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Synthesis of N-Substituted Carbazolocyanines with Absorption in the Near IR Region

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Novel carbazole-fused porphyrazine complexes of zinc and magnesium, as well as corresponding ligand, were obtained starting from 9-(2-ethylhexyl)-9H-carbazole-2,3-dicarbonitrile. The three-step synthetic strategy to N-substituted carbazole-2,3-dicarbonitrile was optimized. The intense absorption in the near IR region (750-780 nm) was found for target carbazolocyanines.

Keywords: Carbazoles, Cadogan synthesis, Suzuki coupling, porphyrazines, near IR absorption.

Синтез N-замещенных карбазолоцианинов с поглощением в ближней ИК области

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На основе 9-(2-этилгексил)-9H-карбазол-2,3-дикарбонитрила получены новые карбазол-аннелированные порфиразиновые комплексы цинка и магния, а также соответствующий лиганд. Оптимизирован трехстадийный метод синтеза N-замещенного карбазол-2,3-дикарбонитрила. Для целевых карбазолоцианинов обнаружено интенсивное поглощение в ближней ИК-области (750 - 780 нм).

Ключевые слова: Карбазолы, синтез по Кадогану, кросс-сочетание по Сузуки, порфиразины, поглощение в ближней ИК области.

Phthalocyanines are tetrapyrrolic macroheterocycles related to porphyrins. The main possibilities for their structure modification are introduction of different peripheral groups (substituents), changing of central metal ion and extension of aromatic π-system. Benzo and naphthyl annulated phthalocyanines, namely naphthalo- and antracocyanines, are well known and widely studied.[1-5] The extension of the aromatic π-system allows using of these compounds in sensors[6] and optical limiters.[7,8] Near IR absorption of π-extended phthalocyanine analogs makes them promising compounds for optical-electronic devices, solar cells,[2,9,10] and photosensitizers for photodynamic therapy.[11]

Heteroannulation of phthalocyanine macrocycle causes additional centers of structural modification and opens new application areas.[12] For instance, pyrazine-fused phthalocyanines (zinc azanaphthalocyanines) in their quaternized

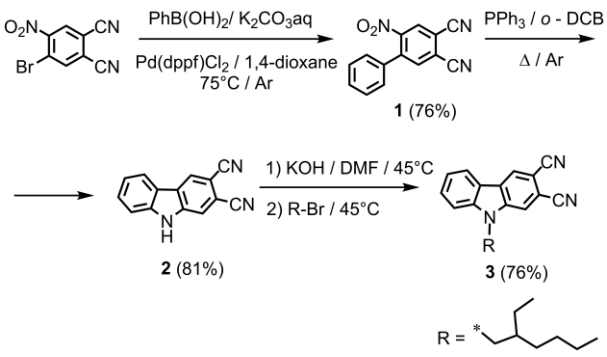
forms demonstrated high photodynamic activity.[13] Thiophene-fused phthalocyanines showed interesting self-organization behavior[14] and can be used as donor material for solar cells.[15]

An interesting structural motif in the chemistry of heteroaromatic compounds is the carbazole molecule. The main peculiarities of carbazole heterocycle are strong electron-releasing effect and a planar structure, which leads to its wide application in organic photoactive materials.[16-21] The most popular method for the introduction of carbazolyl groups is the formation of σ-bonds between the phthalocyanine core and the carbazole unit.[22-25] Carbazole-fused porphyrazines consist of a porphyrazine core with four fused carbazole moieties. They can be called carbazolocyanines by analogy with the azulenocyanines described by Muranaka *et al.*[26] Carbazole-fused porphyrazines were reported only in the pioneer article of Kimura *et al.*[10] Thus, it was of interest to obtain the new carbazolocyanines for further development of this area.

The main purpose of the current work was to develop convenient synthetic approach towards free carbazolocyanine ligand. It is important building block towards mono and multi-decker sandwich-type complexes with different central ions.[27]

4-Bromo-5-nitrophthalonitrile is one of the most versatile precursors towards the synthesis of peripherally substituted and heteroannulated phthalocyanines. There are numerous examples concerning modification of 4-bromo-5-nitrophthalonitrile by aromatic nucleophilic substitution reactions.[28-36] In particular, only bromine or both bromine and nitro groups can be substituted by varying the reaction conditions.[28-30] The synthesis of benzisoxazole-,[36] benzotriazole-,[37] benzofuran- [36] and dibenzofurane- [37] dicarbonitriles was also reported.

Kimura *et al.* for the first time described three-step approach to the N-substituted carbazole dicarbonitriles, including Suzuki cross-coupling reaction, Cadogan cyclization of carbazole and protection of nitrogen atom.[10] The main disadvantage of Kimura's approach is the low yield of the Suzuki cross-coupling reaction. To start with, we chose $Pd(PPh_3)_4$ as a catalyst and K_2CO_3 as a base, instead of $Pd(OAc)_2$/SPhos system and K_3PO_4, and boiling toluene as a reaction media. This catalyst/base system ($Pd(PPh_3)_4/K_2CO_3$) demonstrated high yield for introduction of phenyl group into 1-bromo-3-nitrobenzene and related substrates.[38-40] However, the low conversion of initial compound and formation of phthalocyanine byproduct was observed. The replacement of $Pd(PPh_3)_4$ with sterically hindered [1,1′-*bis*(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) and the conducting of reaction in 1,4-dioxane allowed to obtain 4-phenyl-5-nitrophthalonitrile **1** with 76% yield instead of 46% reported in the literature*.



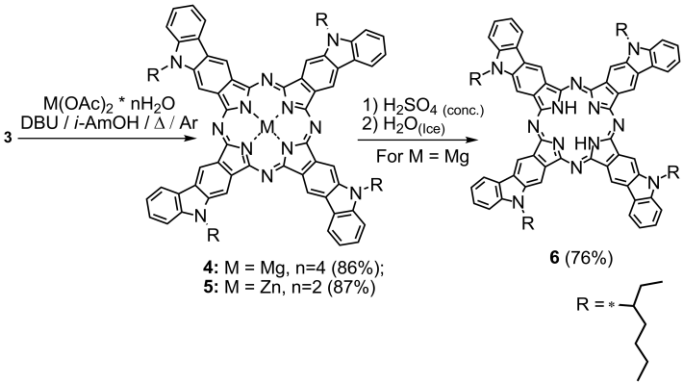
Scheme 1. Synthesis of 9-(2-ethylhexyl)-9*H*-carbazole-2,3-dicarbonitrile **3**.

Further Cadogan cyclization was carried out in the presence of triphenylphosphine in refluxing *o*-DCB[41] to give 9H-carbazole-2,3-dicarbonitrile **2** in good yield (81%)† (Scheme 1). A branched 2-ethylhexyl chain was attached to the nitrogen atom to increase the solubility and suppress the aggregation of target carbazolocyanines. The stirring of compound **2** in the form of potassium salt with bromoalkane gave the desired carbazole **3** ‡.

* *Synthesis of **1***. 1,4-Dioxane (50 mL) was added to the saturated aqueous solution of K_2CO_3 (2.970 g, 18 mmol in 5.5 mL H_2O) and argon was bubbled through the mixture for 15 min. 4-Bromo-5-nitrophthalonitrile (1.500 g, 6 mmol), phenylboronic acid (1.464 g, 12 mmol) and $Pd(dppf)Cl_2$ (0.132 g, 0.18 mmol) were then added and the resulting mixture was stirred for 3 h at 75 °C under argon. The reaction mixture was poured into water and extracted with EtOAc. The collected organic layer was dried over anhydrous $CaCl_2$, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2; EtOAc:*n*-hexane 1:4 V:V) to give compound **1** (1.122 g, 76%). M.p.=159-161 ˚C. ^{1}H NMR (400.13 MHz, [D6]DMSO, 298 K) δ_H ppm: 8.90 (1H, s, H_{Ar}), 8.51 (1H, s, H_{Ar}), 7.43-7.45 and 7.53-7.55 (5H, m, H_{Ph}). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ_C ppm: 140.89, 136.94, 132.93, 130.14, 129.17, 128.48, 127.25, 118.64, 115.30, 113.39, 113.15. IR (diamond) ν_{max} cm^{-1}: 2241 (CN st), 1537 (NO_2 st as), 1356 (NO_2 st sy), 707-907 (arC-H δ).

† *Synthesis of **2***. A mixture of **1** (1.100 g, 4.44 mmol) and PPh_3 (2.900 g, 11.1 mmol) was refluxed in *o*-dichlorobenzene (*o*-DCB) (10 mL) for 2 h under argon (TLC control: SiO_2, EtOAc:*n*-hexane 1:4 V:V). After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure to give dark-brown oil, which solidified on standing. The solid residue was purified by flash chromatography (SiO_2; gradient elution - CH_2Cl_2, then EtOAc:*n*-hexane 3:2 V:V). The EtOAc:*n*-hexane fraction was collected and the solvents were removed under reduced pressure to give compound **2** (0.782 g, 81%). The compound is decomposed under melting (289-291˚C). ^{1}H NMR ([D6]DMSO, 298 K) δ_H ppm: 9.00 (1H, s, H_{Ar}), 8.34 (1H, d, *J*=7.40 Hz, H_{Ar}), 8.25 (1H, s, H_{Ar}), 7.60-7.67 (2H, m, H_{Ar}); 7.35 (1H, t, *J*=7.40 Hz, H_{Ar}). ^{13}C NMR ([D6]DMSO, 298K) δ_C ppm: 141.42, 139.93, 128.76, 127.30, 125.25, 121.82, 120.95, 117.67, 117.51, 117.24, 112.26, 109.30, 102.55. IR (diamond) ν_{max} cm^{-1}: 3349 (N-H st), 2227 (CN st), 1448-1630 (arC-C γ), 728-897 (arC-H δ).

‡ *Synthesis of **3***. Potassium hydroxide (0.206 g, 3.69 mmol) was added to the suspension of **2** (0.400 g, 1.84 mmol) in DMF (8 mL), and stirred for 30 min at 45 °C. Then 2-ethylhexyl bromide (0.652 mL, 3.69 mmol) was added and the resulting mixture was stirred for 24 h at 45 °C (TLC control: SiO_2, EtOAc:*n*-hexane 3:2 V:V). The reaction mixture was poured into water and 5% HCl solution was added dropwise until p*H* = 7. The product was collected by extraction with EtOAc. The organic layer was dried over anhydrous $CaCl_2$, and concentrated under reduced pressure. The residue was dissolved in minimal amount of ethyl acetate and *n*-hexane was added. The resulting solid was filtered off, washed with *n*-hexane and dried at room temperature to give compound **3** (0.462 g, 76%). M.p.=139-140˚C. ^{1}H NMR ([D6]DMSO, 298K) δ_H ppm: 9.02 (1H, s, H_{Ar}), 8.53 (1H, s, H_{Ar}), 8.37 (1H, d, *J*=7.76 Hz, H_{Ar}), 7.65-7.74 (2H, m, H_{Ar}), 7.40 (1H, t, *J*=7.52 Hz, H_{Ar}), 4.38 (2H, d, CH_2), 1.98 (1H, br.s, H_{alkyl}), 1.13-1.30 (8H, m, H_{alkyl}), 0.73-0.83 (6H, m, H_{alkyl}). ^{13}C NMR ([D6]DMSO, 298K) δ_C ppm: 141.91, 140.64, 128.85, 127.22,



Scheme 2. Synthesis of carbazolocyanines. Only one of potential isomers is shown.

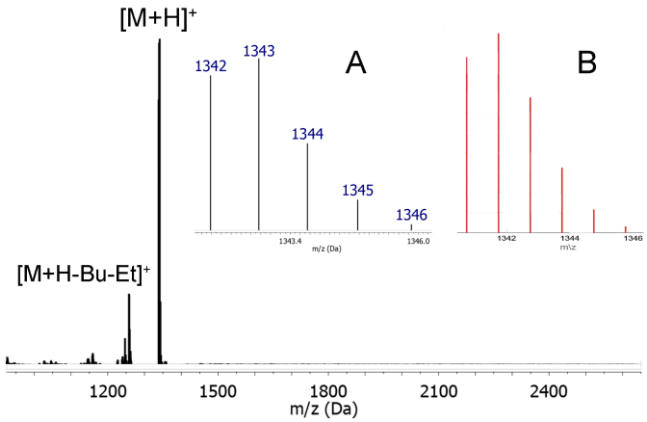


Figure 1. MALDI TOF mass spectrum (positive ion mode) of magnesium complex **4**, isotopic pattern (inset A) and simulated MS pattern (inset B).

9-(2-Ethylhexyl)-9H-carbazole-2,3-dicarbonitrile **3** was introduced into template synthesis with magnesium and zinc acetates [§].

These central ions were chosen because of the possibility of easy removal from the macrocycle. For template cyclization, we have chosen the standard protocol described elsewhere.[42]

The reaction was carried out in boiling isoamyl alcohol in a presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base (Scheme 2). It was found that an additional amount of DBU should be added to speed up the reaction, as electron-rich nitriles are known to be less reactive in this process. Target carbazolocyanines can exist as a mixture of structural isomers (C_{4h}, C_S, D_{2h} and C_{2V}), which cannot be separated using conventional chromatographic techniques.

Then the magnesium complex **4** was stirred in concentrated sulfuric acid, subsequent neutralization by water led to the carbazolocyanine ligand **6** (Scheme 2) [**].

All carbazolocyanines were identified using MALDI TOF mass-spectrometry, NMR, and IR spectroscopy. In mass spectra of metal complexes, the intense molecular ions ($[M+H]^+$) were detected. Experimental isotopic patterns for molecular ions are in agreement with theoretically calculated ones (Figure 1). An additional cleavage of ethyl and butyl groups was observed under laser ionization. The carbazolocyanine ligand **6** possesses a high tendency to aggregation and better solubility can be achieved using DMF and pyridine as solvents. Due to this reason, we found in its mass spectrum adducts with pyridine, which was used as a solvent for the preparation of the sample for MALDI.

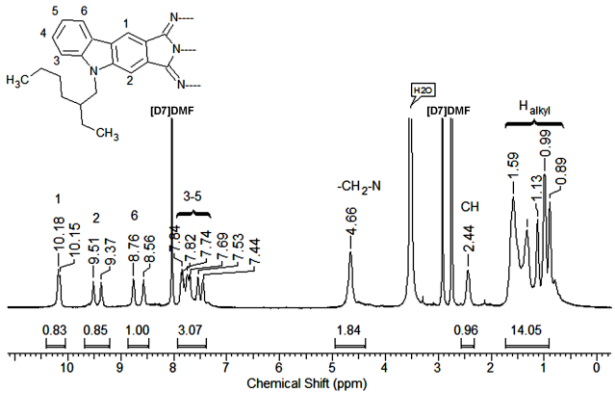


Figure 2. ^{1}H NMR spectrum of magnesium complex **4** measured in [D7]DMF.

124.71, 121.97, 121.20, 120.73, 117.55, 117.25, 116.40, 110.95, 109.46, 102.58, 47.08, 38.41, 29.81, 27.72, 23.38, 22.47, 13.76, 10.55. IR (diamond) ν_{max} cm^{-1}: 2861-2961 (C-H st), 2223 (CN st), 1218-1626 (overlapping of signals of arC-C γ; CH_3 δ; CH_2 δ), 727-903 (arC-H δ).

[§]*General procedure for complexes **4** and **5**.* A mixture of **3** (200 mg, 0.608 mmol) and $M(OAc)_2 \times nH_2O$ (0.304 mmol) was refluxed in isoamyl alcohol (2.5 mL) in the presence of DBU (0.4 mL) for 5 h under argon. The reaction mixture was cooled to room temperature and a MeOH:H_2O (10:1 V:V) mixture was added. The precipitate was filtered off and washed with water and MeOH to give target complexes. Yield of **4**: 175 mg, 86%. UV-Vis (DMF) λ_{max} (lgε) nm: 333 (4.79), 346 (4.80), 665 (4.48), 746 (5.14). IR (diamond) ν_{max} cm^{-1}: 2858-3056 (arC-H st); 1323-1645 (arC-C γ; CH_3 δ; CH_2 δ - overlapping); 1069-1092 (arC-H δ). MS (MALDI-TOF): *m/z* 1342 ($[M+H]^+$, 100%), 1257 ($[M+H-C_4H_9-C_2H_5]^+$, 22%). ^{1}H NMR ([D7]DMF, 298K) δ_H ppm: 10.15-10.18 (1H, br.s, H_1), 9.37-9.51 (1H, br.d, H_2), 8.56-8.76 (1H, br.d, H_6), 7.44-7.84 (3H, m, H_3-H_5), 4.66 (2H, br, -CH_2-N-), 2.44 (1H, br.s, CH), 0.89-1.59 (14H, m, H_{alkyl}).

Yield of **5**: 183 mg, 87%. UV-Vis (DMF) λ_{max} (lgε) nm: 334 (4.83); 343 (4.83); 665 (4.47); 747 (5.13). IR (diamond) ν_{max} cm^{-1}: 2858-3057 (arC-H st); 1329-1624 (arC-C γ; CH_3 δ; CH_2 δ – overlapping); 1070-1097 (arC-H δ). MS (MALDI-TOF/TOF): *m/z* 1382 ($[M+H]^+$, 100%), 1297 ($[M+H-C_4H_9-C_2H_5]^+$, 27%). ^{1}H NMR ([D7]DMF, 298K) δ_H ppm: 9.67-9.84 (1H, br, H_{Ar}), 8.62-8.97 (2H, br, H_{Ar}), 7.57-7.83 (3H, m, H_{Ar}), 4.42-4.53 (2H, br, CH_2), 2.36 (1H, br.s, H_{alkyl}), 1.08-1.57 (14H, m, H_{alkyl}).

[**]*Synthesis of carbazolocyanine ligand **6**.* Powder of complex **4** (164.00 mg, 0.11 mmol) was gradually added to concentrated sulfuric acid (10 mL). The mixture was stirred for 20 min at room temperature and sonicated for 5 min. The resulting viscous solution was poured onto ice and a greenish-brown precipitate immediately formed. The precipitate was filtered off and washed with water until neutral p*H* and then washed with MeOH to give compound **6** (122 mg, 76%). UV–Vis (DMF) λ_{max} nm (lgε): 329 (4.66); 341 (4.65); 417(4.39); 685(4.17); 775(4.78). IR (diamond) ν_{max} cm^{-1}: 3205-3289 (N-H st); 2858-3057 (arC-H st); 1327-1600 (arC-C γ; CH_3 δ; CH_2 δ – overlapping); 1023-1086 (arC-H δ). MS (MALDI-TOF): *m/z* 1634 ($[M+4Py]^+$, 100%), 1555($[M+3Py]^+$, 28%), 1476 ($[M+2Py]^+$, 10%), 1397 ($[M+Py]^+$, 5%) 1318 ($[M]^+$, 20%).

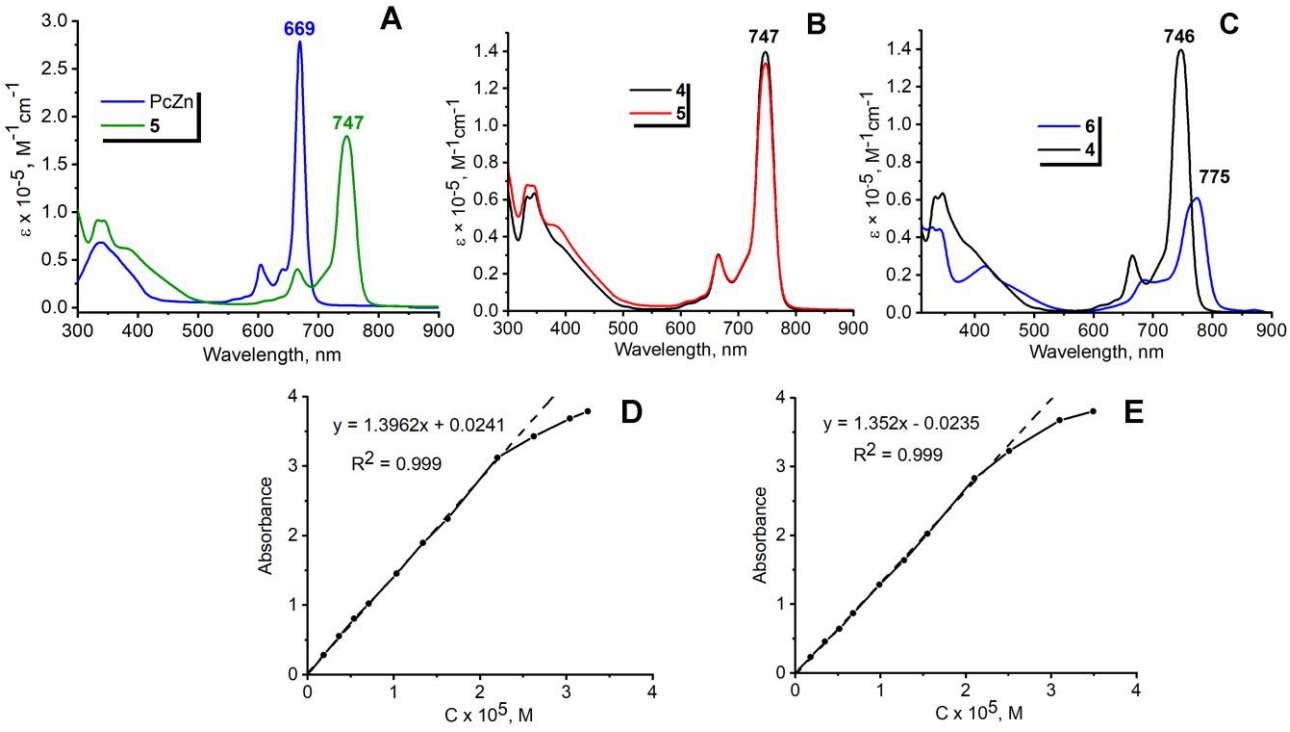


Figure 3. UV-Vis spectra of carbazolocyanines in DMF (B,C) and comparison with unsubstituted zinc phthalocyanine (A). The absorbance of *Q* band *vs*. concentration for magnesium complex **4** (D) and zinc complex **5** (E) (dashed lines demonstrate Beer's law calibration curves).

^{1}H NMR spectra were measured in [D7]DMF since signals of pyridine protons may overlap with those of the carbazole heterocycle. In NMR spectra there are three main groups of signals: aromatic proton signals of carbazole unit, proton signals of the alkyl chain, and broad signal of -CH_2-N- group in the range of 4-5 ppm (Figure 2). All signals are broad probably because of the presence of isomers of the target carbazolocyanines.

UV-Vis spectra of target compounds demonstrate a few regularities. About 80 nm shift of the *Q* band to near IR region was observed going from unsubstituted zinc phthalocyanine to zinc carbazolocyanine **4** (Figure 3A). Broad band in the range of 400-500 nm can be assigned to charge transfer band from heterocyclic periphery to prophyrazine core. Similar peculiarity was observed for thiophene-fused porphyrazines.[43,44] This band is the most pronounced for ligand **6** (Figure 3C).

The changing of central metal ion from Mg to Zn did not affect the position of the *Q* band (Figure 3B), what is following previous data for porphyrazine complexes.[45] The higher affinity between Zn ion and the nitrogen atom of DMF results in slightly more effective suppression of aggregation for zinc complex **5** than it was found for magnesium complex **4**. For the solution of magnesium complex **4** in DMF the Beer's law is not obeyed above $C_{lim} = 2.4 \cdot 10^{-5}$ M *vs* $C_{lim} = 2.7 \cdot 10^{-5}$ M for zinc complex **5** (Figures 3D and 3E).

UV-Vis spectrum of ligand **6** was measured in DMF because of the poor solubility of this compound in other solvents. For instance, UV-Vis spectra in chloroform showed a very broad *Q* band of low intensity. A bathochromic shift of the *Q* band was observed going from the magnesium complex **4** to ligand **6**. In contrast to phthalocyanine ligand, *Q* band of carbazolocyanine ligand **6** do not show splitting. *Q* bands of other π-extended phthalocyanine derivatives (naphthalocyanines and anthracocyanines) also do not split due to the slight splitting of LUMO orbital.[1] At the same time, Kimura *et al.* presented an almost complete degeneration of LUMO and LUMO+1 levels for carbazolocyanine.[10]

It can be concluded that near IR absorbing carbazolocyanine complexes and carbazolocyanine ligand were obtained and identified. Novel carbazolocyanines demonstrated about 80 nm bathochromic shift of *Q* band in comparison with phthalocyanine analogs. In addition we optimised the synthetic strategy to initial N-substituted carbazole-2,3-dicarbonitrile. Replacing the $Pd(OAc)_2$ / SPhos catalytic system with $Pd(dppf)Cl_2$ at the Suzuki cross-coupling stage allowed to obtain 4-phenyl-5-nitrophthalonitrile in 76 % yield instead of 46 % reported in the literature.

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