented with the support of the Global Energy Association. Authors thank P. V. Dmitryakov (National Research Centre “Kurchatov Institute”) for DSC experiments, E.A. Svidchenko

(ISPM RAS) for recording of absorption spectra and S.A. Peregodova (INEOS RAS) for CV experiments. The work was performed in the framework of leading science school NSh-5698.2018.3.

References

- [1] Ilmi R, Haque A and Khan M S 2018 *Organic Electronics* **58** pp 53-62
- [2] Duan L, Qiao J, Sun Y and Qiu Y 2011 *Advanced Materials* **23**(9) pp 1137-1144
- [3] Ponomarenko S A, Luponosov Y N, Min J, Solodukhin A N, Surin N M, Shcherbina M A, Chvalun S N, Ameri T and Brabec C 2014 *Faraday Discuss.* **174** pp 313-339
- [4] Wex B and Kaafarani B R 2017 *J. Mater. Chem. C.* **5**(34) pp 8622-8653
- [5] Jiang H, Sun J and Zhang J 2012 **16**(17) pp 2014-2025
- [6] Kato S, Yamada Y, Hiyoshi H, Umez K and Nakamura Y 2015 *J. Org. Chem.* **80**(18) pp 9076-9090
- [7] Damit E F, Nordin N, Ariffin A and Sulaiman K 2016 *Journal of Chemistry* **2016** pp 1-14
- [8] Higginbotham H, Karon K, Ledwon P and Data P 2016 *Display and Imaging* **2** pp 207-216
- [9] Bakirov A V, Solodukhin A N, Luponosov Yu N, Svidchenko E A, Obrezkova M A, Peregodova SM, Shcherbina MA, Ponomarenko SA and Chvalun SN 2017 *Nanotechnologies in Russia* **12** (7-8) pp 385-394.
- [10] Fell V H K, Mikosch A, Steppert A-K, Ogieglo W, Senol E, Canneson D and Kuehne A J C 2017 *Macromolecules* **50**(6) pp 2338-2343
- [11] Liu Y, Wu S, Wang G, Yu G, Guan J, Pan C and Wang Z 2014 *J. Mater. Chem. A* **2**(21) pp 7795-780
- [12] Min J, Luponosov Y N, Gerl A, Polinskaya M S, Peregodova S M, Dmitryakov P V, Bakirov AV, Shcherbina M A, Chvalun S N, Grigorian S, Kaush-Busies N, Ponomarenko S A, Brabec C J 2013 *Adv. Energy Mater* **4**(5) p 1301234
- [13] Luponosov Y N, Min J, Solodukhin, A N, Bakirov, A V, Dmitryakov, P V, Shcherbina, M A, Peregodova S M, Cherkaev G V, Chvalun S N, Brabec C J, Ponomarenko, S A 2016 *Journal of Materials Chemistry C* **4**(29) pp 7061-7076
- [14] Ponomarenko S A, Kirchmeyer S, Elschner A, Alpatova N M, Halik M, Klauk H, Zschieschang U and Schmid G 2006 *Chem. Mater.* **18** p 579
- [15] Ponomarenko S A, Rasulova N N, Luponosov Y N, Surin N M, Buzin M I, Leshchiner I, Peregodova S M and Muzafarov A M 2012 *Macromolecules* **45** p 2014
- [16] Roquet S, Cravino A, Leriche P, Alévêque O, Frère P and Roncali J. 2006 *Journal of the American Chemical Society* **128**(10) pp 3459-3466
- [17] Kozlov O V, Luponosov Y N, Ponomarenko S A, Kausch-Busies N, Paraschuk D Y, Olivier Y, Beljonne D, Cornil J and Pshenichnikov M S 2015 *Adv. Energy Mater.* **5**(7) p 1401657