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Naphthalene diimides prepared by straightforward method and its characterization for organic electronics

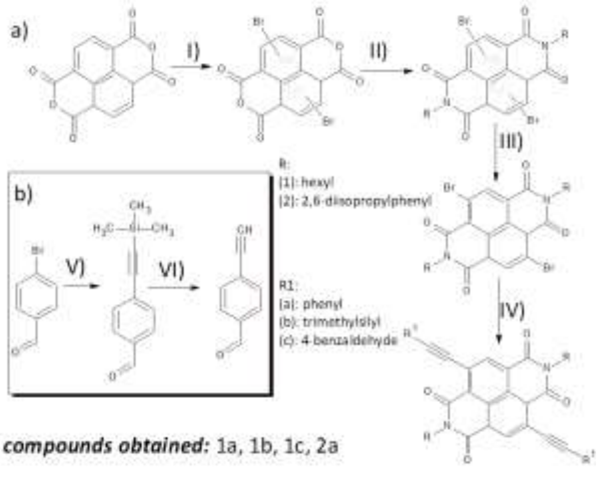
Mateusz Korzec,*[a] Sonia Kotowicz,[a] Katarzyna Łaba,[b] Mieczysław Łapkowski,[b] Jan Grzegorz Małecki,[a] Karolina Smolarek,[c] Sebastian Maćkowski,[c] and Ewa Schab-Balcerzak*[a,b]

Abstract: A new approach in the synthesis of acetylene core substituted naphthalene diimides in polar solvent using $PdCl_2$, Et_3N and powder electrolytic copper was developed. This simplified approach allows for high-throughput synthesis where the reaction products can be easily separated. The DFT studies revealed that electronic structures of these compounds are mainly determined by central naphthalene diimide and acetylene derivatives parts. The obtained thermally stable and soluble compounds undergo reversible reduction with electron affinity from 4.18 to 4.28 eV. They emitted green light with photoluminescence quantum yield of about 6% in chloroform and from 3-12% as thin films. The compounds were applied as emitting layers for both non-doped and doped single layer OLEDs fabricated by solution processing. Under applied external voltage they feature orange or red light electroluminescence.

Conjugated organic compounds are extensively studied in recent years for various organic electronic devices such as organic light emitting diodes (OLED's),[1,2] photovoltaic cells[1,3,4] and field effect transistors.[1,5] Naphthalene diimides (NDI) constitute a family of compounds widely studied for use in organic electronics.[1,6,7] NDI are considered as one of the most promising units for n-type polymer acceptors.[8,9] According to literature, imide-functionalization of NDI has little effect on the molecular-level electronic and optical properties, while the presence of one or more substituents at positions 2, 3, 6, and 7 of the core substituted NDIs, can significantly affect these properties. Thus, although the interest in core substituted naphthalene diimides (cNDIs) has increased in recent years,[8-10] the studies of cNDIs properties are still limited due to synthetic difficulties.[1] Synthesis of cNDIs derivatives is focused on aromatic nucleophilic substitution reactions.[11] The synthetic methodologies for preparing cNDIs with different alkyne core substituents are based mainly on the Stille reaction.[12-16] Utilization of terminal alkyne[17-19] or copper(I) alkyne[20,21] for the preparation of such derivatives is less frequent.

Herein, we report on a new approach to synthesize core-substituted naphthalene diimide, carried out in acetone or water with the presence of catalytic system consisting of $PdCl_2$, Et_3N and powder electrolytic copper without ligands and copper salts. In this way we achieve high-throughput synthesis, in which the reaction products can be easily separated. Using this method we prepared four cNDIs bearing phenyl, trimethylsisyl and 4-benzaldehyde units connected by acetylene linkages with naphthalene diimide core (*Scheme 1a*) with high yields, and studied their thermal, electrochemical, and luminescence properties. Two of the compounds (1b and 1c in *Scheme 1a*) are new and have not been described in literature.

In the first stage of acetylene substituted naphthalene diimides preparation, 2,6-dibromo-1,4,*5,8*-naphthalene-diimide (2,6-BrNDI) was obtained. Synthesis of 2,6-BrNDI involved bromination of dianhydride naphthalene ring and then condensaion reaction with n-hexylamine or 2,6-diisopropylaniline.



Scheme 1. a) Synthesis of cNDIs: I) DBHMH, H_2SO_4, 65ºC, 12 h; II) CH_3COOH, amine, 95ºC, 6h; III) CH_3Cl, SiO_2, hexane; IV) polar solvent, $PdCl_2$, Et_3N, 60ºC, 1h and b) synthesis of 4-ethynylbenzaldehyde: V) $PdCl_2$, Cu, PPh_3, Et_3N, 65ºC, 3 h; VI) MeOH, K_2CO_3, 2h.

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The bromination of 1,4,5,8-naphthalenetetracarboxylic dianhydride can be realized in severalways.[8,22-25] We used 1,3-dibromo-5,5-dimethylhydantoin in H_2SO_4.[8] We have developed method for isolating 2,6-BrNDI through crystallization from chloroform with addition of silica, which allows to bypass the time-consuming chromatographic methods (*Figure 1a, Step III*). After hot filtration, the mixture was concentrated to half the volumen and frozen after adding hexane. For introduction of acetylene linkages and R' substituents we applied Sonogashira reaction of 2,6-BrNDI with selected terminal alkynes that were either commercially available (phenylacetylene and trimethylsilylacetylene) or were prepared in reaction between p-bromobenzaldehyde and trimethylsilylacetylene (TMSA), which were next methanolyzed in the presence of basic catalyst (*Scheme1b).* Cross-coupling, that is, the Sonogashira reaction for final products preparation (**1a-1c** and **2a** in *Scheme 1*), was carried out in the presence of $PdCl_2$ and powder electrolytic copper under aerobic conditions. Such a catalytic system, to the best of our knowledge, has not been yet used for NDIs core modification. We also showed that copper salts can be replaced with powder electrolytic copper. The powder electrolytic copper as carrier for palladium nanoparticles for the Sonogashira reactions was presented first the time in our former works.[26,27] It was found that such catalytic system compare to a standard Sonoghasira protocol resulted in higher reaction yield (from 90 to 100%). The characteristics of applied powder electrolytic copper as carrier for palladium nanoparticles was previously reported[26] and some details are given in Supporting Information. It should be stressed that utilization of powder electrolytic copper can be beneficial because besides metallic copper, Cu oxides (Cu(I) and Cu(II)) are also formed. In particular, copper(I) plays a role of co-catalyst to form the corresponding complexes with terminal alkyne.[28-31] In addition, different Pd(II) systems with copper are formed, e.g., Pd(II)/Cu(II), which can be the source of the active system Pd(0)/Cu(I)[32] or copper systems, e.g., Cu(0) with Cu oxides also having high catalyst activity.[31] So far NDIs core functionalization was carried out in DMF or THF. Here we propose to replace these solvents by acetone or water, which induces product precipitation due to its insolubility. In this way, chromatographic purification method can be avoided.

Table 1. Analysis of reagents for carrying out the coupling to the naphthalene ring.

	R (1 equiv/ NDIs)	*Solvent*	*$PdCl_2$ (equiv/ NDIs)*	*Cu (equiv/ NDIs)*	*Yields[a] [%]*
1[b]	Ph-	acetone	0.045	0.18	79
2	Ph-	H_2O	0.045	0.18	82
3	Ph-	acetone	0.022	-	80
4	Ph-	H_2O	0.022	-	84
5[c]	Ph-	acetone	0.022	0.18	0
6	Ph-	H_2O	-	-	0
7	Ph-	H_2O	-	0.18	0
8	C(HO)Ph-	acetone	0.022	-	59
9	C(HO)Ph-	H_2O	0.022	-	0
10	C(HO)Ph-	H_2O	0.022	0.18	0
11	$(CH_3)_3Si$-	H_2O	0.022	-	0
12	$(CH_3)_3Si$-	H_2O	0.022	0.18	0
13	$(CH_3)_3Si$-	acetone	0.022	-	0
14	$(CH_3)_3Si$-	acetone	0.022	0.18	64
15	$(CH_3)_3Si$-	acetone	0.022	0.09	15

In the reaction was used: 0.253 mmol (0.15 g) NDIs, Et_3N (1 mL) as base, solvent (8 mL) and it was carried out at 60 °C for 1 hour. [a]) Analysis was performed after isolation product and washing with acetone followed by diethyl ether. [b]) reaction with PPh_3 (0.035 eq/NDIs); [c]) reaction without Et_3N.

At the beginning, a catalytic system composition ($PdCl_2$, PPh_3, Et_3N and powder electrolytic copper) in Sonogashira reaction was tested for **1a-1c** compounds (*Table 1*). It was found that the presence of $PdCl_2$, Et_3N and powder electrolytic copper was crucial for cNDIs preparation. The effect of terminal alkynes structure on the course of reaction was pronounced, as utilization of TMSA without any electrolytic copper in both solvents gave no results (*Table 1, entry 11,13)*. On the other hand, reaction with 4-ethynylbenzaldehyde and phenylacetylene without powder electrolytic copper in acetone gives the **1c** and **1a**, respectively (*Table 1*, *entry 3,4,8)*. The synthesis of **1a** can also be carried out in water (*Table 1, entry 4*).

Thermal properties of compounds for organic electronics are of key importance before considering any device applications. In the first differential scanning calorimetry (DSC) scan of cNDIs, endothermic peaks at 254°C (1a) and 253°C (1b) attributed to the melting temperature (T_m) can be distinguished. In the case of compound bearing benzaldehyde structure (2a) during II DSC run glass transition (T_g) at 275°C was seen. T_m and T_g were not observed in DSC thermogram of 1c in the studied temperature range. The temperature of decomposition (T_5) corresponding to 5% weight loss measured by thermogravimetric analysis (TGA) occurred at rather high temperatures of 379°C (1a), 312°C (1b), 305°C (1c) and 370°C (2a) (*Figure S1, S2 in SI*).

The electrochemical properties of synthesized cNDIs were investigated by cyclic voltammetry (CV) (*Figure 2.*). In the negative potential range (vs Fc/Fc^+) two well-separated reversible reduction waves were observed.

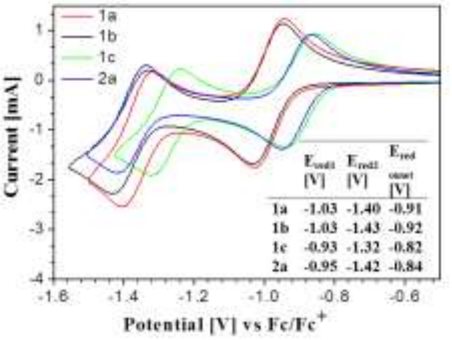

Figure 2. Cyclic voltammograms of studied cNDIs (10^{-3}M) solution of compound in 0.1 M Bu_4NPF_6/ dichloromethane electrolyte.

From the onset of reduction potential the electron affinity (EA) corresponding LUMO level was calculated by using the equation EA = -($E_{red\ onset}$ + 5.1)eV (Figure 2,3). Ionization potentials (IP) can be, in turn, estimated from the optical energy gaps (E_g^{opt}) and the calculated value of EA using the equation IP = -(E_g^{opt} – EA)eV (*Figure 3,4a.*). In light of the distribution of the LUMO level determined with density functional theory (DFT) using the Gaussian09,[33] B3LYP/6-31++ level, is localized on the central molecule core (*Figure 3*). For a more detailed description of the molecular orbitals, the contribution of molecular parts, i.e. central naphthalene diimide, R-C≡C– and aliphatic n-C_6H_{13}– (**1a-1c**) or

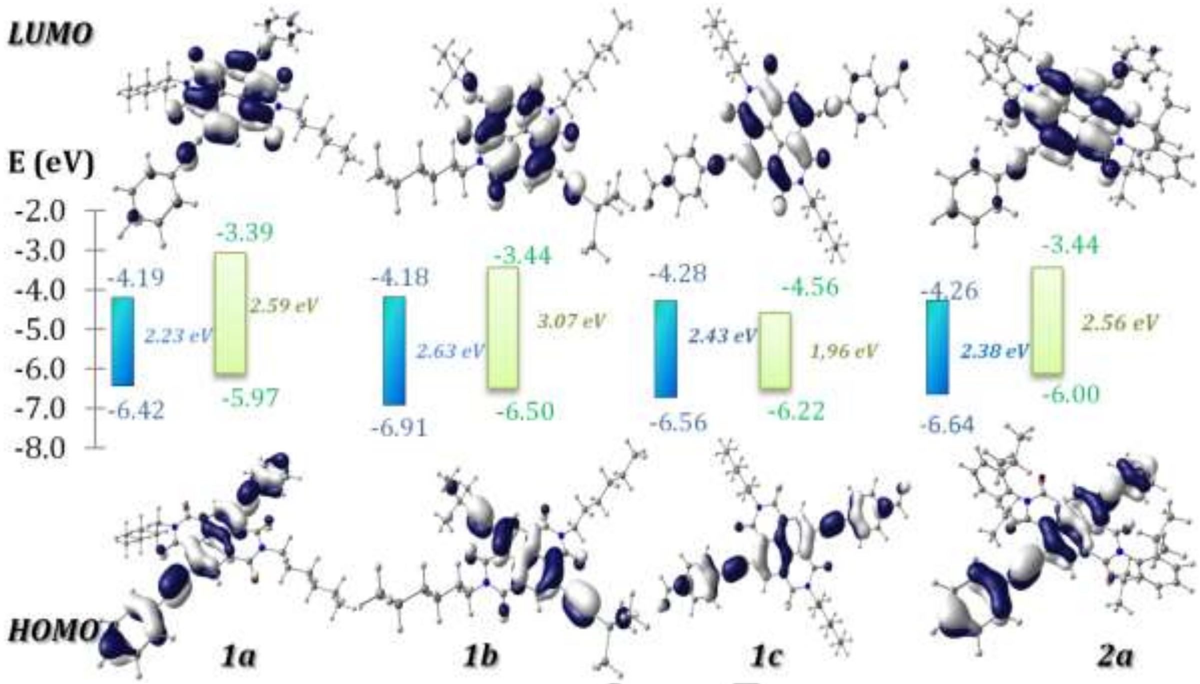

Figure 3. Presentation of the HOMO–LUMO energy levels (***blue***-experimental, EA and IP corresponding LUMO and HOMO respectively, ***green***-theoretical) and orbital composition.

1,3-di(propan-2yl)benzene (**2a**) fragments to a molecular orbital, was calculated using GaussSum 3.0 program.[34] As one can see from the DOS spectra (*Figure S4 in SI*), electronic structures of the compounds are mainly determined by central naphthalene diimide and acetylene derivatives parts. In the HOMOs the share of R-C≡C– fragments predominates over the contribution of central naphthalene diimide part. This is particularly evident in the case of **1a** (*Table S4 in SI*). In case of **1b** HOMO is composed of almost equal shares of naphthalene diimide and trimethylsilylacetylene fragments.

The ground-state absorption spectra of synthesized cNDIs in chloroform, depicted in *Figure 4*, show three absorption bands of a pronounced vibrational structure: one rather intense in the range of 260-350nm, the second, weaker, covering range of data are collected in *Table 2*. Position of maximum absorption 350-400nm, and another from 400 to 525nm. The spectroscopic band (λ_{max}) is affected mainly by the naphthalene core substituents, thus, UV-vis spectra of compounds 1a and 2a are the same. cNDI with aldehyde group (1c) showed λ_{max} bathochromically shifted from 450 to 520nm relative to the compounds without -CHO unit (1a and 2a). UV-vis spectra of cNDI in the form of film are shifted to lower energy in comparison with the corresponding spectra recorded in solution (*Table 2, Figure 4*). The prepared cNDIs were luminescent both in solution and as solid state layers on glass substrates. However, the photoluminescence (PL) of compound bearing trimethylsisyl groups (1b) was very weak both in solution and in film and this data is omitted in *Table 2*. The most intense PL was measured under two excitation wavelengths (λ_{ex}) of 360 and 460nm (*Figure 4, Table 2*). All compound in solution emitted green light with position of maximum emission band (λ_{em}) between 503 – 525nm. The emission band of cNDIs in film was bathochromically shifted with varied degree in comparison with the corresponding emission in solution with the highest PL quantum yield found for 1a. They exhibited very small Stokes shifts in the range of 1172 to 1335cm^{-1} (28 – 34nm), which indicates the rigid nature of studied compounds.

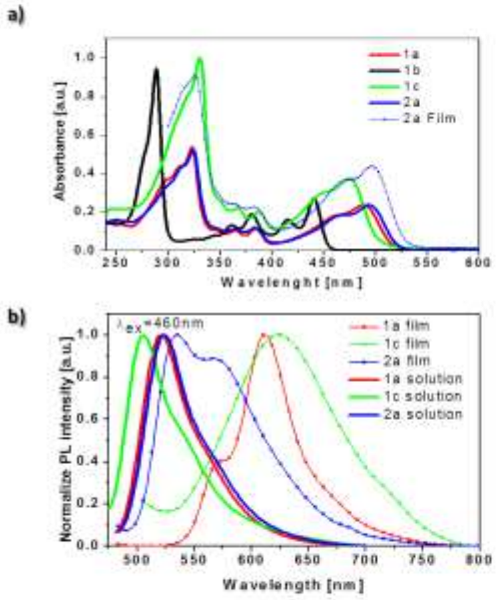

Figure 4. a) UV-vis spectra of cNDIs in chloroform solution (10^{-5}M) and 2a in film and b) PL spectra of cNDIs in chloroform (10^{-5} M) and film.

Table 2. Absorption and photoluminescence of cNDIs

Code	Absorption (UV-vis)		Emission (PL)		Quantum yield (Φ_{PL})	
	CHCl$_3$^{a} λ_{max} ($\varepsilon \cdot 10^{-4}$)^b [nm]	Film λ_{max} [nm]	CHCl$_3$^{a} $\lambda_{em}$$^{(\lambda ex)}$ [nm]	Film $\lambda_{em}$$^{(\lambda ex)}$ [nm]	CHCl$_3$ Φ_{PL} [%]	Film Φ_{PL} [%]
1a	323 (*5.3*); 365 (*1.0*); 384 (*1.1*); 488 (*2.4*)	306; 371; 443; 548	522$^{(360)}$ 522$^{(460)}$	612$^{(360)}$ 612$^{(460)}$	1.07 5.66	12,25 10.71
1b	288 (*9.3*); 361 (*1.3*); 381 (*1.8*); 415 (*1.6*); 440 (*2.6*)	391;422; 445	-	-	-	-
1c	330 (*10.0*); 366 (*2.2*); 387(*2.0*); 475 (*3.7*)	346; 509	503$^{(360)}$ 503$^{(460)}$	624$^{(360)}$ 624$^{(460)}$	1.56 6.28	3.91 3.84
2a	324 (*5.1*); 365 (*1.1*); 384 (*1.1*); 494 (*2.3*)	327; 382; 495	525$^{(360)}$ 525$^{(460)}$	532;568$^{(360)}$ 532;568$^{(460)}$	0.91 6.45	2.95 3.31

[a] c=10^{-5} M;

[b] molecular absorption coefficient [$dm^3 \cdot mol^{-1} \cdot cm^{-1}$]

The electroluminescence (EL) ability of synthesized cNDIs, except for 1b, was tested. The compounds were applied as emitting layers for both non-doped and doped single layer OLEDs fabricated by solution processing. In doped type diodes they were used as a guest in a binary host matrix consisting of poly-(9-vinylcarbazole) (PVK) (50 wt.%): 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole(PBD) (50 wt.%).

Diodes with following structures ITO/PEDOT:PSS/ compound/Al and ITO/PEDOT:PSS/PVK:PBD:compound(15 wt.%)/Al were fabricated. Devices based on neat compounds 1a and 1c did not show any EL response contrary to device with 2a. The current density-voltage characteristics (J-V) and EL spectra of the exemplary devices based on 2a and 1c are depicted in Figure 5. (*Others EL spectra and J-V on Figure S3 in SI*).

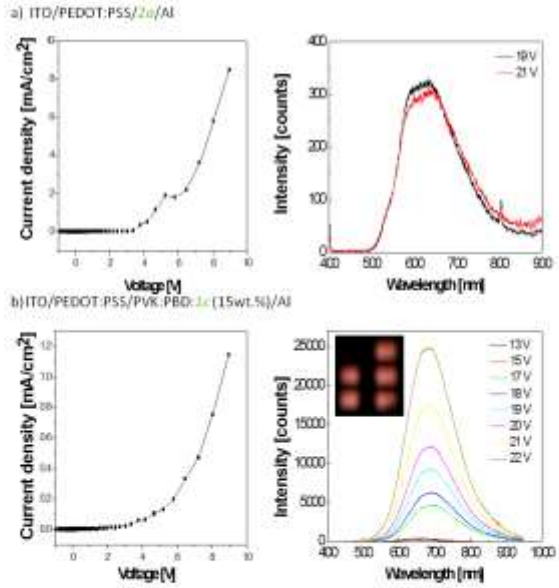

Figure 5. Current density-voltage characteristics and electroluminescence spectra of OLED for increasing and decreasing voltage registered for devices with (a) ITO/PEDOT:PSS/2a/Al and (b) ITO/PEDOT:PSS/PVK:PBD:1c/Al structure.

The turn-on voltage of all diodes was in the similar and low range about 2.27 - 3.08V. The OLEDs exhibited different values of current density (*J*), with the lowest and the highest observed for devices containing **1a** and **2a**, respectively. For all the compounds the EL signal emerged between 8 and 24V.

The fabricated diodes exhibited EL band with maximum at 634nm for ITO/PEDOT:PSS/**2a**/Al and 684nm for ITO/PEDOT:PSS/PVK-PBD:**1c**/Al. In the case of guest-host diodes based on **2a** and **1a**, emission featured three (540, 586 and 659nm) and two maxima (563 and 610nm), respectively (Figure S3 in*SI*).

It seems to be interesting to compare properties important for optoelectronics of presented compounds with similar cNDIs reported in literature. As mentioned cNDI bearing as a core substituents ethynylene bonds are seldom reported. Y. Li and coworkers[15] described sNDI with N-hexyl group in which arylacetylene bonds were substituted with pyridine, phenyl, thiophene and benzothiophene rings. One of them with phenyl rings is the same as compound presented in this work denoted as 1a. It was found that pyridine and thiophene units compare to phenyl structure, hypsochromically and bathochromically shifted λ_{em} in solid state, respectively. The highest Φ_{PL} was registered for cNDI with phenyl structure (1a). Compound with thiophene rings showed the lowest E_g value (1.94 eV). Thin films of these cNDI exhibited air-unstable *n* type semiconducting properties contrary to compounds with imide nitrogen substituted by longer aliphatic chain (-$C_{20}H_{41}$). N-hexyl cNDIs were nitrogen-stable *n* semiconductors. Their semiconducting properties were studied by characterizing OFETs with their thin films. It was concluded that presented cNDI exhibited dual functions, that is, light emitting and semiconducting. However, their ability for EL was not tested. S. Chopin et all[1,17] reported two arylacetylene-substituted cNDIs, one, which was the same as our 2a with ethynylphenyl structure and second containing the ethynylphenyl substituted with N,N-dihexylamino group. It was showed that only luminescent was cNDI bearing ethynylphenyl units. cNDI bearing trimethylsilylacetylene moieties and N-substituted with octyl group (C_8H_{17}) were used as a fluorogenic probe for the selective detection of fluoride ions and their PL, thermal and electrochemical properties are not presented.[1] It can be concluded that introduction of the substituted acetylene units into naphthalene structure of NDI (1a) resulted in lowering of reduction potential form -0.5 to -1.0 V and as a result, the narrowing of E_g from 2.8 to 2.23 eV in relation to N,N'-dihexyl-NDI without substituted core.[35] Additionally, the bathochromic shift of λ_{EL} is seen compare 1a substituted NDI and unsubstituted N,N'-dihexyl-NDI.[36].

In summary, acetylene substituted naphthalene diimides were synthesized *via* an efficient and straightforward approach. The electroluminescence ability of such types of compounds was demonstrated for the first time. The compounds bearing aldehyde (**1c**) and trimethylsilyl (**1b**) units can be considered as substrates for further synthesis of molecules with a core consisting of acetylene substituted naphthalene diimides for organic electronics devices. Further modifications of these compounds are in progress.

Acknowledgements

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Keywords: core-substituted naphthalene diimides • photoluminescence • elcetrochemistry • electroluminescence

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Entry for the Table of Contents (Please choose one layout)

Layout 2:

FULL PAPER

- The simply method synthesis of acetylene substituted naphthalene diimides was developed
- Electroluminescence of prototype diodes with new compounds was demonstrated

M. Korzec, S. Kotowicz, K. Łaba, M. Łapkowski, J.G. Małecki, K. Smolarek, S. Maćkowski, E. Schab-Balcerzak**

A new approach in the synthesis of acetylene substituted naphthalene diimide was developed. The obtained compounds emitted green light with quantum photoluminescence yield of about 6% in chloroform and from 3-12% as thin films. Under applied external voltage they feature orange or red light electroluminescence.

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Simply strategy of naphthalene diimides preparation and characterization for organic electronic