ORIGINAL PAPER

Comparative Studies of Diphenyl-Diketo-Pyrrolopyrrole Derivatives for Electroluminescence Applications

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Abstract Four different derivatives of diphenyl-diketo-pyrrolopyrrole (DPP) with alkyl side groups were synthesized to increase their solubility. Quantum chemical calculations revealed that the substitution influenced molecular geometry and subsequently modified absorption and photoluminescence spectra. The theoretical results were confirmed by experimental characterization. With increasing phenyl torsion the vibrational structure was less pronounced and larger Stokes shift was observed. Simultaneously, the molar absorption coefficient decreased as the deformation increased. On the other hand, the measured fluorescence quantum yields were modified only slightly. This indicates the possibility to prepare soluble derivatives without loss of quantum yields and to use these materials for construction of efficient and stable electroluminescent devices. Furthermore, the electroluminescence of the thin layer devices based on the soluble low molecular DPPs were characterized and discussed.

Keywords Diphenyl-diketo-pyrrolopyrrole ·
Organic light emitting diodes · OLED · Organic electronics ·
Electroluminescence

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Introduction

Nowadays, we can notice the strong effort to produce organic electroluminescent devices (OLED) that can be used as a completely new generation of lamps and full colour flat panel displays. The potential advantages of these devices are high efficiency, low driving voltage, versatility in its application (flexibility, transparency), low weight, relatively cheap production, environmentally friendly materials, etc. There is a big deal of discussion whether low molecular materials with high stability or polymeric ones with excellent film forming properties and therefore offering low-cost solution-based processing are more advantageous [1]. Nowadays, the most efficient devices used in display prototypes utilise combination of the materials providing specific functionality, e.g. hole or electron transport, reduction of injection barrier for holes and electrons, and of course the exciton formation and efficient radiative recombination. The materials chosen to build the device have to fulfil not only those requirements mentioned, but also their IP (ionisation potential) and EA (electron affinity) have to be aligned to allow effective charge migration [2]. As can be seen, only one advantageous attribute, e.g. high fluorescence quantum yield, is not enough to build efficient electroluminescent device. It is therefore common to functionalise promising material in such way, which does not affect the intrinsic desired properties.

In this study we investigated group of several derivatives of *3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4 dione*, also known as DPP, see Fig. 1. DPP itself has a high quantum yield of fluorescence (Φ_F), as well as a high molar absorption coefficient. Although it has been already reported that some derivatives are potentially suitable for electro-optical applications [3], these materials are mainly used as high performance pigments and are valued for their fatigue resistance. Several derivatives have been synthesised and studied to increase solubility of the DPP in organic solvents and thus offer cheap solution-based deposition techniques. The article discuss the influence of the change of the structure on the electronic spectra, fluorescence quantum yields, position of HOMO and LUMO orbitals necessary for efficient charge transfer, etc. In addition to experimental optical characterization, quantum chemical calculations were employed to determine these parameters and to find links between structure and functionality.

Experimental

The synthesised materials were analysed to confirm the molecule structure by A Bruker AMX 360 NMR spectrometer, ion trap mass spectrometer MSD TRAP XCT equipped with APCI, EA 1108 FISONS instrument for elemental analysis and Fourier transform infrared spectrometer. The referred ultraviolet-visible spectroscopy (UV-VIS) absorption spectra were recorded in dimethylsufoxide (DMSO). The molar absorption coefficients were calculated from the dependence of absorption on concentration $A=\mathrm{f}(c)$ measured in 5 cm quartz cuvette ($c<10^{-5}$ M) in linear part of the dependence. The fluorescence spectra and quantum yields (Φ_F) were obtained according to the comparative method [4] where for each test sample gradient of integrated fluorescence intensity *vs* absorbance $FL=\mathrm{f}(A)$ is used to calculate the Φ_F using two known standards. The standards were previously cross-calibrated to verify the method. The electroluminescence was measured on thin layers prepared

by spin-casting method. The layer of the DPP derivative (~100 nm thick) was sandwiched between indium tin oxide anode and aluminium cathode. Layer of PEDOT:PSS (poly (2,3-dihydrothieno-1,4-dioxin) doped with poly(styrensulfonate)) (~100 nm thick) from the anode side and Alq3 (8-hydroxyquinoline aluminium salt; ~40 nm thick) from the cathode side were introduced to lower the potential barrier for holes and electrons respectively. All of the electrical measurements were performed under vacuum to prevent oxidation of the samples.
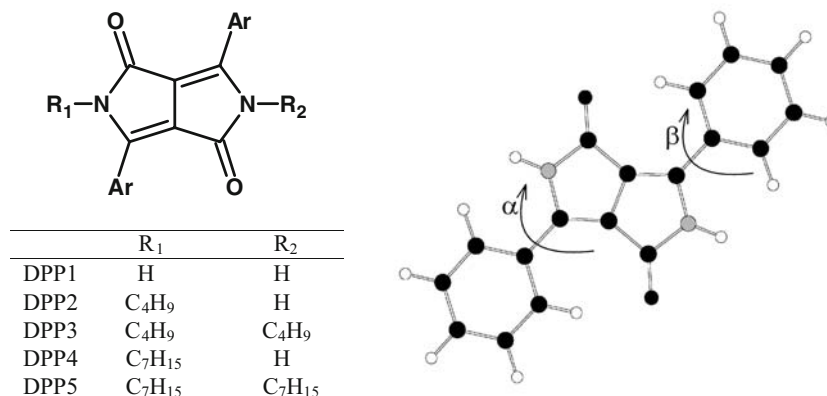
Synthesis

Synthesis of DPP1

1,300 ml of tert-amylalcohol and 69 g (3 mol) of natrium (in three portions) were charged into the 2,5 l Keller flask equipped with a stirrer, a condenser, a thermometer and a supply of nitrogen. Natrium was dissolved under the reflux and the catalytic presence of $FeCl_3$ (it takes approximately 2 h) and 217 g (2.1 mol) of benzonitrile was added. After that 202 g (1 mol) of diisopropyl succinate was continuously batched within 2 h. Subsequently, this mixture was stirred under the reflux for 2.5 h. Reaction mixture was cooled down to 60°C and then 0.8 l of 2-propanol and 1.2 l of distilled water were added to protolyse it. The protolysis was carried out at 60°C for 2 h; the reaction mixture was heated up to 80°C and kept for stirring for 1 h. The hot suspension was filtrated and the filter cake was washed with 2 l of hot 2-propanol to the slight yellowish filtrates and 2 l of hot water to the neutral pH. The filter cake was dried and charged into 3 l of ethanol. Suspension was heated up and kept under reflux for 2 h. The hot suspension was filtrated, washed with 2 l of ethanol and finally with hot water. We obtained 161 g of the product.

NMR: ^{1}H chemical shifts: 11.39 (br. s 2H, NH); 8.53 (4H, m, H-ortho); 7.63 (6H, m, H-meta+H-para) ^{13}C chemical shifts were not determined due to very low

Fig. 1 The basic structure of *3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4 dione*, also known as DPP and the four derivatives prepared. Calculated DPP conformation, definition of the phenyl torsion angles α and β

	R_1	R_2
DPP1	H	H
DPP2	C_4H_9	H
DPP3	C_4H_9	C_4H_9
DPP4	C_7H_{15}	H
DPP5	C_7H_{15}	C_7H_{15}

solubility of the sample. MS analysis, M=288: positive-ion MS: m/z 289 [M+H]$^+$, 100%. Elemental analysis: calculated: C (74.99), H (4.20), N (9.72); found: C (74.99), H (4.20), N (9.72).

Synthesis of DPP2 and DPP3

11.6 g (0.04 mol) of the intermediate DPP1 and 120 g of dried dimethylformamide (DMF) were charged into the evaporative flask. The suspension was shortly stirred up. Subsequently, 16.2 g of 30% methanolic solution of sodium methylate was added. The fine slurry of sodium salt of DPP1 was stirred for 20 min, methanol was distilled out under the vacuum (t<40°C, p=40 mbar) and than was added 16.8 g (0.123 mol) of n-butyl bromide. The mixture was heated up to 80°C and stirred for 20 h. After that the temperature was increased to 80–100°C and suspension was kept for stirring for further 2 h. The reaction mixture was filled into 1 l of distilled water and heated up to boiling point. The final mixture was cooled to 10°C and the product was filtrated. The filter cake was reslurried in 200 ml of methanol; suspension was heated up to boiling point and filtrated. After cooling of the filtrates, the reddish brown substance (mixture of DPP2 and DPP3) was obtained. This substance was recrystallized from 200 ml of cyclohexane. 1.29 g of bright red product DPP3 was obtained. The saved filter cake from previous step was reslurried in 200 ml of methanol; suspension was shortly heated up to boiling point and filtrated. The filter cake (2.99 g) was identified as the starting compound DPP1. After cooling of the filtrate, 0.61 g of reddish orange product DPP2 was obtained.

NMR data of DPP2: ^{1}H chemical shifts: 11.30 (br. s 1H, NH); 8.53 (2H, m, H-ortho); 7.87 (2H, m, H-ortho); 7.64 (6H, m, H-meta+H-para); 3.82 (2H, t, NCH$_2$); 1.46 (2H, m, CH$_2$); 1.20 (2H, m, CH$_2$); 0.80 (3H, t, CH$_3$); ^{13}C chemical shifts: 162.6; 161.7; 146.1; 146.0; 132.4; 131.1; 129.2; 129.0; 128.7; 128.0; 127.7; 110.9; 108.6; 40.9; 30.9; 19.4, 13.5. MS analysis of DPP2, M=344: positive-ion MS: m/z 345 [M+H]$^+$, 100%. Elemental analysis of DPP2: calculated: C (76.72), H (5.85), N (8.13); found: C (76.72), H (5.9), N (8.16).

NMR data of DPP3: ^{1}H chemical shifts: 7.87 (4H, m, H-ortho); 7.66 (6H, m, H-meta+H-para); 3.76 (4H, t, NCH$_2$); 1.43 (4H, m, CH$_2$); 1.18 (4H, m, CH$_2$); 0.79 (6H, t, CH$_3$); ^{13}C chemical shifts: 164.8; 148.0; 131.4; 129.0; 128.7; 127.9; 108.8; 40.6; 30.8; 19.4, 13.4. MS analysis of DPP3, M=400: positive-ion MS: m/z 401 [M+H]$^+$, 100%. Elemental analysis of DPP3: calculated: C (77.97), H (7.05), N (6.99); found: C (79.09), H (7.05), N (7.02).

The infrared spectra showed the shift of C=O stretching from 1,637 to 1,660 cm^{-1} for samples DPP1 and DPP2, respectively to 1,678 cm^{-1} for sample DPP3. This shift is caused by the hydrogen lost bond.

Synthesis of DPP4 and DPP5

11.6 g (0.04 mol) of the intermediate DPP1 and 120 g of dried DMF were charged into the evaporative flask. The suspension was shortly stirred up. Subsequently, 16.2 g of 30% methanolic solution of sodium methylate was added. The fine slurry of sodium salt of DPP1 was stirred for 20 min, methanol was distilled out under the vacuum (t<40°C, p=40 mbar) and than was added 20 g (0.112 mol) of 1-bromohexane. The mixture was heated up to 80°C and stirred for 20 h. After that the temperature was increased to 80–100°C and suspension was kept for stirring for further 2 h. The reaction mixture was filled into 1 l of distilled water and heated up to boiling point. The final mixture was cooled to 10°C and the product was filtrated. The filter cake was reslurried in 400 ml of methanol; suspension was heated up to boiling point and filtrated. 3.78 g of filter cake (starting compound) was obtained. After cooling of the filtrates, the yellowish-orange substance (mixture of DPP4 and DPP5) was obtained and reslurried in 200 ml of n-hexane. The suspension was heated up to boiling point and filtrated. 0.66 g of filter cake (DPP4) was obtained. After cooling of the filtrates 1.88 g of product DPP5 was obtained.

NMR data of U11: ^{1}H chemical shifts: 11.30 (br. s 1H, NH); 8.52 (2H, m, H-ortho); 7.86 (2H, m, H-ortho); 7.63 (6H, m, H-meta+H-para); 3.81 (2H, t, NCH$_2$); 1.47 (2H, m, CH$_2$); 1.20 (8H, m, CH$_2$); 0.83 (3H, t, CH$_3$); ^{13}C chemical shifts: 162.5; 161.6; 146.1; 146.0; 132.3; 131.1; 129.2; 129.0; 128.6; 128.0; 127.6; 110.8; 108.5; 41.0; 31.1; 28.6; 28.0; 26.0, 22.0, 14.0. MS analysis of DPP4, M=386: positive-ion MS: m/z 387 [M+H]$^+$, 100%. Elemental analysis of DPP4: calculated: C (77.69), H (6.78), N (7.25); found: C (77.66), H (6.79), N (7.39).

NMR data of DPP5: ^{1}H chemical shifts: 7.87 (4H, m, H-ortho); 7.65 (6H, m, H-meta+H-para); 3.75 (4H, t, NCH$_2$); 1.43 (4H, m, CH$_2$); 1.15 (16H, m, CH$_2$); 0.83 (6H, t, CH$_3$). ^{13}C chemical shifts were not determined due to very low solubility of the sample. MS analysis of DPP5, M=484: positive-ion MS: m/z 485 [M+H]$^+$, 100%. Elemental analysis of DPP5: calculated: C (79.3), H (8.32), N (5.78), found: C (79.35), H (8.46), N (5.90).

The IR spectra showed the shift of C=O stretching from 1,637 to 1,660 cm^{-1} for samples DPP1 and DPP4, respectively to 1,684 cm^{-1} for sample DPP5. This shift is caused by the hydrogen lost bond independently from the type of alkyl group used.

Quantum chemical modeling

Ground state molecular conformations

Quantum mechanical calculations were performed with the Gaussian 03 [5] software package. The equilibrium molec-

ular conformations of the selected DPP derivatives were determined by means of the Hartree-Fock (HF) and B3LYP methods at 6–31G* level. The molecules were considered to be isolated, geometry was fully optimized with no molecular symmetry taken a priori into account. B3LYP is a hybrid HF/density functional theory (DFT) method, which combines Becke's three-parameter exchange functional [6] with the Lee–Yang–Paar correlation functional [7]. It was successfully used for the calculations of the conformations of the different π-conjugated systems [8–10]. At the same time, the computer requirements of this method are comparable rather with the HF method than other "correlated" methods. However, the B3LYP method has also some disadvantages. B3LYP method, like other DFT-type methods, overestimates the electron delocalization and the degree of conjugation. The second drawback is that standard DFT-type methods cannot be used in combination with the configuration interaction (CI) method for the calculation of the relaxed excited state conformations. For this reason, molecular conformations were also calculated using HF method. For all the studied molecules we found only usual differences between HF and B3LYP calculated conformations, that are connected with the inclusion of the correlation energy in the B3LYP method.

The optimized conformations show that some of the substituents influence the molecular geometry of the central DPP unit. The most important conformational parameters are the torsion angles α and β of the phenyls (see Fig. 1). While the unsubstituted DPP molecule is planar $\alpha = \beta = 0°$, derivatives denoted as DPP3 and DPP5 possess significantly rotated phenyl groups (see Table 1); in DPP2 and DPP4 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 and many electronic properties like absorption and luminescence are modified.

Absorption and luminescence

First excited states S_1 of the studied molecules were calculated using ab initio configuration interaction method using single-excitation (CIS method) at the geometry optimized by the HF method. Absorption excitation energies $E_{S_0 \rightarrow S_1}$ are shown in Table 1. The ab initio CIS method enables to determine the trends in the excited state properties connected with the conformation change of the central DPP unit. However, the calculated absolute values of the excitation energies poorly reproduce the experimental results.

The full UV–VIS absorption spectra of the studied molecules were calculated using time-dependent B3LYP (TD-B3LYP) method at the B3LYP optimized geometry. Time-dependent density functional methods recently became an effective and rather accurate tool for single point calculations of electronic excitations in various, namely conjugated, molecular systems [11–13], but they are not suitable for the excited state conformation optimization necessary for luminescence spectra calculations. They rather well reproduce the experimental peak positions, but obviously without a strong vibrational structure of the first transition.

To obtain information about luminescence transitions, relaxed conformations of the S_1 state were optimized by means of ab initio CIS method. During the S_1 state relaxation the bond length alternation in the central DPP unit is reversed and the phenyl character becomes partly quinoidal. Finding relaxed conformations enabled determination of the first luminescence peak energy E_{lum}, Stokes shift ΔE_{Stokes}, and deformation energy E_{def} of the relaxed excited state (see Table 1). It was found that the excitation energies $E_{S_0 \rightarrow S_1}$ of the derivatives with the rotated phenyl groups exhibit a hypsochromic shift strongly correlated with the values of the torsion angles α and β. Similarly also ΔE_{Stokes} and E_{def} are significantly influenced by the phenyl

Table 1 Phenyl torsion angles calculated by the HF and B3LYP methods, lowest absorption energy $E_{S_0 \rightarrow S_1}$, first luminescence peak E_{lum}, Stokes shift ΔE_{Stokes}, and deformation energy E_{def} of the relaxed excited state

Derivative	B3LYP method		HF method		$E_{S_0 \rightarrow S_1}$	E_{lum}	ΔE_{Stokes}	E_{def}
	α [°]	β [°]	α [°]	β [°]	[eV]	[eV]	[eV]	[eV]
DPP1	0.0	0.0	0.0	0.0	2.837	2.427	0.410	0.339
DPP2	36.0	6.7	46.9	16.9	2.935	2.424	0.511	0.437
DPP3	36.5	36.5	46.1	46.1	3.012	2.441	0.571	0.482
DPP4	36.7	7.7	46.9	16.9	2.933	2.422	0.511	0.437
DPP5	35.9	35.9	46.0	46.0	3.010	2.438	0.571	0.482

For the absorption and luminescence calculations, the ground state conformations were optimized by means of the HF method and the relaxed excited state conformations were calculated using the ab initio CIS method

rotation. The calculated first luminescence peak changes only slightly.

Optical and optoelectrical characterisation

The substitution of central DPP unit by alkyl side chains resulted in hypsochromic shift of the absorption (see Fig. 2a). This shift increases with the number of alkyl groups but is not affected by the length of the alkyls used. Furthermore, the vibration modes present in the spectrum of the non-substituted molecules were reduced. This tendency is further amplified as the substitution introduces second alkyl group. The spectral shift is accompanied with decrease of molar absorption coefficient (see Table 2). The fluorescence spectra of the synthesized derivatives (Fig. 2b) shows bathochromic shift with respect to the primary DPP1. The increasing Stokes shift is also accom-

Table 2 Experimental values for molar absorption coefficient ε, position of absorption λ_{AbsMax} and luminescence λ_{FLMax} peak maximums, Stokes shift $\Delta\lambda_{Stokes}$ and fluorescence quantum yield Φ_F ($\Delta\Phi_F < 0.05$)

Derivative	ε [mol·l^{-1}·cm^{-1}]	λ_{AbsMax} [nm]	λ_{FLMax} [nm]	$\Delta\lambda_{Stokes}$ [nm]	Φ_F [-]
DPP1	34,300	507	519	12	0.74
DPP2	21,300	493	525	32	0.69
DPP3	18,500	467	530	63	0.69
DPP4	32,800	493	524	31	0.78
DPP5	19,500	466	529	63	0.77

panied with the broadening of the spectra as was observed in the case of absorption. The measured fluorescence quantum yields were practically not modified in the range of accuracy of the method (see Table 2).

The observed behaviour can be explained according to the quantum chemical calculations described above. Substitution of alkyl group lead to the rotation of the adjacent phenyl group and therefore cause lost of planarity and effective conjugation. This is exemplified as the decrease of molar absorption coefficient and hypsochromic shift of the absorption [14]. Introduction of the second alkyl rotates also the second phenyl and the effective conjugation is even more decreased.

All of the prepared derivatives exhibited electroluminescence behaviour. Example of the electroluminescence spectra of thin layer devices based on DPP5 together with the fluorescence spectra of the solution and thin film layer prepared from DPP5 are shown on Fig. 3. It was found that the thin layers prepared either by spin casting, inkjet printing or vacuum evaporation technique showed high portion of crystallinity. The size of the crystals formed depends on the regularity of the molecule. The planar DPP1 forms nano-sized crystals as observed by the AFM
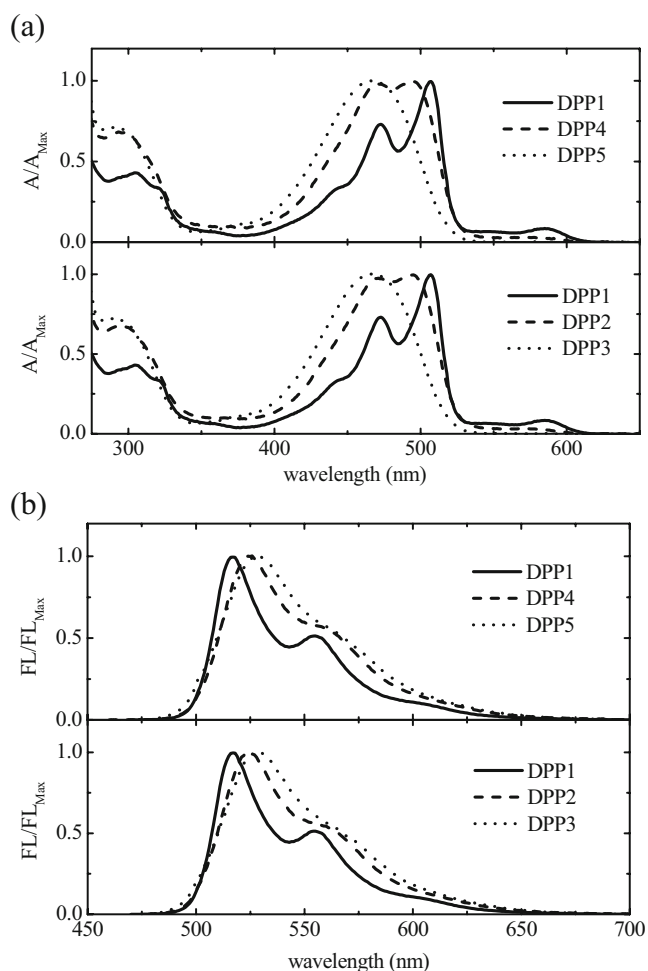

Fig. 2 Absorption **a** and fluorescence **b** spectra measured in dimethylsulfoxide. The spectra were normalized to the longer wavelength band. Clear hypsochromic shift in absorption and bathochromic shift in fluorescence (FL) spectra accompanied with the lost of vibronic structure can be observed as the substitution takes place
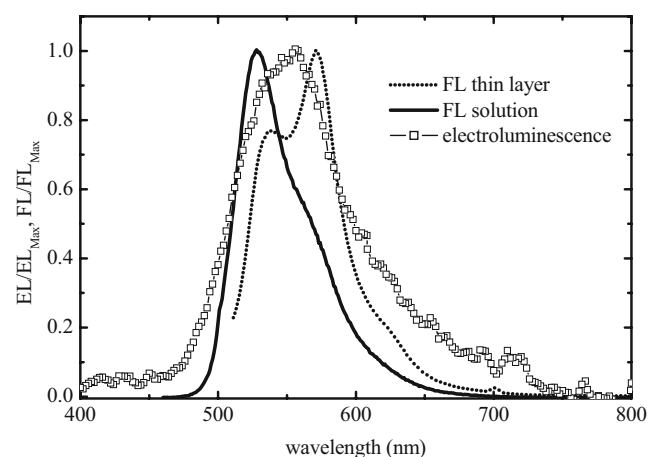

Fig. 3 Normalized electroluminescence (EL) response of the device prepared from DPP5 derivative, fluorescence of the thin layer and fluorescence of solution in dimethylsulfoxide

technique. It has to be mentioned that the DPP1 is not soluble enough for spin casting technique and was prepared by thermal vacuum evaporation. The mono substituted derivatives prepared by spin casting showed tendency to form highly rough (tens of nanometer) and up to more than 5 μm long curved "lying grass" like structures. The symmetrically substituted derivatives formed large crystals up to tens of μm long tightly packed together. This film-forming properties influence the electric response and therefore the electroluminescence behaviour to a considerable extent.

Conclusions

Basic structure and four derivatives of diphenyl-diketo-pyrrolopyrrole were synthesized and compared from the point of view of their potential use as light emitting layer for organic electroluminescence device. It was found that the electronic properties strongly depend on the planarity of the molecules, which was decreased by the substitution. The measurements showed that the original high fluorescence quantum yield reminds nearly the same. This indicates the possibility to prepare derivatives soluble in solvents suitable for cheap large-scale production without loss of fluorescence quantum yields and therefore to use these materials for construction of efficient electroluminescent devices. In order to get the best performance it is necessary to optimise the OLED structure for each derivative.

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