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Structure-property relationship of isomeric diphenylethenyl-disubstituted dimethoxycarbazoles

Audrius Bucinskas, a Gintautas Bagdziunas, a Ausra Tomkevičienė, a Dmytro Volynyuk, a Nataly Kostiv, a Dalius Gudeika, a Vyginas Jankauskas, a Martins Rutkis, c and Juozas V. Gražulevičius*

Isomeric 3,6-dimethoxy- and 2,7-dimethoxycarbazoles containing diphenylethenyl moieties were synthesized by condensation of the appropriate dimethoxycarbazoles with diphenylacetaldehyde. The solid-state structures and the molecular order of the compounds were proven by X-ray crystallography. Both compounds were found to be capable of glass formation with the comparable glass transition temperatures (70-71 °C). They exhibited high thermal stabilities, with the 5 % weight loss temperatures exceeding 375 °C. The isomer having diphenylethenyl groups at C-3 and C-6 positions and methoxy groups at C-2 and C-7 positions (3a) exhibited aggregation-induced emission (AIE), while its counterpart having diphenylethenyl groups at C-2 and C-7 positions and methoxy groups at C-3 and C-6 positions (3b) showed the opposite effect, i.e. aggregation-caused quenching (ACQ). The derivative 3b showed superior charge transporting properties. Time-of-flight hole drift mobilities in its layers approached 10⁻³ cm²/Vs at high electric fields. A comparative theoretical analysis of the compounds was performed using density functional theory (DFT) and time-dependent DFT calculations. They proved more effective π-conjugation in the derivative of 3,6-dimethoxycarbazole (3b), which was also observed by UV and fluorescence spectroscopies. The theoretical study revealed relatively low ground state dipole moment of 0.69 D of the isomer 3b, while its counterpart (3a) showed much higher ground state dipole moment of 5.98 D. The difference in polarity was found to have the crucial effect on the molecular arrangement in the crystals and consequently, on the thermal transitions and charge-transporting properties.

Keywords: Carbazole; Charge mobility; DFT; AIE; ACQ; Reorganization energy; Marcus theory; X-ray crystallography.

Introduction

The search for new π-conjugated organic compounds with advanced properties is still the challenge for many laboratories working on the synthesis of organic electroactive materials for optoelectronic applications. Carbazole derivatives have attracted much attention because of their flexible synthesis and wide range of applications, such as organic light-emitting diodes (OLEDs), organic thin-film transistors, solid-state dye-sensitized solar cells.¹⁴ The carbazole moiety can be easily modified via its C-3 and C-6 positions.⁵ There is a substantial number of studies on 3,6-substituted carbazole derivatives and on their optoelectronic applications. Incomparably less research was done on 2,7-substituted carbazole derivatives. The main obstacle until recently was the lack of an efficient synthesis procedure for these compounds. The obstacle disappeared when the convenient synthetic pathways towards 2,7-dihalocarbazoles were reported.⁶,⁷ Since then ongoing studies of 2,7-disubstituted carbazole compounds revealed substantially higher hole mobilities compared to those of 3,6-disubstituted counterparts.⁸ In this work we demonstrate the convenient synthetic method of 2,7-diphenylethenyl disubstituted carbazole derivative by the direct reaction of 3,6-dimethoxy substituted carbazole derivative with diphenylacetaldehyde. We also synthesized the isomeric derivative from 2,7-dimethoxy substituted carbazole derivative and performed the comparative study of the properties of the obtained materials by the theoretical and experimental tools.

Diphenylethenyl-disubstituted derivatives of carbazole were earlier prepared by the multi-step synthetic route, the last step of which was Pd-catalyzed Suzuki coupling of diphenylethenyl borolane with the corresponding dibromocarbazole derivatives.⁹,¹⁰ They showed good performance as hole-transporting blue emitters in electroluminescent devices.

In some fields of application, such as dye-sensitized solar cells, electrochemically stable hole-transporting materials with low ionization potentials are required. It is known that introduction of methoxy groups into the structures of aromatic amines as well as the attachment of methoxy-substituted
diphenylamino groups to the carbazole moieties lead to the decrease of the ionization potential.\textsuperscript{11,12} The possibility to monitor ionization potentials is also important in the fabrication of OLEDs. The hole-injection barrier differences can strongly affect the efficiency of the devices. The role of the methoxy groups is found to be related to the mesomeric (\(p\)-donor) effect and the possibility to establish hydrogen bonds.\textsuperscript{13} The stronger influence was observed for \(para\)-methoxy substituted derivatives, as compared to \(ortho\)- and \(meta\)-methoxy substituted derivatives.\textsuperscript{12,13} The \(para\)-methoxy substituted derivatives also showed the highest hole mobilities.\textsuperscript{12,13} The effect of the methoxy substitution in carbazole derivatives on their photophysical and photoelectrical properties, to the best of our knowledge, has not yet been studied. Electrochemical and thermal stability is another important property of organic semiconductors. This can lead to the corresponding device degradation.\textsuperscript{14-17} It is known that \(2,7\)-substituted derivatives of carbazole show irreversible oxidation with the formation of new carbazolyl derivative.\textsuperscript{18} By introducing methoxy or diphenylethenyl groups into C-3 and C-6 positions of carbazole moiety we obtain compounds which demonstrate reversible oxidation and higher electrochemical and thermal stability, in contrast to the non-substituted counterparts.\textsuperscript{8,9}

Results and discussion

Synthesis

Diphenylethenyl-substituted dimethoxycarbazoles (3a, 3b) were synthesized by condensation of the appropriate derivative of dimethoxycarbazole with diphenylethanaldehyde (Scheme 1). This synthetic method of diphenylethenyl-disubstituted derivatives is superior with respect of that reported earlier for the synthesis of the similar derivatives containing no methoxy groups.\textsuperscript{7} It does not require the preparation of diphenylethenyl borolane and bromination of carbazole.

Scheme 1. Synthesis of 3a and 3b.

The starting compound 2a was prepared by three steps. 2,7-Dimethoxycarbazole (1a) was obtained by an Ullmann-coupling followed by a Cadogan cyclization reaction using triphenylphosphine as reported in the literature.\textsuperscript{19,20} Alkylation with 2-ethylhexylbromide was performed by the conventional procedure.\textsuperscript{21} Compound 2b was synthesized starting from 3,6-dimethoxycarbazole (1b) which was prepared by bromination of carbazole with N-bromosuccinimide (NBS) in dimethylformamide (DMF), followed by the direct methoxide displacement of bromine\textsuperscript{22,23} and alkylation by the same procedure as mentioned above. The synthesized compounds were identified by elemental analysis, IR, \(^1\)H and \(^{13}\)C NMR, and MS. Compounds 3a, 3b were found to be soluble in common organic solvents such as tetrahydrofuran, toluene and chloroform.

Figure 1. ORTEP diagrams, packing in the crystals and the possible intermolecular charge-hopping channels of 3a-3b.
Crystal structures

According to quantum chemical calculations molecular structures of 2,7-dimethoxycarbazole derivatives (2a, 3a) exhibit relatively high ground state dipole moments (4.53 and 5.98 D, accordingly). At the same time the derivatives of 3,6-dimethoxycarbazole (2b, 3b) are non-polar with low ground state dipole moments (0.30 and 0.69 D). Therefore, one could expect much stronger intermolecular dipole–dipole interaction in case of crystals of 3a than for 3b. The thermal properties of the synthesized compounds were estimated by differential scanning calorimetry (DSC) and thermogravimetric analysis of the packing pattern of the molecules of molecular materials.

The DSC measurements showed that compounds 3a and 3b possess high thermal stability with 5% weight loss temperatures (T_d) of 376 °C and 405 °C, respectively. The DSC measurements showed that 3a and 3b are able to form molecular glasses. Compounds 3a and 3b were isolated after the synthesis as crystalline substances and their first DSC heating scans revealed endothermal melting signals (Figure 2). Due to the presence of stronger dipole–dipole interactions the crystals of 3a showed by 25 °C higher melting point than those of 3b. Compound 3b exhibited polymorphism which is rather often observed for organic glass forming molecular materials. The ability to form more than one crystal structure could be the result of the weak dipole-dipole interaction between the molecules of 3b. No crystallization was observed during the cooling scans, which indicated the transition from the melt to the glassy state. In the second and the following DSC heating scans 3a and 3b exhibited glass transitions at 70 and 71 °C, respectively. This observation shows that the linking topology of 3a-b has no effect on their glass transition temperatures.

Optical and photophysical properties

The normalized absorption and fluorescence spectra of the dilute solutions in THF and the solid films of 3a and 3b are shown in Figure 3. The optical and photophysical characteristics are summarized in Table 1. The absorption maxima of the dilute solutions of 3a and 3b were detected at 362 nm and 392 nm, respectively. UV-vis spectrum of 3b showed considerable bathochromic effect of 30 nm with respect to the spectrum of its counterpart 3a. These results provide evidence for more effective and prolonged conjugation length in 3b compared to 3a. Compounds 3a and 3b showed emission in a blue and green regions with the emission maxima at 473 and 501 nm, respectively. Fluorescence spectra of 3a and 3b exhibited considerable red shifts with respect to those of the starting compounds (2a and 2b, sup. info. Figure S2). Table 1. The absorption and emission maxima of the dilute solutions of 3a, 3b, sup. info. Figure S2).

Thermal properties

The thermal properties of the synthesized compounds were estimated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The thermal characteristics are collected in Table 1. Compounds 3a and 3b possess high thermal stability with 5% weight loss temperatures (T_d) of 376 °C and 405 °C, respectively. The DSC measurements showed that 3a and 3b are able to form molecular glasses. Compounds 3a and 3b were isolated after the synthesis as crystalline substances and their first DSC heating scans revealed endothermal melting signals (Figure 2). Due to the presence of stronger dipole–dipole interactions the crystals of 3a showed by 25 °C higher melting point than those of 3b. Compound 3b exhibited polymorphism which is rather often observed for organic glass forming molecular materials.
The target compounds 3a and 3b are characterized by long Stokes shifts (~110 nm) which implies that the structures of the emitting state and ground state are rather different. This difference apparently originates from the zwitterionic state of the excited molecules 3a-b. The absorption and emission spectra of the solvent casted solid amorphous films of 3a and 3b were found to be similar to the corresponding spectra of the solutions, but exhibited small red-shifts. Both the solid films and the dilute solutions of 3b showed higher fluorescence quantum yields as compared to those of 3a. This observation can be explained by the different zwitterionic states of 3,6-dimethoxy- and 2,7-dimethoxycarbazoles containing diphenylethenyl moieties. Compound 3a exhibited the phenomenon of aggregation induced emission which is illustrated by Figure 4a.

![Fluorescence spectra of the dispersions of 3a (a) and 3b (b) in water–THF mixtures (10^{-4}–10^{-3} M). The inset depicts the changes of fluorescence peak intensity. λ_ex = 350 nm.](image)

Figure 4. Fluorescence spectra of the dispersions of 3a (a) and 3b (b) in water–THF mixtures (10^{-4}–10^{-3} M). The inset depicts the changes of fluorescence peak intensity. λ_ex = 350 nm.

The FL intensity of the THF solution was very low and was almost unchanged when water was added up to 60% (v/v), and then started to increase sharply upon further addition of water. These results indicate that the molecules of compound 3a started to aggregate when the volume fraction of water reached 70%. Clearly, the fluorescence behavior of 3a is typical of an AIE luminogen. The high ground state dipole moment and high dipole-dipole interaction between the molecules of compound 3a results the restrictions of the molecular motions which can be a key factor explaining the aggregation induced emission. The X-ray analysis data of 3a (Figure 1) show that the neighboring dimers, which are arranged parallel but with the opposite induced dipole moments (IDM) of the excited state, can form configuration favorable for the formation of J-aggregates. This presumption is confirmed by fluorescence spectroscopy. The intensity maxima of aggregation induced emission are bathochromically shifted by ca. 15 nm compared to the emission maxima of dilute solutions in THF. The totally opposite effect of aggregation-caused quenching was observed for isomer 3b (Figure 4b). In case of 3b, the closest dimers are parallel and IDM (Figure 1) are of the opposite direction. However, the ground state dipole moment of 3b is very small (0.69 D). Therefore IDM is also small and there has no substantial effect on IDM of the surrounding molecules. For this reason no shift in fluorescence spectra was observed and the aggregation induced quenching was monitored. Figure 5 shows fluorescence decay curves of the dilute THF solutions and of the solid films of 3a and 3b.

![Fluorescence decay curves of the dilute (10^{-5} M) solutions in THF and of the solid films of 3a (a,b) and 3b (c,d). Blue lines indicate single or double exponential fits to the experimental data. Fluorescence lifetimes (τ) are indicated.](image)

Figure 5. Fluorescence decay curves of the dilute (10^{-5} M) solutions in THF and of the solid films of 3a (a,b) and 3b (c,d). Blue lines indicate single or double exponential fits to the experimental data. Fluorescence lifetimes (τ) are indicated.

### Table 1. Thermal, optical and photophysical characteristics of compounds 3a and 3b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_m / T_g</th>
<th>λ_{max, sol}</th>
<th>λ_{max, film}</th>
<th>Stokes shift, nm</th>
<th>Φ_{film}</th>
<th>Φ_{sol}</th>
<th>τ_{film}</th>
<th>k_{film}</th>
<th>k_{sol}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>168 / 70 / 405</td>
<td>362 / 365</td>
<td>473 / 476</td>
<td>111</td>
<td>1.20 / 2.20</td>
<td>0.10 (96%), 5.48 (4%) / 0.28 (86%), 3.7 (14%)</td>
<td>1.08 / 1.18</td>
<td>1.2 / 0.8</td>
<td>98.8 / 34.9</td>
</tr>
<tr>
<td>3b</td>
<td>128,143 / 71 / 376</td>
<td>392 / 396</td>
<td>501 / 510</td>
<td>109</td>
<td>34.9 / 11.8</td>
<td>3.96 / 0.69 (77%), 3.03 (23%)</td>
<td>1.07 / 1.21</td>
<td>0.9 / 1.7</td>
<td>1.6 / 12.8</td>
</tr>
</tbody>
</table>

*a* - determined by DSC, scan rate 10 °C/min, N_{2} atmosphere; *b* - 5% weight loss determined by TGA, heating rate 10 °C/min, N_{2} atmosphere; *c* counted for the most prevalent state; *d* the chi-square values show the quality of the fit.
The derivative 3a exhibited double exponential fluorescence decays originating from two different molecular excited states with the fluorescence life times (τ) of 0.10 and 5.48 ns for the solution and 0.28 ns 3.7 ns for the film with χ2 ranging from 1.08 to 1.18 respectively. The fluorescence decay of the film of compound 3b can also be described by the double exponential fit with the fluorescence lifetimes of 0.69 ns and 3.03 ns with χ2 value of 1.21, while fluorescence decay of the dilute solution of 3b was adequately described by the single exponential curve with the lifetime of 3.96 ns (χ2 = 1.07). We presume that the emission with the shorter life time (0.1-0.7 ns) originates from the excited dimethoxycarbazole moiety, while the emission with the longer life time (3.0-5.5 ns) originates from the excited zwitterionic states of 3a-b derivatives.

To unveil the contributions of the competing radiative and nonradiative relaxation processes, we calculated the radiative (k_r) and nonradiative (k_nr) decay rate constants from the excited state using the obtained values of Φ and τ by the following relations: k_r = Φ / τ, k_nr = (1-Φ) / τ. The results are summarized in Table 1. Interestingly, the calculated k_r and k_nr values of 3a-b were found to be highly dependent on the position of methoxy and diphenylethenyl moieties. For both the isomers 3a-b the k_r values obtained for the solutions and the solid films showed no any big differences, while the values of k_nr observed for the solutions and films of 3a were found to be significantly higher than those of 3b. Thus the nonradiative processes are predominant in the relaxation processes of excited states of compound 3a.

In order to get more insight on the nature of the absorption bands of 3a-b, TD-DFT calculations were performed. The significant similarities between the theoretical and experimental UV-vis spectra of 3a-b were observed (Figure 6). The excitation energies and oscillator strengths for the molecules 3a-b are presented in Table 2.

![Image](329x293 to 420x339)

**Table 2.** Properties of the selected transitions and their contribution to the UV-vis spectra of 3a-b calculated at the B3LYP/6-31G(d,p)/PCM(THF) level.

<table>
<thead>
<tr>
<th>Exp. UV λ_0 nm</th>
<th>Cal UV λ nm</th>
<th>Tr.</th>
<th>Osc. Stren. a.u.</th>
<th>Contributions (more than 20%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>362</td>
<td>376</td>
<td>1</td>
<td>0.637</td>
<td>H→L (95%)</td>
</tr>
<tr>
<td>362</td>
<td>326</td>
<td>2</td>
<td>0.254</td>
<td>H→L (90%)</td>
</tr>
<tr>
<td>312</td>
<td>307</td>
<td>5</td>
<td>0.443</td>
<td>H→L+2 (77%)</td>
</tr>
<tr>
<td>296</td>
<td>6</td>
<td>6</td>
<td>0.265</td>
<td>H→L+2 (63%)</td>
</tr>
<tr>
<td>392</td>
<td>434</td>
<td>1</td>
<td>0.181</td>
<td>H→L (63%),H→→L (35%)</td>
</tr>
<tr>
<td>317</td>
<td>327</td>
<td>2</td>
<td>1.363</td>
<td>H→L (35%),H→→L (63%)</td>
</tr>
<tr>
<td>317</td>
<td>327</td>
<td>5</td>
<td>0.253</td>
<td>H→L (67%)</td>
</tr>
</tbody>
</table>

The absorption band with the similar wavelength for N-substituted 2,7-dimethoxycarbazole was observed experimentally. Therefore, these excitations are assigned to π-π’ transition in the dimethoxycarbazole moiety.

![Image](333x435 to 418x490)

**Figure 6.** Comparison of the experimental (black-dot) and calculated 3a and 3b (red) UV-vis spectra at the B3LYP/6-31G(d,p)/PCM(THF) level (σ = 0.25 eV); bars represent the oscillator strength.

The lowest energy band for 3a is influenced by two transitions S_0→S_1 and S_0→S_2 with the maxima of ε at 376 and 362 nm, respectively. The first excitation with the oscillator strength of 0.637 for 3a corresponds to the HOMO→LUMO transition (figure 7). This transition is localized on the diphenylethenyl and dimethoxycarbazole moieties. Therefore, this excitation corresponds to π-π’ transition for both conjugated chromophores. The absorption band with the maximum at 312 nm of 3a corresponds to the calculated S_0→S_5 and S_0→S_6 transitions. The S_0→S_5 transition, according to the nomenclature of Platt, is named as 1_La transition because the orbitals on the carbazole moiety are oriented along the symmetry axis.

![Image](337x238 to 412x277)

**Figure 7.** The computed spatial distributions of HOMO and LUMO orbitals for 3a and 3b.

The situation with 3b was found to be different. The lowest energy absorption band of 3b is influenced by two lower energy transitions compared to those of 3a, i.e. S_0→S_1 and S_0→S_2 transitions which manifest themselves at 434 and 425 nm, respectively. The attachment of methoxy groups at C_p3 and Cp6 positions of the carbazole moiety and a negative charge is on diphenylethenyl moiety. The first S_0→S_1 excitation with the oscillator strength
of 0.181 a.u. of 3b corresponds to the HOMO→LUMO and HOMO-1→LUMO transitions with 63 and 35 % contributions, respectively (figure 7). This excitation is a mixture of the π-π* transitions of both conjugated chromophores and ICT transition from carbazole to diphenylethenyl moieties. In other words, S2→S1 can be regarded as zwitterionic transition in nature.

The electron density in the carbazole ring is delocalized symmetrically because of the ICT transition. The second S2→S1 excitation at 425 nm corresponds to the same S2→S1 transition, but the orbital contributions are 35 and 63 %, respectively. Similarly, this excitation is a mixture of the π-π* transition of both conjugated chromophores and ICT transition from the carbazole to the diphenylethenyl moiety. The obtained oscillator strength (0.181 a.u) of the first excitation of 3b is lower than that of 3a. The UV absorption band at 317 nm is influenced by S0→S1 excitation which corresponds to the HOMO-2→LUMO transition. This S0→S1 excitation is the mixture of π-π* transitions in the diphenylethenyl and carbazole chromophores.

The energies of HOMO and LUMO of 3a-b were calculated using the same method as for UV-vis spectra. The energies of HOMO and LUMO for 3a were found to be -4.97 eV and -1.16 eV, respectively, and those observed for 3b were -4.93 eV and -1.60 eV, respectively. The calculated HOMO energy levels are in good agreement with the experimental values (Table 3).

### Electrochemical properties and ionization potentials

Electrochemical properties of the solutions of the compounds in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte were studied by the cyclic voltammetry (CV) using Ag/AgNO3 as the reference electrode and a Pt wire counter electrode. The electrochemical characteristics are summarized in Table 3. The CV curves of 3a-b are shown in Figure 8.

![Figure 8. Cyclic voltammograms of 3a-b at 10⁻³ mol L⁻¹ in a solution of argon-purged TBAP (0.1M) in CH₂Cl₂, v= 50 mV/s.](image)

No reduction waves was observed down to ca -1.5 V in CV curves of all the studied compounds. However, all the compounds showed the oxidation waves up to ca 0.31 V. The oxidation was found to be irreversible only for compound 2a (Figure S2), having unsubstituted C-3 and C-6 positions of carbazole ring. It was found to be quasi-reversible for 2b. Irreversible oxidation of 2a was followed by coupling of carbazole radical cations because of higher electron spin density at C-3 and C-6 positions and formation of new carbazolyl-containing compounds.

The oxidation of 3a and 3b was found to be reversible up to ca 0.55 V. Precursor 2b and compounds 3a-b showed oxidation peaks at 0.51V, 0.45V and 0.43V, respectively, and after five repeated oxidation and reduction cycles their CV curves did not change. The oxidation of compound 2a started at 0.41 V and, subsequently, the oxidation peak at 0.53 V was observed. The HOMO energy levels were determined using the relationship E\text{HOMO}(eV) = -1.4E\text{onset,ox}(V) - 4.6. The HOMO energy levels of the derivatives 3a and 3b were found to be comparable and a little higher with respect to those of compounds 2a-b.

<table>
<thead>
<tr>
<th>E\text{onset,ox} (V)</th>
<th>E\text{HOMO, DFT} (eV)</th>
<th>E\text{IP} (eV)</th>
<th>IP, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a 0.41</td>
<td>-5.17 / -</td>
<td>3.69</td>
<td>5.68</td>
</tr>
<tr>
<td>2b 0.35</td>
<td>-5.09 / -</td>
<td>3.16</td>
<td>5.50</td>
</tr>
<tr>
<td>3a 0.33</td>
<td>-5.06 / -4.97</td>
<td>3.05</td>
<td>5.38</td>
</tr>
<tr>
<td>3b 0.31</td>
<td>-5.03 / -4.93</td>
<td>2.72</td>
<td>5.41</td>
</tr>
</tbody>
</table>

*Onset, oxidation and reduction potentials vs Fe. E\text{HOMO}(eV) = -1.4E\text{onset,ox}(V) - 4.6, where E\text{onset,ox} was determined by solution-based cyclic voltammetry. The optical bandgap energies estimated from the absorption edges. Ionization energy (IP) for the solid films was measured by the electron photoemission in air method. Irreversible oxidation.

The HOMO levels acquired from the DFT calculations and from CV measurements were found to be in good agreement for compounds 3a-b and showed higher values compared to the diphenylethenyl-substituted derivatives of carbazole containing no methoxy groups.

The ionization potentials (IP) of the synthesized compounds were measured by the electron photoemission in air technique. The results are presented in Table 3. Usually the photoemission experiments are carried out in vacuum but, in our case, the investigated organic compounds were stable with respect to oxygen and the measurements could be carried out in air. All the synthesized compounds showed lower IP values compared to compounds containing electronically isolated carbazole moieties having no substituents at the aromatic rings. Methoxy-disubstituted carbazoles (2a,b) showed a little higher IP than the target compounds (3a,b). Compounds 3a and 3b were found to exhibit the comparable IP values. This observation proves our earlier finding that the alteration of the substitution patterns of carbazole moiety practically does not affect the ionization energy values.

### Charge-transporting properties

The hole-transporting properties of the layers of compounds 3a and 3b were studied by the xerographic time-of-flight (XTOF) and the time of flight (TOF) techniques. The sample of compound 3b for the XTOF measurements was prepared by drop casting technique with the layer thickness of ca. 2.5 µm. Because of high disposition to crystallization it was not possible to obtain good quality amorphous film of compound 3a using the same film preparation method. The value of hole drift mobilities of the layer 3b was found to be 4.1×10⁻³ cm²/Vs at electric field of 1.23×10⁶ V/cm. Figure 9a shows hole photocurrent transients on log-log and linear ( insets) scales that were observed for the layer of 3b. No transit times were detect-
Figure 9. XTOF transients for the drop-casted layer of 3b (a) and TOF transients for the vacuum deposited layers of 3a (b) and 3b (c). The insets show transient curves in the linear plot.

The zero field hole drift mobility (µ0) and the field dependence parameter (α) was obtained by the extrapolation of the electric-field dependences of the hole drift mobilities to the zero electric field (Figure 10, Table 4):

Figure 10 shows the electric field dependencies of hole-drift mobility values (µ) for the layers of 3a and 3b. The logarithm of the hole-drift mobility values showed linear dependencies on the square root of the electric field. The similar characteristic dependences were observed for many amorphous (disordered) organic semiconductors and were explained in terms of the Bassler and Borsenberger model.

The zero field hole drift mobility (µ0) and the field dependence parameter (α) was obtained by the extrapolation of the electric-field dependences of the hole drift mobilities to the zero electric field (Figure 10, Table 4):

<table>
<thead>
<tr>
<th>µ0 / µ0 in free, cm²/Vs</th>
<th>µ, cm²/Vs</th>
<th>α, 10⁻³ cm/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>1.8×10⁻³ / 7.7×10⁻³</td>
<td>2.6×10⁻⁴</td>
</tr>
<tr>
<td>3b</td>
<td>1.4×10⁻³ / 1.5×10⁻³</td>
<td>6.2×10⁻⁴</td>
</tr>
</tbody>
</table>

Table 4. The hole mobility data for compounds 3a and 3b.

Compound 3b showed higher hole mobility and a little lower field dependence parameter than 3a.

To get deeper insight into the hole-transporting properties of the isomers 3a-b the theoretical calculations were performed. The crystal structure to the large extent determines the charge carrier transport pathways and charge mobilities in organic molecular crystals. For some compounds the mesoscopically connected networks in the amorphous films are possible even without a periodic order.

In this work, the crystal structures of 3a-b were used to generate a wide variety of possible hopping pathways (dimmers) showed in Figure 1 and Figure S4. According to the Holstein small polaron limit, the charge is localized on a single molecule. The standard Marcus-Hush model (1) describes the rate of charge transfer between molecules:

\[
k_i = \frac{2\pi}{\hbar} |H_i|^2 \frac{1}{\sqrt{4\pi k_B T}} \exp \left( -\frac{(\lambda + \Delta G^0)^2}{4k_B T} \right)
\]

where \(k_i\) is the electron transfer rate constant for pathway \(i\), \(H_i\) is the electronic coupling between the initial and final states, \(\lambda\) is the reorganization energy (\(\lambda = \lambda_{in} + \lambda_{out}\), i.e. the sum of both inner and outer-sphere), \(\Delta G^0\) is the total Gibbs free energy change for the electron transfer reaction, \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature (298 K).

Many theoretical and experimental studies concerning \(\lambda\) of single molecules were reported. However, relevant for charge mobility is the charge reorganization energy of organic solids.
The charge reorganization energy is the sum of inter- and intramolecular effects, where the intramolecular effects dominate the charge–phonon coupling. However, their energy is very small (10–100 meV) and the crucial point to access the impact to charge mobility in the solid state is not performed.\(^\text{35}\)

The other factor is a charge carrier polarization energy. The polarization energy is significant for the organic materials and includes both an electrostatic and a polarization contribution.\(^\text{47}\) The polarization energy is defined as the difference between the solid state and gas phase values of ionization potential.\(^\text{48}\)

We assume that the Gibbs free energy (\(\Delta G^0\)) is approximately equal to the polarization energy for one dimension of the crystal for holes and can be described as \(\Delta G^0 \approx -\frac{1}{2}P^r\). The \(P^r\) energy can be estimated theoretically from the stand-alone molecule ionization potential (IP) (it can be obtained from vertical IP calculation in vacuum) and the IP of the solid state (it can be obtained from vertical IP calculation in one crystal lattice) using the formula \(P^r = IP_{\text{solid}} - IP_{\text{vacuum}}\). The calculated \(P^r\) energy values were found to be \(-0.69\) eV for \(3a\) and \(-0.57\) eV for \(3b\).

The internal reorganization energy (\(\lambda_{in}\)) values were calculated using the normal-mode analysis method.\(^\text{49}\) This value for the model compound was calculated at the B3LYP/6-311+G(d,p) level in vacuum according to the following equation:

\[
\lambda_{in} = [E^a(g^0) - E^b(g^0)] + [E^a(g^0) - E^b(g^0)]
\]

In this equation, \(E\) corresponds to the energy of the neutral molecule (\(g^0\)) in the geometry of the cation/anionic species (\(g^0\)). The reorganization energies of \(3a\) and \(3b\) for holes (\(\lambda_h\)) were found to be 0.32 and 0.26 eV, and for electrons (\(\lambda_e\)) they were found to be 0.31 and 0.36 eV. These results show that the reorganization energies for holes and electrons of \(3a\) and \(3b\) are somewhat similar.

The electronic coupling (transfer) integrals \(H_i\) for the pathways (see Figure 1) were estimated using the energy splitting in dimmer method (3) at the long-range corrected hybrid density functional wb97X-D\(^3\) and 6-31G(d) basis set using the Spartan’14 package in vacuum:

\[
H_i = \frac{E_{L+1(H)} - E_{L(H-1)}}{2}
\]

where \(E_{L+1}\) and \(E_{L+1}\) are the energies of the LUMO and LUMO+1 (HOMO and HOMO–1) levels taken from the neutral state from the crystal structures of \(3a\) and \(3b\). The molecules in the crystal structures were not optimized. The 2-ethylhexyl chains were approximated by methyl groups to reduce computational time for the calculation of the reorganization energies and the electronic coupling integrals.

The diffusion coefficient (\(D\)) for migration of electrons or holes in the dimmers is given by the equation (4):

\[
D = \frac{1}{2N} \sum \frac{d_i^2}{k_i^2}
\]

where \(N\) is the dimensionality of the crystal (\(N=3\)) and \(d_i\) is the distance between the dimmers mass centers. Then, according to the Einstein equation (5), the final drift mobility (\(\mu_0\)) in the absence of electric field was calculated using the single-step approximation:

\[
\mu_0 = \frac{e \cdot D}{k^\text{B}T}
\]
higher induced dipole moment may cause lower charge mobility.

**Experimental**

**Instrumentation**

\(^1\)H and \(^13\)C NMR spectra were recorded using Varian Unity Inova (300 MHz \((^1\)H), 75.4 MHz \((^13\)C)) and Bruker Avance III 400 spectrometer (400 MHz \((^1\)H), 100 MHz \((^13\)C)) apparatus. Chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane or internal (NMR) solvent signal. Infrared (IR) spectra were recorded on Perkin Elmer Spectrum GX spectrometer. The spectra of the solid compounds were recorded using KBr pellets. Mass (MS) spectra were obtained on Bruker maxis 4G. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental. Melting points (m.p.) of the synthesized compounds were estimated using Electrothermal Mel-Temp apparatus. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental.

For X-ray crystallography analysis diffraction data were collected on a Bruker-Nonius Kappa CCD single diffractometer using graphite monochromated Mo-Kα radiation (\(λ = 0.71073 \ Å\)). The crystal structure was solved by direct methods [SIR-97] and reﬁned by full-matrix least squares [SHELXL-97]. Mercury 3.3 software was used for molecular graphics.

UV spectra were recorded with Aventes AvaSpec-2048XL spectrometer. Fluorescence (FL) spectra and fluorescence decay curves of the dilute THF solutions and of the solid films of the compounds were recorded by Edinburgh Instruments FLS980 spectrometer. Fluorescence quantum yields were measured using integrated sphere calibrated with two standards: quinine sulfate in 0.1 M H₂SO₄ and rhodamine 6G in ethanol.

DSC measurements were carried out in a nitrogen atmosphere with a Perkin Elmer at DSC 8500 equipment at heating rate of 10 °C/min. TGA was performed on a Perkin Elmer TGA 400 apparatus in a nitrogen atmosphere at a heating rate of 10 °C/min.

Cyclic voltammetry measurements were carried out by a three-electrode assembly cell from a Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The samples for the measurements were prepared on precleaned ITO coated glass substrates from Sigma-Aldrich with a sheet resistance of 70–100 Ω/sq. Then ITO electrodes were evaporated at a pressure below 5×10⁻⁵ mbar. ITO-coated glass substrates were cleaned by successive washing with deionized water, THF, and trichloroethane in an ultrasonic bath. Each operation lasted over 5 minutes. The deposition rates of materials and Al were 0.2–0.3 Å/s and ~15 Å/s, respectively. The thicknesses of the films of target compounds vary from 0.65 to 2.5 µm, respectively, and active area of that obtained samples was 6 mm². The layers were undertaken by exciting materials through the ITO layer. The charge carriers were generated at the layer surface by illumination with a Nd:YAG laser EKSPLA NL300 (pulse duration was 3-6 ns, wavelength 355 nm). The total photogenerated charge was kept small enough to avoid space charge effects. The electronic time response of the measurement circuit \((τ = RC)\) was always selected to be smaller than the transit time \((τ = τ_o)\). The transit time \(τ_o\) with the applied bias \((V)\) indicates the passage of holes through the entire thickness of the cell \((d)\) and enables determination of the hole mobility as \(μ=ε/(τ_o)\). The experimental setup consisted of a delay generator Tektronix AFG 3102C and a digital storage oscilloscope Tektronix TDS 3032C.

**Computational details**

Time dependent density function (TD-DFT) calculations of UV-vis spectra of 3a-b were performed with the Gaussian 09 software package. The geometries of the molecules of 3a and 3b were optimized from X-ray data as the starting point using B3LYP functional and 6-31G(d,p) basis set, followed by calculations of their harmonic vibrational frequencies to verify their stability. All the calculated vibrational frequencies are real, which indicates the true minimum of the total energy on the potential energy hypersurface. The alkyl chains were approximated by methyl groups to reduce the computational time. The simulations were performed for THF solutions using a polarizable continuum model (IEFPCM) to assess the influence of the solvent polarity onto the molecular vertical excitation energies. The half-width at 1/e of the peak maximum \(σ\) value of 0.25 eV was used in this work. Up to 10 lowest energies of the excited states were calculated.

**Materials**

Carbazole, N-bromosuccinimide, chloroform, potassium hydroxide, copper(I) iodide, dry methanol, dry dimethylformamide (DMF), sodium, 2-ethylhexylbromide, potassium carbonate, acetone, diphenylacetalddehyde, (rac)-camphor-10-sulfonic acid (CSA) were purchased from Aldrich and used as received without further purification.

2,7-Dimethoxycarbazole (1a, WF=227 g/mol, m.p.: 270-272 °C, lit.: 272-274 °C) was achieved by an Ullmann-coupling and a Cadogan cyclization as reported in the literature.\(^{19,20}\) \(^1\)H NMR (400 MHz, DMSO) δ 10.98 (s, 1H), 7.83 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 2.2 Hz, 2H), 6.72 (dd, J = 8.5, 2.3 Hz, 2H), 3.82 (s, 6H). \(^13\)C NMR (101 MHz, DMSO) δ 157.6, 141.0, 120.0, 116.5, 107.3, 94.7, 55.2.

3,6-Dimethoxycarbazole (1b, WF=227 g/mol, m.p.: 130-131 °C, lit.: 131-133 °C) was prepared by bromination and methoxylation reactions by the procedures described in literature.\(^{22,23}\) \(^1\)H NMR (300 MHz, CDCl₃) δ 8.8, 0.5 Hz, 2H), 7.03 (dd, J = 8.8, 2.5 Hz, 2H), 3.91 (s, 6H). \(^13\)C NMR (75 MHz, CDCl₃) δ 153.7, 135.4, 123.8, 115.3, 102.9, 94.7, 55.2.

9-(2-Ethylhexyl)-2,7-dimethoxycarbazole (2a) was prepared by the reaction of 2,7-dimethoxycarbazole with an excess of 2-ethylhexylbromide under the basic conditions in the presence of a phase transfer catalyst. 2,7-Dimethoxycarbazole (1a, 0.40 g, 1.8 mmol), 2-ethylhexylbromide (0.38 g, 2.1 mmol), potassium carbonate (0.10 g, 0.70 mmol), potassium hydroxide (0.30 g, 5.3 mmol) and catalytic amount of tetrabutylammonium hydrogensulfate were refluxed (2 h) in acetonitrile (14 ml). After TLC (acetonewater, 2:1), the resulting slurry was filtered and the solid residue was washed with methanol and tetrahydrofuran.
1:10) control, when the starting compound 1a disappeared, the reaction was terminated, cooled down to the room temperature, treated with ethyl acetate and washed with distilled water. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and the solvents were removed. The residue was purified by silica-gel column chromatography using the mixture of hexane and acetone (20:1) as the eluent. The yield of yellow crystals was 31 % (0.32 g, FW = 695 g/mol, m.p.: 144-145 °C).

1H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.32 – 7.16 (m, 24H), 6.59 (s, 2H), 3.89 (s, 6H), 3.19 – 3.07 (m, 2H), 1.53 – 1.47 (m, 1H), 1.14 – 1.05 (m, 2H), 0.97 – 0.87 (m, 3H), 0.79 (t, J = 7.3 Hz, 3H), 0.71 – 0.64 (m, 2H), 0.52 (t, J = 7.3 Hz, 3H). 13C NMR (100 MHz, CDCl$_3$, δ, ppm): 152.1, 144.0, 141.8, 141.2, 136.2, 130.8, 128.8, 128.2, 128.0, 127.4, 127.2, 125.7, 124.3, 121.6, 110.8, 101.0, 56.5, 47.4, 38.5, 30.6, 28.4, 27.1, 24.0, 23.4, 14.3, 10.9. v$_{\text{max}}$(KBr): 3077, 3054, 3021 (aromatic C = H, 3000-3000 cm$^{-1}$); 2954, 2930, 2870, 2858 (aliphatic C = H, 3000-2850 cm$^{-1}$); 1597, 1490, 1470, 1429 (C=C in Ar, 1600-1585, 1500-1400 cm$^{-1}$); 1310, 1269 (C=N in Ar, 1335-1250 cm$^{-1}$); 1201, 1160, 1063 (C–O–C, 1250-1050 cm$^{-1}$); 823, 774, 764, 696 (C–H in Ar, 900-675 cm$^{-1}$). EI-MS m/z 695.3740 (M$^+$) (calcd 695.3763). Anal. Caled for C$_{30}$H$_{29}$N$_2$O$_2$: C 86.19, H 7.17, N 2.08. Found (%): C 86.19, H 7.17, N 2.08.

The structures of 3a-b were also proven by X-ray crystallography. The single-crystal of 3a suitable for X-ray diffraction was grown from dilute hexane/THF solution while the crystal for 3b was grown from the dilute methanol/THF solution at the room temperature. Crystal visualization and analysis were conducted using Mercury 3.3. Crystallographic data for compounds 3a and 3b are stored in open-access collection of crystal structures database in the Cambridge Crystallographic Data Centre with the following numbers: 1042467 and 1042468. These data can be obtained via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +4 4 1223 326033.

Conclusions
2,7-Dimethoxy and 3,6-dimethoxy carbazoles derivatives possessing diphenylethenyl moieties (3a-b) were synthesized by condensation of the corresponding derivative of dimethoxy carbazole (2a-b) with diphenylacetaldehyde. The structures of the synthesized compounds were proven by X-ray crystallography. Both of the isomers exhibit high thermal stability and form molecular glasses. Since the majority of molecules in crystal structure of 3a form J-aggregates, this compound showed the effect of aggregation-induced emission, while the other isomer, i.e. 3b, showed the effect of aggregation-caused quenching. Both target compounds (3a-b) showed comparable ionization potentials of ca. 5.4 eV, which are lower compared to those of the parent dimethoxy carbazoles (2a-b). The derivative 3b showed superior charge transporting properties relative to its counterpart 3a. The time-of-flight hole drift mobilities in its amorphous layers exceeded 10$^{-5}$ cm$^2$/Vs at high electric fields. The pronounced differences in charge carrier mobility, thermal and optical properties were justified by the theoretical study using DFT and TD-DFT calculations. According to these results, the target molecules of 3a were found to be highly polar with the ground state dipole moment of 5.98 D, in contrast to the molecules of 3b having the ground state dipole moment of ca. 0.69 D. The polarity was shown to a crucial effect on the molecular arrangement in the crystals, consequently on the thermal transitions (polymorphism) and on the charge-transporting properties of the isomers.

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