SOLUBLE DIKETO-PYRROLO-PYRROLES FOR ORGANIC ELECTRONICS AND PHOTONICS

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Abstract
Novel derivatives of DPPs and PCs with different side groups were synthesized to increase their solubility. Simultaneously, groups with various electron donating or withdrawing ability were linked to the basic pyrrolinone core to improve some of their optical and electrical properties such as absorption molar coefficient, conductivity, photogeneration yield and others. Thermal and thermooxidative stability was studied by thermal gravimetry and differential scanning calorimetry in either nitrogen or air. Relationship between the molecular structure of DPPs and PCs, organic thin film morphology and their optical and optoelectronic properties such as charge transport and photogeneration were studied. The experimental characterizations were accompanied with quantum chemical calculations.

It was shown, that depending on the side groups substitution, studied materials exhibit high molar absorption coefficient as well as high quantum yield of fluorescence or significant quantum yield of photogeneration. Some derivatives exhibit gas sensing properties. In spite of the fact, that most of the derivatives exhibit hole conductivity, the derivatives with significant electron conductivity were prepared recently in our labs. These properties together with chemical, light and thermal stability and reasonable solubility predestines them as potential candidates for printed electronics and optical applications.

Key words:
Organic semiconductors, Nanotechnology, Organic electronics, Photonics

1. INTRODUCTION
Nowadays, we can see a strong effort in seeking for highly performing materials for cheap organic electronics. Together with high performance of the materials, the usual second requirement is their high photo- and thermal- stability. Among other materials, the diketo-pyrrolo-pyrroles (DPPs) are suitable candidates due to these requirements. DPPs were widely used in inks and paints for their great colour properties. In recent years interest of DPPs increases in the field of optical and electrical application for the great fluorescent properties and good charge carrier mobility. Therefore a several tens of soluble derivatives of DPPs were prepared and investigated with respect to their molecular structure.

2. WET DEPOSITION: NEED FOR SOLUBILITY
The DPPs are insoluble in majority of common solvents. Whilst this is favourable for many applications, the ability to solubilize the compounds would offer the possibility of using wet solution-based techniques (spin-coating, drop-casting, inkjet printing, etc.) to prepare organic electronic devices from DPPs. Therefore, we performed study targeting to obtain solubilised DPPs [1]. One reason for their insolubility is the existence of H-bonds between the –NH group and oxygen (see the parent structure in Figure 1). Since the basic DPP
core is perfectly planar, $\pi-\pi$ electron overlap occurs in the solid state and also contributes to their insolubility. These interactions can be so strong as to impart colour change between the solid and dissolve forms and influence other properties, such as fluorescence and Stokes shift [2]. It is therefore clear, that modified solubility can be achieved either through $N$-substitution and/or disruption of molecular planarity [1].

We designed and investigated group of several DPP derivatives in order to increase the solubility for utilization of these materials as the active media in organic light emitting diodes (OLEDs) [1]. The DPP itself has a high quantum yield of fluorescence ($\Phi_F$) which is the key prerequisite for this application. To alter the solubility we used the $N$-substitution by different alkyls (R$_1$ and R$_2$ in Figure 1).

The quantum mechanical computations were used to obtain optimised conformations. The results shows, that the $N$-substitution influences the molecular geometry of the central DPP unit. The most important conformational parameters are the torsion angles $\alpha$ and $\beta$ of the phenyls (see Figure 1). While the unsubstituted DPP molecule is planar $\alpha = \beta = 0^\circ$, derivatives with substitution on both nitrogens possess significantly rotated phenyl groups. For the unsymmetrically substituted ones, only the phenyl next to the substituted nitrogen atom is rotated. Phenyl group rotation significantly reduces the charge transfer integral between phenyls and the central DPP unit. Consequently the effective extent of conjugation is decreased due to the reduction of charge transfer integral between phenyls and central pyrrolo-pyrrole part. Therefore, many electronic properties like absorption and luminescence are modified.

3. MULTICOLOUR EMISSION BY SUBSTITUENT TUNING

Various electronic applications require materials with different energy of electronic states and transitions. For example, to tune the colour of emitted light one has to utilise materials with wide band-gap (blue), small-band gap (red) and also in between (e.g. green). The possibility to have all of the emitters from one family (having not too much different structure) is particularly favourable for white light emitting diodes due to the reduction of possible structural defects. Another example might be the organic solar cells where the band-gap should be matched to the solar radiation in order to maximize the performance. And finally the charge conducting layers have to have matched the positions of the bands with the electrodes to allow for efficient charge injection. Therefore, we modified the DPP to obtain such multicolour emission by substituent tuning [3].

In case of organic semiconductors, the spectral engineering can be done by introduction of polar substituents into organic chromophores which causes a redistribution of electronic density in both the ground state and the excited state. This can strongly modify their absorption and fluorescence properties [4]. The important parameters such as positions of the electron and/or hole transport levels, the absorption coefficients and fluorescence quantum yields, etc. are modified. Furthermore, the push–pull substituted organic $\pi$ conjugated compounds are at the centre of interest of physicists, because they can produce strong second-order nonlinear optical effects [5]. On the other hand, quadrupolar chromophores are suitable for producing NLO behaviour, which we also demonstrated [6]. As organic pigments generally represent photostable systems, their modification by introduction of polar substituents to get dipolar or quadrupolar molecules is very promising in this respect.

We investigated the effect of electron-donor (piperidino) and electron-acceptor (cyano) groups attached to the phenyls (R$_3$ and R$_4$ in Figure 1) on the electronic spectra both, experimentally and theoretically [3].

It was found, that in general, cyano group stabilizes both phenyl molecular orbitals, while piperidino group destabilizes them (and even to a greater extent). An electron-donor substituent increases the electron density on the phenyl group to which it is attached, and on acceptor C=O group of the second pyrrolinone ring in HOMO, while in LUMO further CT is observed to the opposite phenyl group. This indicates the electron-acceptor character of the whole central dipyrrolinone is mainly localized on keto groups.

The absorption spectra show poor resolution of vibronic structure in the case of asymmetrically piperidino substituted and push-pull piperidino–cyano substituted compounds. We ascribed this to the significantly higher dipole moment interacting with the polar solvent by dipole–dipole interaction.
The fluorescence spectra of DPPs usually show small Stokes shifts, which are significantly increased by N-substitution (e.g. alkylation) inducing higher degree of nonplanarity [1]. Thus the N-substituted derivatives are promising with respect to applications like OLED, laser, etc.

![Figure 1](image)

**Fig 1.** The basic structure of 3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4 dione, also known as DPP (R₁=R₂=R₃=R₄=H) and the definition of the phenyl torsion angles α and β.

4. **SOLUBLE SPECTRALLY TUNED DPP DERIVATIVES**

For practical applications also other properties than the main functionality are important. Therefore, we combined the spectral tuning with improved solubility to obtain materials for cheap wet solution based production with precisely tuned energetic states [7] and [8].

We showed also for other electron-donating group (dimethylamin), that the molar absorption coefficient $\varepsilon$ increased and was accompanied with strong bathochromic shift. This behaviour implies that charge separation occurs via electron delocalization leading to creation of permanent dipole moment. Blurring of vibration structure in absorption spectra of mono substituted derivatives imply interaction with polar dimethylsulfoxide (DMSO) and shows polar character of the mono substituted DPP [7].

Introduction of the N-alkylation led to the decrease of the $\varepsilon$ and hypsochromic shift. First N-alkylation causes only small change, whereas second alkylation lead to the value of $\varepsilon$ almost similar to the parent, non N-substituted, DPP. This decrease is accompanied by the hypsochromic shift and loss of vibrational structure. We proposed the same mechanism as for the N-alkylated only derivatives discussed above: the N-alkylation causes rotation of the phenyls and consequently breaks the molecule symmetry, and hence, the effective conjugation and increases the polarity.

The introduction of one electron-donating group to the DPP led to a smaller fluorescence quantum yield (PLQY) compared to the N,N-disubstituted molecules. This is in accordance with the obtained values of the absorption coefficient: the polarity of the mono-substituted molecule is higher compared to the symmetric ones. The observed higher Stokes shifts for mono substituted than to the di-substituted DPP also confirmed this hypothesis. The N-alkylation of the functionalised DPPs by electron-donating or withdrawing groups caused further decrease of PLQY accompanied with increasing Stokes shift similarly to the N-alkylated only derivatives.

The calculated molecular parameters of the studied derivatives showed that the substitution of phenyls by donor or acceptor groups has almost no influence on the phenyl torsion angles and the molecular conformation of the central DPP unit. However, it leads to the bathochromic shift of the absorption and luminescence peaks due to the increased effective extent of the conjugation and support the conclusions drawn above.

The studied DPP derivatives with N-substitution show pronounced solid state fluorescence [8], on the contrary to any of their non-alkylated precursors. The fluorescence of symmetrically phenyl substituted
derivatives is strong, easily observable by naked eye under UV irradiation. Solid-state fluorescence of push-pull derivative is almost not observable partly because of its significantly lower intensity and also as it falls almost fully into the infrared region, where the solid-state fluorescence is quite rare [9].

5. MODEL ELECTRONIC DEVICES MADE FROM DPPS

Organic electronic devices based on different types of organic semiconductors (among them also based on the small organic molecules, e.g. DPPs) are subject of intense research activity. As already mentioned, the only one advantageous attribute of the material used is not enough to build an efficient device and therefore we introduced soluble functionalised derivatives discussed above. The performance of small molecular organic devices has been shown to be highly sensitive to film morphology and processing conditions. Therefore, we focused also on the role of different preparation techniques on the consequent thin film morphology and corollary the device performance [10].

Thin films of small molecular semiconductors can be prepared by means of a variety of complex techniques including physical or chemical vapour deposition, organic molecular beam epitaxy or solution-based deposition techniques. Often, the solution deposited active layers of devices (e.g. spin cast films) exhibit a high portion of microcrystallites and aggregates whereas the vapour deposition techniques provide high quality crystalline films, characterized by improved charge transport properties compared with those of solution deposited films.

In [10] we investigated the morphology and properties of thin films made from a group of five DPP derivatives prepared and characterized in [1, 7]. These derivatives were modified in order to increase solubility required for low cost wet solution-based casting.

We have shown that the thin layers prepared by both spin casting and vacuum depositions were polycrystalline but the shapes and dimensions of crystallites were found to be dependent on the structure of the materials and temperature of the substrate during deposition ($T_s$). The formation of larger clusters with increasing $T_s$ was described as a thermally activated process where a particle impinged onto the substrate surface can move laterally unless it loses its kinetic energy and finds the energy potential well.

The studies we made with different substrates show that the morphology is practically independent on the nature of the substrate. The key impact on the morphology of thin layers was found to be based on the N-substitution of central DPP unit by alkyl side chains. The crucial factor is the type of substitution: the unsymmetrical (one substituted alkyl chain) or symmetrical (two substituted alkyl chains). The symmetrically substituted derivatives form planar large crystallites with sizes increasing up to 1 $\mu$m, whereas the asymmetrically substituted derivatives form highly rough fiber crystallites, their lengths being up to 1 $\mu$m.

On the basis of the findings described above, the symmetrically substituted derivatives resulted as suitable for construction of electroluminescence devices (organic light emitting diodes – OLEDs). The prepared organic diode from the phenyl di-piperidino substituted N,N-alkylated DPP showed that the turn-on voltage for this diode is ~3V. At this voltage the previously ohmic nature of the I–V characteristics changes to the space-charge-limited, where the current flow is bulk-limited. The low value of the turn-on voltage implies that reasonable charge balancing was achieved due to the barrier reducing pre-contact layers (PEDOT:PSS and Alq3). This allowed us to measure also the spectrally resolved electroluminescence of several selected derivatives.

The electroluminescence spectra show that the EL depends on the substitution used rather than on the length of the alkyl chains used, which is in accordance with the quantum chemical calculations and optical spectroscopy characterization [1,3].

We also performed comparative study of acid protonation of pyridyl functionalised diketopyrrolopyrrole derivatives. Such derivatives (also with piperidyl or a morpholinyl ring) change their colour after protonation [11]. Since these materials are also semiconductive the protonation can influence their conductivity. The
mechanism of the material conductivity change is based on the donor function of protonated quaternary nitrogen in a pyridyl ring. The electron contributes to the conductivity after hydrogen capture.

We described influence of acid vapour treatment on DPP thin films by means of changes of UV-VIS spectra, IR spectra and electrical conductivity. UV-VIS absorption exhibits hypsochromic shift and significant growth of the absorption at 580 nm and decrease at 470 nm that results in a colour shift from red to violet. The protonation releases conductive electrons enhancing conductivity in orders of magnitude $10^{-10}$ to $10^{-6} \Omega^{-1}\cdot\text{cm}^{-1}$. All processes described are reversible and the material can be recovered by annealing at 170 °C. These results were further used to construct hydrogen sensor [12].

6. SUMMARY

In summary, we have shown, that depending on the side groups substitution, studied materials can be precisely tuned with respect to their optical, optoelectrical, electrical properties. Based on these optimizations, we were able to demonstrate the possibility to prepare low turn-on voltage OLED devices, gas sensing devices etc. These properties together with chemical, light and thermal stability and reasonable solubility predestine them as potential candidates for printed electronics and optical applications.

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