Synthesis of new polyconjugated molecules with biphenyl, dibenzothiophene, carbazole and phenanthrene units

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Dedicated to Prof. Oleg Kulinkovich on the occasion of his 60th birthday

Abstract
The simple methods of synthesis of hardly accessible substituted biphenyl, dibenzothiophene, carbazole and phenanthrene derivatives were elaborated starting from dimethyl 4,4'-biphenyldicarboxylate. The series of new luminophores with extended π-conjugated chains based on combinations of biphenyl, carbazole, dibenzothiophene, phenanthrene fragments and alternating phenyl, vinyl or heterocyclic units were synthesized by the Wittig and the Knoevenagel reactions of corresponding aromatic dialdehydes and different CH-acids or phosphonium salts. Investigation of the effect of various substituents on the luminescent properties has been presented. The new luminophores could be used as emissive or charge transport layers in organic light emitting diodes (OLEDs).

Keywords: Biphenyl, carbazole, dibenzothiophene, phenanthrene, conjugated system

Introduction

The biaryl axis is the central building block in a very large number of various molecules such as natural and pharmacologically active products,[1] chiral reagents,[2] as the source of chiral phases for chromatography,[3] as inflexible "spacers" between two parts of a molecule,[4, 5] as the basis of liquid crystals[6] and fluorescent layers in OLEDs.[7] Different substituted biphenyls very often are used as suitable synthetic intermediates for synthesis heteroaromatic and polycyclic aromatic compounds.[8] The key step in such synthesis almost always is the coupling of two matched aromatic parts of the target molecule. Another way is the directed modification of easily accessible biphenyls such as, for example, 4, 4'-biphenyldicarboxylic acid.

Methyl ester of 4, 4'-biphenyldicarboxylic acid **1** is a very convenient and cheap starting material for synthesis of wide range of various biphenyl derivatives, especially because it can be separated from wastes of DMT manufacture.[9, 10] Owing to presence of two *para*-carboxylic groups in this molecule, the conjugated system of biphenyl can be easily involved in construction of extensive polyconjugated molecules like **2**, which are potential luminophores and electroactive materials. Additional fuctionalization of biphenyl rings allows varying properties of synthesized molecules.[7, 11-13]

Similar heteroaromatic and polycyclic aromatic compounds **3-5** are of great interest as intermediates for synthesis of such kind polyconjugated systems. The analysis of literature shows that whereas of 2, 7-carbazolyl, 2,7-phenanthrenyl and 3,7-dibenzothiophenyl fragments have the lengthiest conjugation, they are not very often used as chromophores for preparation of dyes and luminophores. First of all, it is connected with difficulties of the direct functionalization of C2, C3 and C7 positions in these ring systems by simple electrophilic substitution.[14-17]

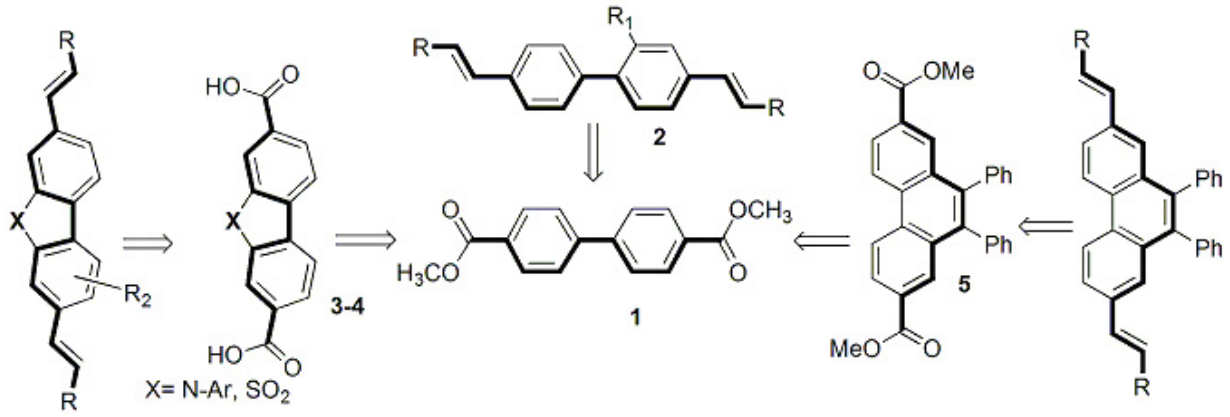


Figure 1

The object of this work was elaboration of effective methods of synthesis of difficult-to-access 4,4'-disubstituted biphenyl, 3,7-disubstituted dibenzothiophene, 2,7-disubstituted carbazole and phenanthrene derivatives followed by their application in synthesis of polyconjugated systems – potential electroluminescent and electroactive materials (Figure 1).

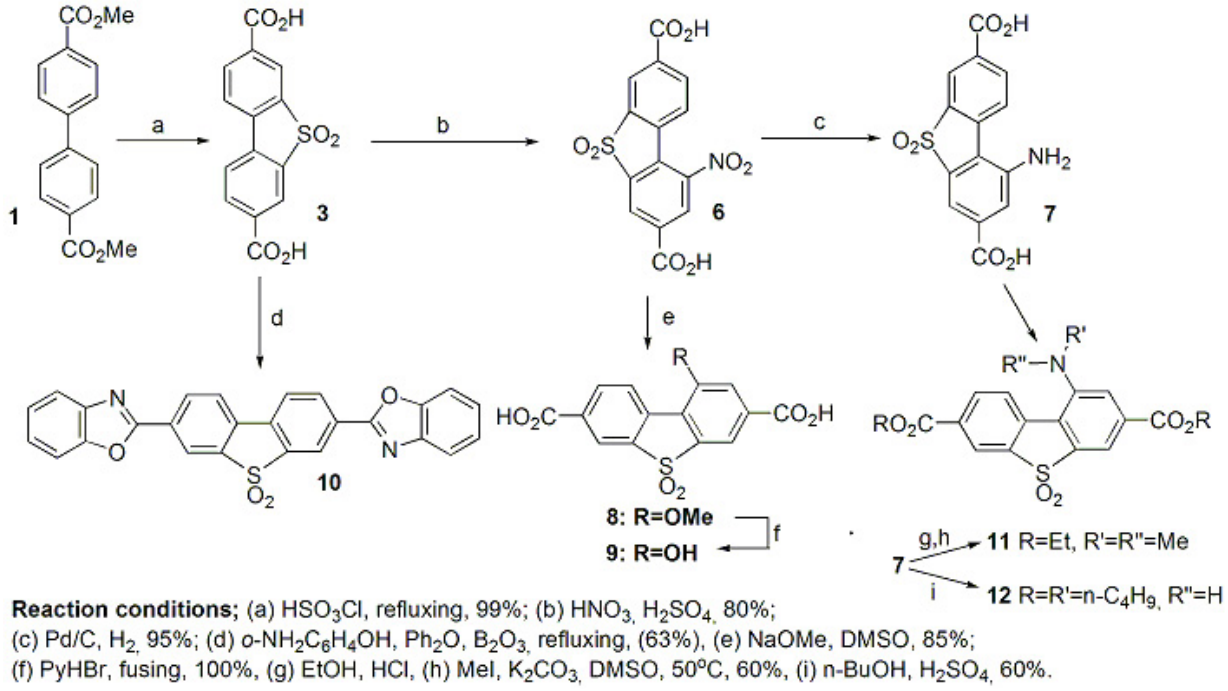
Results and Discussion

There are at least two reasons to consider 4, 4'-biphenyldicarboxylic acid as a versatile starting material for synthesis of the above mentioned system. First, two carboxylic groups in this molecule are the very convenient functions to develop and to lengthen side chains. Second, the cross-effect of the *para*-carboxylic group and the second ring gives the only answer about the

direction of electrophilic substitution in this molecule and allows the carrying out a necessary functionalization of the ring system.

The double sulphurization of diester **1** with chlorosulphonic acid gives 5, 5-dioxodibenzothiophen-3, 7-dicarboxylic acid **3** in quantitative yield (Scheme 1). This compound itself is the suitable chromophoric building block for synthesis of the rod-shaped molecules with a lengthy π-conjugated system like **10**, which are potential electroluminescent materials. The dioxazole derivative **10** was prepared in one step by refluxing of acid **3** with *o*-aminophenol in the presence of boric acid[10] in diphenyl ether.

The molecule of dibenzothiophene **3** contains three electron-withdrawing groups and we anticipated that the introduction of an additional electron-donating function in this molecule could dramatically affect its properties as a chromophor. Amino and hydroxy derivatives **7, 9** are the most interesting from the viewpoint of their further use in synthesis of luminescent materials. The key intermediate in the synthesis of both amino and hydroxy derivatives is the nitro dibenzothiophene **6**. The nitration of diacid **3** with nitric acid in concentrated H_2SO_4 proceeded with the highest regioselectivity giving 1-nitro-5,5-dioxodibenzothiophen **6** in 80% yield.



Reaction conditions; (a) HSO_3Cl, refluxing, 99%; (b) HNO_3, H_2SO_4, 80%;
(c) Pd/C, H_2, 95%; (d) *o*-$NH_2C_6H_4OH$, Ph_2O, B_2O_3, refluxing, (63%), (e) NaOMe, DMSO, 85%;
(f) PyHBr, fusing, 100%, (g) EtOH, HCl, (h) MeI, K_2CO_3, DMSO, 50°C, 60%, (i) n-BuOH, H_2SO_4, 60%.

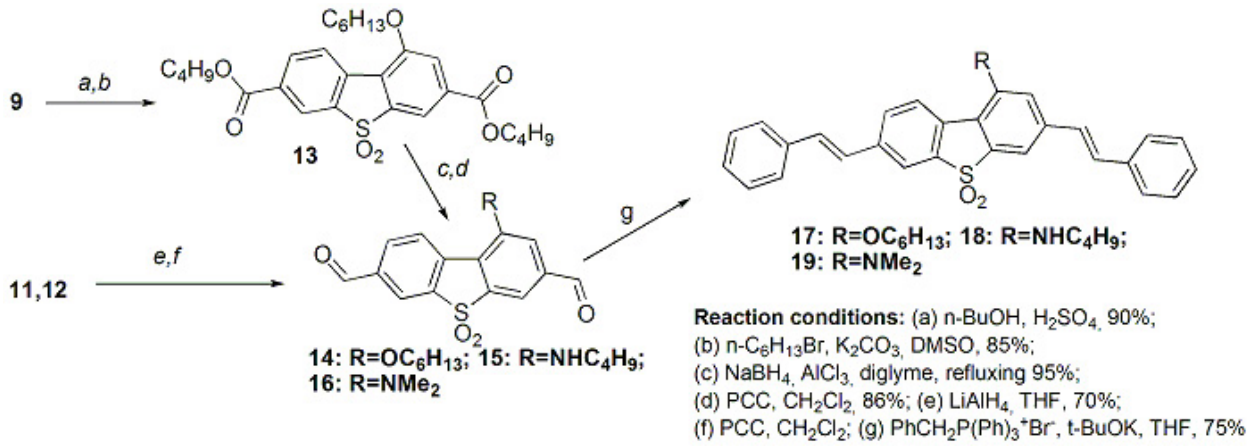
Scheme 1. Synthesis of 5, 5-dioxo-5*H*-dibenzo[*b,d*]thiophene derivatives.

The minor 2-nitro derivative (5-7%) was easily separated with thrice-repeated crystallization from isopropyl alcohol. The presence of two carboxylic and sulfo electron-withdrawing groups in the molecule makes possible the direct nucleophilic substitution of the nitro group in relatively mild conditions, and, therefore, 1-hydroxy derivative **9** was obtained by treatment of nitro

compound **6** with NaOMe in DMSO at 100°C followed by fusion with pyridine hydrobromide. In contrast to the starting compound **3** 1-hydroxy-5,5-dioxodibenzothiophen-3,7-dicarboxylic acid **9** intensively fluoresces in solutions and displays the strong red solvatochromic shift in emission spectra ($\lambda_{fluor.}$= 395 (toluene), $\lambda_{fluor.}$= 525 (ethanol)).

1-Amino-5, 5-dioxodibenzothiophen-3,7-dicarboxylic acid **7** was obtained by palladium catalyzed hydrogenation of nitro derivative **6** in 95% yield. Both the amino **7** and the alkylamino derivatives **11, 12** intensively fluoresce in the solid state and solutions in the blue-green region spectra ($\lambda_{fluor.}$=470-510 nm) and show high thermal and light stability.

We used these chromophores for the synthesis of new polyconjugated systems, which comprised dibenzothiophene and stilbene structural elements. The simplest model compounds

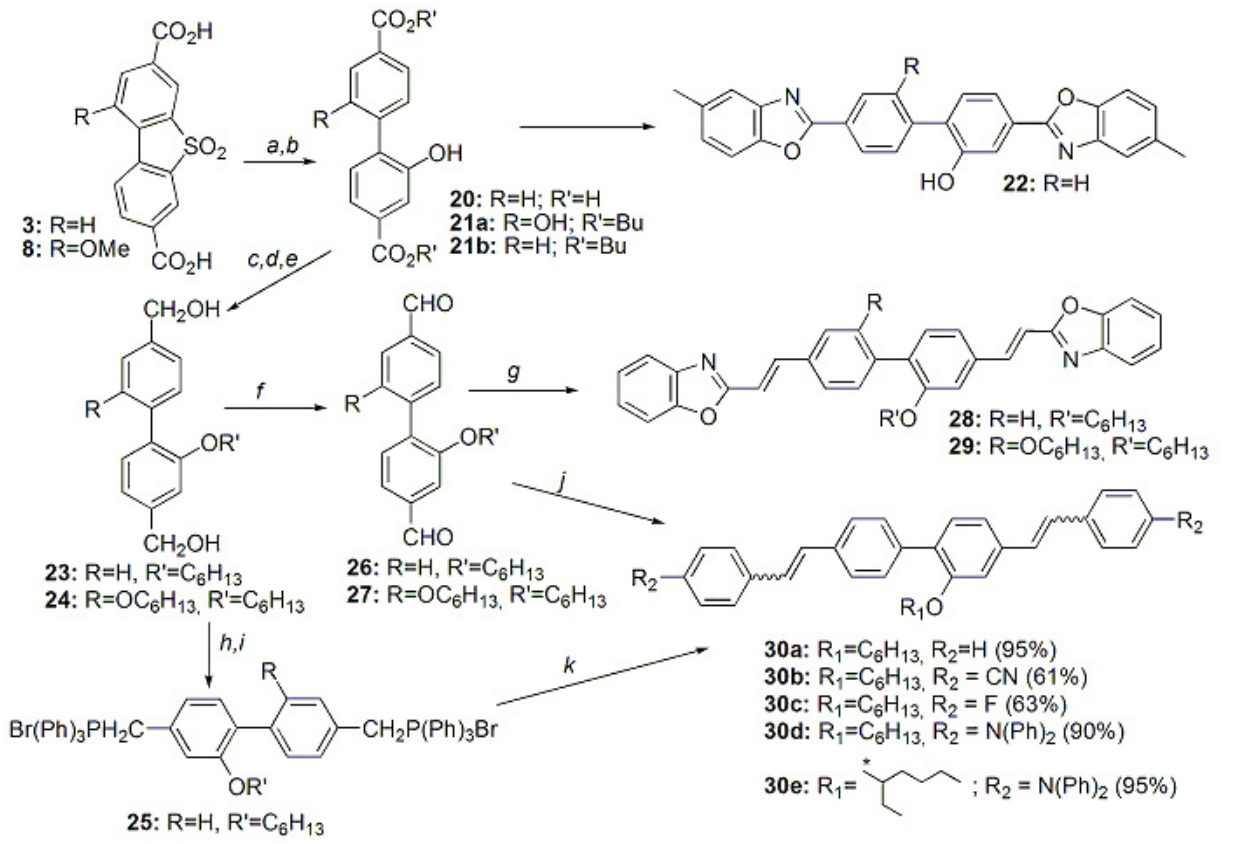


Scheme 2

17-19 with phenylenevinylene fragments in main chain were prepared by the Wittig reaction of aldehydes **14-16** with benzyltriphenylphosphonium bromide as depicted in the Scheme 2.

The aldehydes were synthesized in two steps by the reduction of esters **11-13** followed by oxidation of corresponding alcohols with PCC. The ylide was generated under treatment of the phosphnium salt with *t*-BuOK in THF and the only *trans-trans* isomers of **17-19** were isolated in 45-75% yields. In comparison with the starting diesters, the highest effect was observed in the emission spectra of 2-alkoxy derivative **17**. The red-shift of luminescence maximum was 50 nm ($\lambda_{fluor.}$= 397 (**13**), $\lambda_{fluor.}$= 448 (**17**)) because of expanding of π-conjugated backbone. In the case of amines **18, 19** only as much as three times the increase of emission intensity was observed without any changes of maximums positions in PL spectra.

Prepared from 4,4'-biphenyldicarboxylic acid dibenzothiophenes **3, 8** in their turn are very convenient intermediates to obtain 2- and 2,2'-subsituted 4,4'-biphenyldicarboxylic acids **20, 21**, which could be used as starting materials for the synthesis of luminophores with conjugated extended chains of alternating phenyl, vinyl or heterocyclic units – potential electroluminescent (EL) materials (Scheme 3).



Scheme 3. Synthesis of policonjugated molecules on basis of 2-substituted biphenyls.

Generally, luminophores from non-substituted biphenyls have low solubility and high crystallization tendency that impedes their application as EL materials,[18,19] but owing to presence of hydroxy functions in compounds **28-30,** one can correct their solubility and the glass transition temperature by introduction of long alkoxy groups.

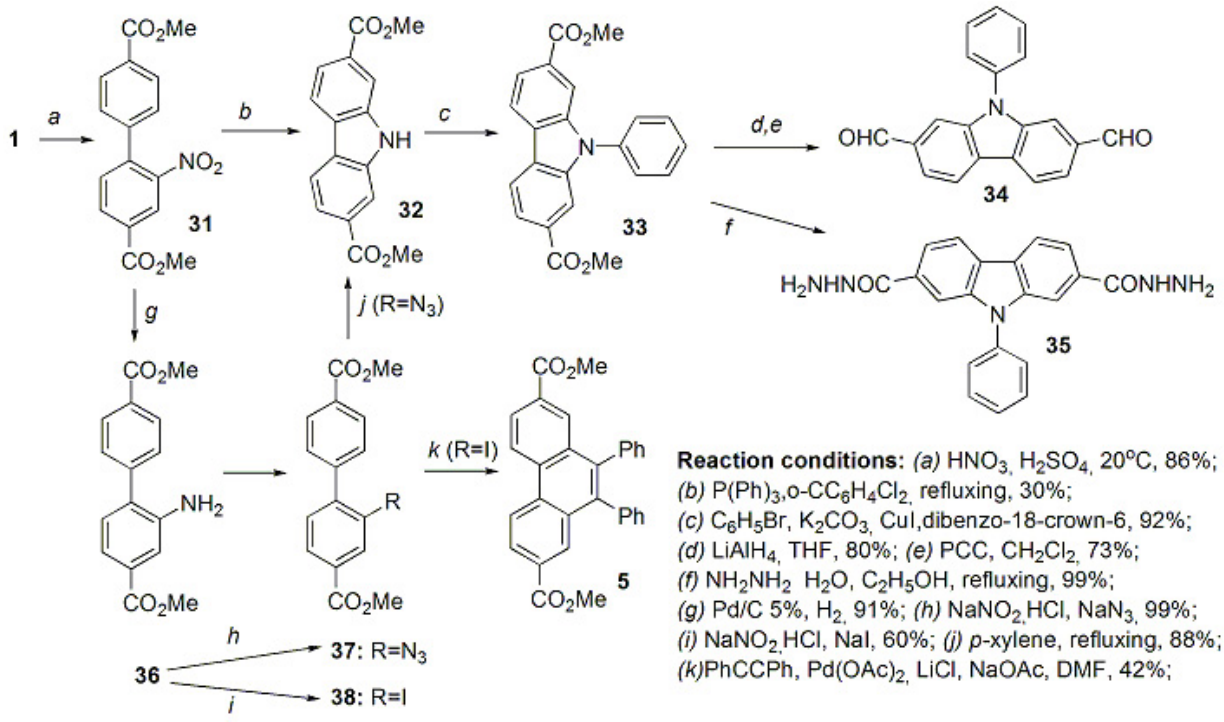
2-Hydroxy-4, 4'-biphenyldicarboxylic acid **20** was obtained in high yield by simply fusing of sulphone **3** with NaOH at 250-280°C.[10] The same procedure with 2-methoxy sulphone **8** gave the mixture of 2- and 2, 2'-dihydroxy derivatives in a ratio 1:2 and 80% total yield, and their dibutyl esters **21 a-b** can be easy separated by extraction of monoester with petroleum ether in the Soxhlet extractor. The strong influence of the substituent at C2 position on luminescence was demonstrated by the example of bis-benzoxazolyl derivative **22**, which was synthesized by condensation of diacid **20** with 4-methyl-2-aminophenole in mixture of diphenyl ether/pyridine and boric acid as catalyst. This compound shows intensive blue photoluminescence in DMSO solution ($\lambda_{max.}$ = 420 nm) and, in the same time, luminescence of its salt form solution has maximum at 570 nm with the anomalous big Stokes shift (~240 nm), when pair electrons of phenolate can be drawn into conjugated system.[11]

The synthesis of the rod-shaped molecules with ethenyl linkers between the biphenyl moiety and electron-withdrawing 1,3-oxazole group was fulfilled by the Knoevenagel reaction of 2-substituted-4,4'-biphenyldicarbaldehydes **26** and **27** with 2-methyl-1,3-benzoxazole. The benzoxazole **28**, due to its electron-rich and good thermal stability, was used as emissive layer to enhance organic light-emitting diodes (OLEDs).[13]

A series of new soluble compounds based on a combination of biphenyl and stilbene structural elements were synthesized by the Wittig reaction of the aldehyde **26** with benzyl (triphenyl)phosphonium salts or diphosphonium bromide **25** with various aromatic aldehydes. The dimethyl ester of **20** was reduced with $LiAlH_4$ in THF and the resulting alcohol **23** was used for preparation both dialdehyde **26** and diphosphonium salt **25** as key intermediates in the synthesis of the EL dyes.

The stereochemistry of Wittig reaction products **30a-e** depends very much on the structure of aromatic aldehydes. In case of relatively small molecules of benzaldehyde, 4-cyano- and 4-fluorbenzaldehyde, the coupling of phosphorane generated from **25** does not proceed stereoselectively and inseparable mixtures of all four isomers (*trans-trans, cis-cis, trans-cis*) are formed. The same result was obtained when the aldehyde **26** reacted with benzyltriphenylphosphonium bromide. In both cases *t*-BuOK was used as base to generate corresponding ylides. The substances **30a-c** show strong blue photoluminescence in solutions and, in spite of the fact that they are mixture of isomers, could be used as electroactive materials in manufacturing of OLEDs. Stereoselectivity of the reaction increased when we used the bulky 4-(diphenylamino)benzcarbaldehyde[20] and the *trans-trans* isomer of **30d** was separated in 75% yield. The rest, approx. 15%, was a mixture of other isomers, which were completely converted in the more stable *trans-trans* isomer of **30d** by the refluxing in toluene with catalytic amount of iodine under argon atmosphere. The diphosphonium bromide **25,** where R' is the branched 2-ethyl-1-hexenyl, reacts with 4-(diphenylamino)benzcarbaldehyde giving the only *trans-trans* isomer **30e** in 95% yield. We anticipated that the luminophores like **30d,e** with electron donating aromatic amines in the main chain of conjugation have to possess the balanced hole and electron injection abilities and could be promising EL materials.

The most commonly used the hole-transporting materials in organic light-emitting devices are triarylamines like 4, 4'-bis [*N*-(1-naphthyl-)-*N*-phenyl-amino]-biphenyl (NPB).[21] N-Arylated carbazole can be regarded as structural analog of triarylamines but having flat and rigid structure. That allows expecting good charge transporting properties, high termo- and light stability of polyconjugated molecules on their basis.[22] One of the most common methods for synthesis of carbazole derivatives is the Cadogan reaction of 2-nitrobiphenyls in the presence of organophosphorus reagents.[23] A requisite dimethyl 2-nitro [1, 1-biphenyl]-4,4'-dicarboxylate **31** was synthesized in high yield by nitration of diester **1** under thoroughly controlled temperature conditions. Unfortunately, the reductive intramolecular cyclization of **31** in the presence of triphenylphosphine gave only 30% yield of desired dimethyl 9*H*-carbazole-2,7-dicarboxylate **32** (Scheme 4).



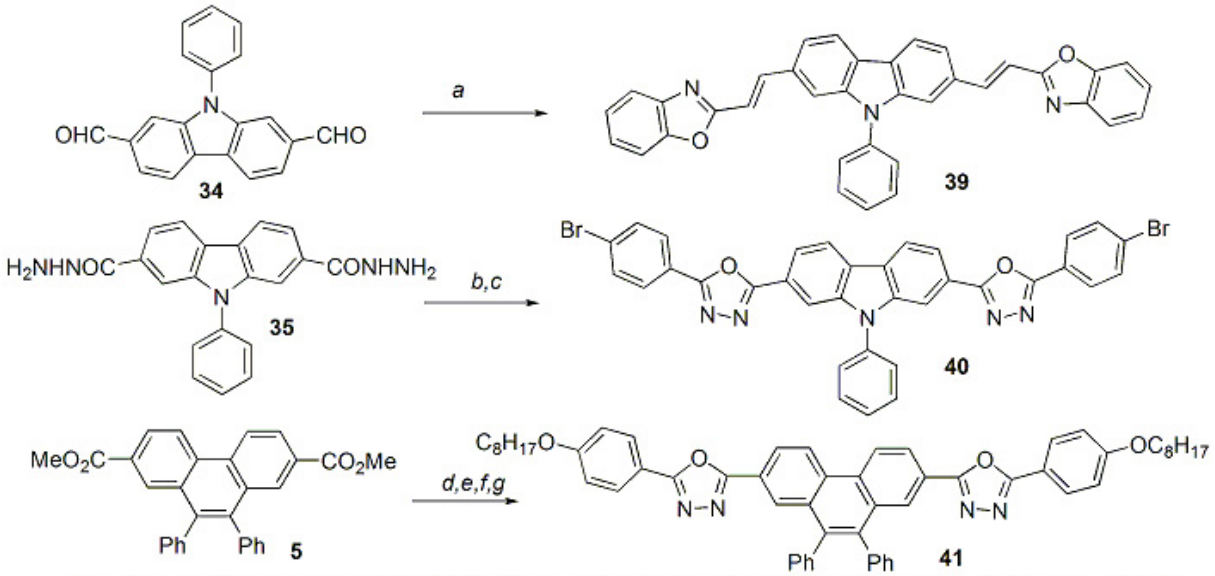
Scheme 4. Synthesis of carbazole and phenanthrene derivatives.

Furthermore, the reaction mixture was contaminated by a number of byproducts that were diddicult to separate. Another way for generation of singlet nitrenes that easily react with introduction into aromatic C-H bond is thermo- or photocyclization of 2-azidobiphenyls. The chain of transformations involved the reduction of nitro derivative **31** in amine **36**, formation diazonium salt, its substitution with NaN_3 and thermocyclyzation of the azide **37.** These transformations gave the carbazole **32** in 80% total yield, starting from nitrobiphenyl **31**. The arylation of the electron-deficient nitrogen atom in dimethyl carbazole-2,7-dicarboxylate **32** demands harsh reaction conditions, however, the refluxing of it with bromobenzene in the presence of K_2CO_3, CuI and dibenzo-18-crown-6 gave the desired N-aryl carbazole **33** in unexpectedly high yield (92%). The corresponding dialdehyde **34** was obtained in two steps as depicted in Scheme 4. The carbazole-2, 7-dicarbohydrazide **35** was synthesized in quantitative yield by refluxing with hydrazine hydrate in ethanol.

Palladium-catalyzed annulation of aryl iodides with alkynes has been proved to be a useful method of forming polycyclic aromatic compounds, in particular substituted phenanthrenes.[24, 25] The crucial 2-iodobiphenyl **38** was obtained by nucleophilic substitution of the amino group in **36** via the corresponding diazonium salt. To synthesize 9, 10-diphenylphenanthrene **5** we used an annulation procedure described for monosubstituted 2-iodobiphenyls.[25]

Both the carbazoles **34, 35** and phenanthrene **5** are versatile building blocks for synthesis of lengthy π-conjugated systems with alternating electron donor and electron acceptor groups in the main chain of conjugation, which could show good balanced luminescence and charge transport

properties. The electron withdrawing ability of the 1, 3, 4-oxadiazole and 1,3-oxazole groups are very strong and comparable to the nitrile one. The presence of double bonds in these heterocycles allows using them as chromophore elements and in the same time as linkers for extending of a conjugated system. The synthesis of the carbazole derivative **39** with benzoxazole units in the side chain was accomplished by the condensation of the dialdehyde **34** with 2-methyl-1,3-benzoxazole under the Knoevenagel reaction conditions (Scheme 5). The oligomer **40,** in which carbazole moiety is connected with bromophenyl unit via 1,3,4-oxadiazole linkers, was synthesized in 42% total yield by reaction of the dihydrazide **35** with 4-bromobenzoyl chloride followed by cyclization of the corresponding dibenzoyl carbazole-2,7-dicarbohydrazide in boiling



Reaction conditions: *(a)* *t*-BuOK, DMSO,2-methyl-1,3-benzoxazole, 78%; *(b)* 4-BrC_6H_4COCl, Py; *(c)* $POCl_3$, refluxing, 46%; *(d)* NaOH, EtOH/THF; *(e)* $SOCl_2$, DMF; *(f)* p-$C_8H_{17}OC_6H_4CONHNH_2$, THF, Et_3N; *(g)* $POCl_3$, refluxing 66%

Scheme 5

$POCl_3$. The dibromide **40** itself intensively luminesces in the blue region (λ_{max} = 428.5 nm) and could be used in synthesis of polymeric EL materials by the Suzuki-Miyaura cross coupling with boric acids.[26] The invert succession of transformations was realized for preparation of phenanthrene **41** because of poor solubility of the diester **5** and the corresponding dihydrazide. 9,10-Diphenyl-2,7-phenanthrenedicarbonyl dichloride was synthesized in two steps, and without further purification was condensed with 4-(octyloxy)benzenecarbohydrazide to give the mixed dihydrazide, which was cyclized in compound **41** in high total yield. This dye has strong blue fluorescence and good solubility in common organic solvents.

Experimental Section

General Procedures. All melting points were measured using a Boetius apparatus and are uncorrected. IR spectra were recorded using a UR-20 IR spectrometer. ^{1}H NMR (100 or 500, 13 MHz) and ^{13}C NMR (125,75 MHz) spectra were recorded as $CDCl_3$ and DMSO-d_6 solutions on a Tesla BS-567A and Bruker AVANCE-500 instruments respectively. Chemical shifts (δ) are given from TMS (0 ppm) as internal standard for ^{1}H-NMR, and $^{13}CDCl_3$ (77.0 ppm) for ^{13}C-NMR. TLC was performed on aluminum backed silica gel 60 F254 plates and visualized by UV and/or exposure to I_2. Column chromatography was conducted with Merck Kieselgel 60: 70-230 mesh. Solvents were dried and freshly distilled according to common practice.

5, 5-Dioxo-5*H*-dibenzo[*b,d*]thiophene-3,7-dicarboxylic acid (3). A solution of 27 g (0.1 mol) dimethyl ester of 4,4'-biphenyldicarboxylic acid in 116.5 g (1 mol) chlorosulfonic acid was heated at reflux for 3 h (cease of evolution of HCl). The reaction mixture was cooled and poured on 1 kg of crushed ice. The precipitated crystals were filtered off, washed with water up to neutral medium and dried. The yield was 30.21 g (99%). MP > 400^{o}C (dec.); Elemental Anal. Calcd for $C_{14}H_8O_6S$: C 55.26, H 2.65, S 10.54 Found: C 55.01, H 2.53, S 10.36; ^{1}H NMR (DMSO-d_6, 100 MHz), δ: 4.5-6.2 (br s, 2H, -OH), 8.3 (s, 6H, Ar); IR (KBr, ν cm^{-1}): 3430, 2630, 2530, 1710, 1670, 1620, 1450, 1420, 1310, 1260, 1180, 1150, 1090, 950, 860, 770, 710.

Dimethyl 9, 10-diphenylphenanthrene-2,7-dicarboxylate (5). A mixture of dimethyl 2-iodobiphenyl-4, 4'-dicarboxylate **(38)** (1.3 g, 3.2 mmol), LiCl (0.138 g, 3.2 mmol), 1,2-diphenylethyne (0.65 g, 3.5 mmol), palladium diacetate (0.04 g, 5 mol %) and sodium acetate 0.5 g, 6.4 mmol) in 50 ml of DMFA was stirred at 95–105°C for 3 days. After cooling, the reaction mixture was poured into 100 ml of water and the precipitate was filtered off and washed with hexane. After drying, 0.61 g (42%) of **5** as a yellow powder was obtained. MP = 309-310°C; Elemental Anal. Calcd for $C_{30}H_{22}O_4$: C 80.70, H 4.97 Found: C 80.47, H 4.88; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 3.81 (s, 6H, $-CH_3$), 7.2–7.4 (m, 10H, -Ph), 8.09 (s, 2H, 1-, 8-H), 8.22 (d, 2H, J^{ortho} = 9 Hz, 3-, 6-H), 9.13 (d, 2H, J^{ortho} = 9 Hz, 3-, 6-H). IR (KBr, ν cm^{-1}): 3100, 3050, 2970, 1730, 1570, 1440, 1390, 1340, 1300, 1260, 1210, 1130, 1020, 970, 830, 770, 710.

1-Nitro-5, 5-dioxo-5*H*-dibenzo [*b,d*]thiophene-3,7-dicarboxylic acid (6). To a solution of 2 g (0.0065 mol) 5, 5'-dioxodibenzothiophen-3, 7-dicarboxylic acid **(3)** in 60 ml of H_2SO_4, 0.64 ml (0.013 mol) HNO_3 (70%) was added dropwise at 80°C. The resulting reaction mixture was stirred for 40 min, then was cooled and diluted with 100 ml of water. The precipitate was filtered off and washed with water up to neutral medium. Recrystallization from toluene gave white crystals. Yield: 2.07 g (90%), MP = 335-337°C; Elemental Anal. Calcd for $C_{14}H_7NO_8S$: C 48.14, H 2.02, N 4.01, S 9.18 Found: C 47.80, H 1.89, N 3.99, S 9.09; ^{1}H NMR (DMSO-d_6, 100 MHz), δ: 7.98 (dd, 1 H, J^{ortho} = 8.4 Hz, J^{para} = 0.5 Hz, 9-H), 8,38 (dd, 1 H, J^{ortho} = 8.4 Hz, J^{meta} = 1.6 Hz, 8-H), 8.54 (dd, 1 H, J^{meta} = 1.6 Hz, J^{para} = 0.5 Hz, 6-H), 8.72 (d, 1 H, J^{meta} = 1.6 Hz, 4-H), 8.74 (d, 1 H, J^{meta}= 1.6 Hz, 2-H); IR (KBr, ν cm^{-1}): 3090, 2630, 1730, 1610, 1540, 1400, 1370, 1315, 1230, 1170, 1155, 1060, 940, 920, 910, 865, 810, 775, 755, 745, 700, 650, 575, 535, 520.

1-Amino-5,5-dioxo-5*H*-dibenzo[*b,d*]thiophene-3,7-dicarboxylic acid (7). To a solution of 5 g (0.015 mol) nitro derivative (6) in 100 ml of THF, 0.5 g 5 % Pd/C was added and the resulting mixture was placed in hydrogenating apparatus and stirred at 60°C under 10 atm. pressure of hydrogen for 48 h. The catalyst was filtered off and washed with THF. Solvent was removed in vacuum, the residue was recrystallized from toluene to give yellow crystals. Yield: 3.29 g (70%). MP = 360°C; Elemental Anal. Calcd for $C_{14}H_9NO_6S$: C 52.66, H 2.84, N 4.39, S 10.04 Found: C 52.60, H 2.73, N 4.28, S 9.87; ^{1}H NMR (DMSO-d_6, 100 MHz), δ: 7.9 (dd, 1 H, J^{ortho} = 8.4 Hz, J^{meta} = 1.4 Hz, 8-H), 8.3-8.5 (m, 4 H); IR (KBr, ν cm^{-1}): 3450, 3300, 1725, 1640, 1610, 1560, 1430, 1410, 1310, 1275, 1190, 1120, 1040, 1015, 980, 900, 875, 865, 825, 805, 760, 700, 635.

1-Methoxy-5, 5-dioxo-5*H*-dibenzo [*b,d*]thiophene-3,7-dicarboxylic acid (8). To a solution of 1-nitro-5, 5-dioxodibenzothiophen-3, 7-dicarboxylic acid **6** (3 g, 10 mmol) in 50 ml of DMSO, 1.56 g (0,029 mol) MeONa was added. The reaction mixture was heated at 110°C and was stirred for 2 h. Then the reaction mixture was cooled, the formed crystals were filtered off, washed with acetone and then solved in water. The solution was acidified with 10% hydrochloric acid The precipitated crystals were separated by filtration and washed with water. Recrystallization from ethanol gave white crystals. Yield: 2.14 g (75%). MP = 360-361°C. Elemental Anal. Calcd for $C_{15}H_{10}O_7S$: C 53.89, H 3.02, S 9.59 Found: C 53.50, H 2.91, S 9.42; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 4.13 (s, 3H, -OCH_3), 7,87 (d, 1H, J^{meta} = 1 Hz, 2- or 4-H), 7.93 (d, 1H, J ^{meta}= 1 Hz, 2- or 4-H), 8.2-8.5 (m, 3 H, 6-, 8-, 9-H); IR (KBr, ν cm^{-1}): 3460, 2985, 2640, 2590, 1840, 1705, 1615, 1500, 1480, 1440, 1425, 1410, 1320, 1265, 1185, 1155, 1145, 1060, 1020, 950, 925, 870, 760, 730, 710, 655.

1-Hydroxy-5, 5-dioxo-5*H*-dibenzo [*b,d*]thiophen-3,7-dicarboxylic acid (9). A mixture composed of 5 g (0.012 mmol) methyl ether **8** and 20 g (0.17 mmol) pyridine hydrochloride was heated at 220°C and the resulting fusion was held at this temperature for 30 min. Then the mixture was cooled down and diluted with 50 ml of water. Precipitated crystals were filtered off and washed with water. Recrystallization from ethanol gave white crystals. Yield: 4.2 g (87.5%). MP > 380°C (subl.); Elemental Anal. Calcd for $C_{14}H_8O_7S$: C 52.50, H 2.52, S 10.01 Found: C 52.27, H 2.41, S 9.88; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 7.79 (d, 1H, J^{meta} = 1 Hz, 2- or 4-H), 7.81 (d, 1H, J^{meta} = 1 Hz, 2- or 4-H), 8.33 (m, 1H, 6-H), 8.34 (dd, 1H, J^{ortho} = 7 Hz, J^{meta} = 1.5 Hz, 8-H), 8.50 (dd, 1H, J^{ortho} = 7 Hz, J^{para} = 0.7 Hz, 9-H). IR (KBr, ν cm^{-1}): 3465, 3100, 1735, 1595, 1610, 1435, 1410, 1310, 1265, 1195, 1070, 985, 920, 880, 780, 765, 720, 690, 650.

3, 7-Bis [5-methylbenzoxazol-2-yl]-5, 5-dioxo-5*H*-dibenzo [*b,d*]thiophene (10). A reaction mixture composed of 3 g (0.01 mol) 5,5'-dioxodibenzothiophen-3,7-dicarboxylic acid **3**, 2 g (0.02 mol) 2-amino-4-methylphenol, 0.2 g (0,003 mol) H_3BO_3, 50 ml diphenyl ether and 10 g (0.13 mol) pyridine was heated at 180°C with stirring under argon atmosphere for 2 h. Then the temperature was raised up to 220°C and the reaction mixture was stirred for additional 3 h with slow distillation of pyridine and nascent water. The reaction mixture was cooled at RT and precipitated crystals were filtered off and washed successively with toluene and acetone. Recrystallization from toluene gave yellow crystals. Yield 2.7 g (63%). MP >250°C (dec.); Elemental Anal. Calcd for $C_{28}H_{18}N_2O_4S$: C 70.28, H 3.79, N 5.85, S 6.70 Found: C 69.85, H

3.67, N 5.76, S 6.59; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 2.31 (s, 6H, –CH_3), 7.01 (d, J^{ortho} = 8.0 Hz, 2H, 6',6''/7',7''-benzooxazolyl), 7.14 (d, J^{ortho} = 8.0 Hz, 2H, 6',6''/7',7''-benzooxazolyl), 7.76 (s, 2H, 4',4''-benzooxazolyl), 8.43 (d, J^{ortho} = 7.0 Hz, 2H, 2,8/1,9- H thioph.), 8.47 (d, J^{ortho} = 7.0 Hz, 2H, 2,8/1,9-H thioph.), 8,63 (s, 2H, 4,6- H thioph.); IR (KBr, ν cm^{-1}): 3100, 3047, 2997, 2963, 2893, 1750, 1687, 1667, 1623, 1580, 1567, 1545, 1497, 1480, 1430, 1380, 1367, 1342, 1306, 1290, 1277, 1232, 1206, 1180, 1168, 1116, 1100, 1043, 1023, 980, 932, 874, 845, 829, 800, 760; UV (DMF, λ_{max}, nm (ε, l/(mol*cm))): 368.5 (19600); FLU (DMF, λ_{max}, nm, λ_{EX} = 365.0 nm) 443.5.

***N, N*-Dimethyl-1-amino-5,5-dioxo-5*H*-dibenzo[*b,d*]thiophen-3,7-dicarboxylic acid diethyl ether (11).** 1-Amino-5,5-dioxodibenzothiophen-3,7-dicarboxylic acid **7 (**3.3 g, 10 mmol) was dissolved in 60 ml of ethanol saturated with HCl , then the reaction mixture was heated at reflux and stirred for 12 h. After cooling, a precipitate was filtered off and successively washed with ethanol and water. Dried crystals were solved in 40 ml of DMSO, 2,5 g (18.7 mmol) K_2CO_3 and 2,5 g (17.7 mmol) CH_3I were added, and then the reaction mixture was heated at 60°C and stirred for 140 h. The reaction mixture was diluted with water and extracted with CH_3Cl. Combined organic solution was dried over Na_2SO_4. Concentration of the solution in vacuum afforded a residue, which was purified by column chromatography on silica gel (toluene) to give 1.9 g (60%) of **11** as a green solid. Recrystallization from ethanol afforded green needles with mp = 210–212°C. Elemental Anal. Calcd for $C_{20}H_{21}NO_6S$: C 59.54, H 5.25, N 3.47, S 7.95 Found: C 59.18, H 5.13, N 3.41, S 7.82; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.87 (t, 6H, J = 7 Hz, $(CH_3)_2$), 2.88 (s, 6H, $N(CH_3)_2$), 4.41- 4.45 (m, 4H, -CH_2-), 8.06 (s, 1H, 2-H), 8.17 (s, 1H, 4-H), 8.35 (d, 1H, J^{ortho} = 8 Hz, 9-H), 8.45 (d, 1H, J^{ortho} = 8,5 Hz, 8-H), 8.50 (s, 1H, 6-H); IR (KBr, ν cm^{-1}): 3435, 3000, 2960, 2805, 1720, 1605, 1540, 1450, 1395, 1370, 1345, 1305, 1255, 1165, 1115, 1025, 985, 905, 860, 830, 805, 770, 755,720, 685.

***N*-Butyl-1-amino-5, 5-dioxo-5*H*-dibenzo [*b,d*]thiophene-3,7-dicarboxylic acid dibutyl ether (12).** A solution of 2.4 g (0.75 mmol) amine **(7)** and 0.5 ml H_2SO_4 in 30 ml of butanol was heated 7 h with regular distillation of nascent water. The reaction mixture was cooled, diluted with $CHCl_3$ and washed with 100 ml of 5% $NaHCO_3$ and water. Concentration of the solution in vacuum afforded a residue, which was purified by column chromatography on silica gel (toluene) to give 2 g (55%) of **12** as a green solid. Recrystallization from toluene afforded green crystals with mp = 171-172°C. Elemental Anal. Calcd for $C_{26}H_{33}NO_6S$: C 64.04, H 6.82, N 2.87, S 6.58 Found: C 63.76, H 6.69, N 2.75, S 6.49; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 0.92-1.06 (m, 9H, CH_3-), 1.45-1.60 (m, 6H, -CH_2-), 1.75-1.82 (m, 6H, -CH_2 -), 3.33-3.36 (m, 2H, -NH-CH_2-), 4.34-4.40 (m, 4H, -OCH_2-), 4.40 (s, 1H, -NH-), 7.26 (s, 1H, 2-H), 7.84 (d, 1H, J^{meta} = 1,5 Hz, 4-H), 7.87 (d, 1H, J^{ortho} = 8 Hz, 9-H), 8.36 (dd, 1H, J^{meta} = 1.5 Hz, J^{ortho} = 8 Hz, 8-H), 8.46 (d, 1H, J^{meta} = 1.5 Hz, 6-H); IR (KBr, ν cm^{-1}): 2975, 2950, 2890, 1730, 1610, 1585, 1490, 1395, 1305, 1255, 1180, 1155, 1130, 1070, 1035, 950, 900, 860, 775, 750, 640, 600.

1-Hexyloxy-5, 5-dioxo-5*H*-dibenzo [*b,d*]thiophen-3,7-dicarboxylic acid dibutyl ether (13). A mixture composed of 1-hydroxy-5,5-dioxodibenzothiophen-3,7-dicarboxylic acid **(9)** (2.2 g, 7 mmol), 30 ml butanol and 0.5 ml H_2SO_4 was boiled for 10 h with regular distillation of nascent

water. Then the reaction mixture was cooled, diluted with toluene and washed with 100 ml of 5% solution of $NaHCO_3$. The organic phase was dried over sodium sulfate and solvent was removed in vacuum. The residue without additional purification was solved in 40 ml of DMSO, 2, 5 g (18.9 mmol) of K_2CO_3 and 2, 0 g (12.1 mmol) of 1-bromhexane were added. The reaction mixture was heated at 60°C and stirred for 12 h. After cooling-off, the mixture was diluted with water and was extracted with chloroform. Combined organic phases were dried over Na_2SO_4. Concentration of the solution in vacuum afforded a residue, which was purified by recrystallization from toluene to give **13** (3 g, 85%) as white crystals. MP= 80-82°C; Elemental Anal. Calcd for $C_{28}H_{36}O_7S$: C 65.09, H 7.02, S 6.21 Found: C 64.73, H 6.86, S 6.08; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 0.94 (t, 3H, J = 7 Hz -C<u>H</u>$_3$), 1.01 (t, 6H, J=7 Hz, -C<u>H</u>$_3$), 1.36-1.60 (m, 12H, -CH_2-), 1.77 (m, 4H, -$(CH_2)_2$-), 1.83 (m, 2H, -CH_2-), 4.28 (t, 2H, J = 6.5 Hz, Hex-OCH_2-), 4.38 (t, 4H, J=6.5, Hz, Bu-OCH_2-), 7.85 (d, 1H, J^{meta} = 1 Hz, 2-H), 8,09 (d, 1H, J^{meta} = 1 Hz, 4-H), 8.33 (m, 1H, J^{ortho} = 8.5 Hz, J^{meta} = 1.5 Hz, 8-H), 8.42 (d, 1H, J^{ortho} = 8.5 Hz, 9-H), 8.48 (d, 1H, J^{meta} = 1.5 Hz, 6-H); IR (KBr, ν cm^{-1}): 2985, 2640, 2590, 1840, 1705, 1615, 1500, 1480, 1440, 1425, 1410, 1320, 1265, 1185, 1155, 1145, 1060, 1020, 950, 925, 870, 760, 730, 710, 655.

1-Hexyloxy-5, 5-dioxo-5*H*-dibenzo [*b,d*]thiophene-3,7-dicarbaldehyde (14). To a stirred solution of 11.6 g (0.3 mol) $NaBH_4$ in 60 ml of diglyme, 3.8 g (0.02 mol) of $AlCl_3$ was added and, after 15 min, 4.5 g (0.009 mol) of dibutyl ether **13** was added. The resulting reaction mixture was heated at 110°C and was intensively stirred for 6 h, then was cooled at RT and quenched with 100 ml of water. Precipitated crystals were filtered off and washed with water. The crude product was dissolved in 30 ml of $CHCl_3$, 3 g PCC was added and the reaction mixture was stirred at RT for 10 h. Then 5 ml of isopropanol was added to quench excess of PCC, the resulting solution was filtered through a layer of silica gel, the filtrate was concentrated in vacuum and the residue was purified by column chromatography to give **14** (2.8 g, 86%) as a white solid. Recrystallization from toluene gives white crystals. MP=142-144°C; Elemental Anal. Calcd for $C_{20}H_{20}O_5S$: C 64.50, H 5.41, S 8.61 Found: C 64.12, H 5.28, S 8.25; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 0.89 (t, 3H, J = 7 Hz, CH_3), 1.30-1.39 (m, 4H, $(CH_2)_2$), 1.53 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 4.39 (t, 2H, J = 6,5 Hz, -OCH_2-), 7.96 (s, 1H, 2-H), 8.12 (d, 1H, J^{meta} = 1 Hz, 4-H), 8.33 (m, 1H, J^{ortho} = 8.5 Hz, J^{meta} = 1.5 Hz, 8-H), 8.54 (s, 1H, 6-H), 8.56 (d, 1H, J^{ortho} = 8.5 Hz, 9-H), 10.09 (s, 1H, -CHO), 10.10 (s, 1H, -CHO); IR (KBr, ν cm^{-1}): 3450, 3080, 2975, 2950, 2875, 1700, 1610, 1570, 1490, 1440, 1400, 1350, 1325, 1290, 1215, 1160, 1050, 920, 875, 860, 725, 626.

***N*-Butyl-1-amino-5, 5-dioxo-5*H*-dibenzo [*b,d*]thiophen-3,7-dicarbaldehyde (15).** To a suspension of 0.37 g (10 mmol) $LiAlH_4$ in 50 ml of THF, 3.0 g (6 mmol) of N-butyl-1-amino-5, 5-dioxodibenzothiophen-3,7-dicarboxylic acid dibutyl ether **12** in 30 ml of THF was added. The reaction mixture was stirred for 12 h, excess of $LiAlH_4$ was quenched with 1 ml of 5% NaOH, and then an inorganic precipitate was filtered off and washed with THF. The filtrate was dried over sodium sulfate and concentration of the solution in vacuum afforded 1.6 g (74%) of 1-butylamino-3, 7-bis (hydroxymethyl)-5*H*-dibenzo[*b*,*d*]thiophene-5,5-dione as a green solid, which was recrystallized from ethanol. MP= 210-212°C. Elemental Anal. Calcd. for

$C_{18}H_{21}NO_4S$: C 62.23, H 6.09, N 4.03, S 9.23 Found: C 61.89, H 6.00, N 3.96, S 9.07; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 0.87 (t, 3H, J = 8 Hz, CH_3), 1.41 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 3.23 (m, 2H, N-CH_2), 4.54 (t, 2H, J = 6 Hz, CH_2-O), 4.59 (t, 2H, J = 6 Hz, CH_2-O), 5.42 (t, 1H, J = 6 Hz, OH), 5.48 (t, 1H, J = 6 Hz, OH), 5.89 (t, J = 5,5 Hz, NH), 6.99 (s, 1H, 2-H), 7.06 (d, 1H, J^{meta} = 0.5 Hz, 4-H), 7.65 (dd, 1H, J^{ortho} = 8 Hz, J^{meta} = 1,5 Hz, 8-H), 7.79 (d, 1H, J^{meta} = 1,5 Hz, 6-H), 8.12 (d, 1H, J = 8.5 Hz, 9-H); IR (KBr, ν cm^{-1}): 3400, 2975, 2950, 2880, 1610, 1570, 1450, 1410, 1285, 1210, 1150, 1065, 1010, 930, 890, 820, 720, 625. The oxidation of the obtained bis(hydroxymethyl) derivative (1 g, 2 mmol) with PCC (2 g) in 20 ml of $CHCl_3$ according to the procedure for **34** gave 0.6 g of **15** as a orange solid, which was used in next stage without purification.

1-Dimethylamino-5, 5-dioxo-5*H*dibenzo [*b*,*d*]thiophene-3,7-dicarbaldehyde (16). The dialdehyde **16** (0.3 g) was obtained as an orange solid according to the procedure for **15** from 2 g (4 mmol) of diester **11.** The crude product was used in the next stage without any purification.

1-Hexyloxy-3, 7-bis [(*E*)-2-phenylethenyl]-5*H*-dibenzo [*b*,*d*]thiophene-5,5-dione (17). To a stirred suspension of triphenylbenzylphosphonium bromide (0.5 g, 1, 1 mmol) in 40 ml of dry THF, *t*-BuOK (0.12 g, 1 mmol) was added. The reaction mixture was stirred approx. for 15 min until a homogeneous dark-red solution formed. Then a solution of **14** (185 mg, 0.5 mmol) in 10 ml of THF was added dropwise and stirring was continued for 40 min. Concentration of reaction mixture in vacuum afforded a residue, which was purified by column chromatography on silica gel (toluene) to give 194 mg (75%) of **17** as a yellow solid. Recrystallization from toluene afforded yellow crystals. MP=172-173°C; Elemental Anal. Calcd for $C_{34}H_{32}O_3S$: C 78.43, H 6.19, S 6.16 Found: C 78.71, H 5.58, S 6.42; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 0.90 (t, 3H, J = 7.5 Hz, CH_3), 0.91-1.57 (m, 4H, $(CH_2)_2$), 1.53 (m, 2H, CH_2), 1.94 (m, 2H, CH_2), 4.33 (t, 2H, J = 6.5 Hz, -OCH_2), 7.41-7.30 (m, 8H, arom), 7.55-7.84 (m, 7H, arom), 7.84 (s, 1H, 4-H thioph.), 7.96 (dd, 1H, J^{ortho} = 8 Hz, J^{meta} = 1.5 Hz, 8-H thioph.), 8.21 (d, 1H, J^{ortho} = 8 Hz, 9-H thioph.), 8.26 (d, 1H, J^{meta} = 1.5 Hz, 6-H thioph.); ^{13}C NMR (DMSO-d6, 125.75 MHz), δ: 14.11, 22.68, 25.81, 26.89, 29.12, 31.49, 31.87, 69.01, 111.12, 114.63, 118.84, 126.07, 126.46, 126.58, 126.80, 126.86, 128.35, 128.49, 128.82, 131.08, 131.60, 132.05, 136.29, 136.47, 141.26, 156.20; IR (KBr, ν cm^{-1}): 3040, 2950, 2870, 1630, 1590, 1500, 1450, 1415, 1300, 1160, 995, 820, 845, 790, 700, 620; FLU (toluene, λ_{max}, nm, λ_{EX} = 383.0 nm) 448.0.

1-Butylamino-3, 7-bis [(*E*)-2-phenylethenyl]-5*H*-dibenzo [*b*,*d*]thiophene-5,5-dione (18). According to the procedure for obtaining of **17**: triphenylbenzylphosphonium bromide (1.8 g, 4 mmol), *t*-BuOK (0.45 g, 4 mmol), the crude product **15 (**0.6 g). After purification **18** (486 mg, 20% calculated from diester **12**) was obtained as a yellow solid. MP=262-264°C (toluene). Elemental Anal. Calcd for $C_{32}H_{29}NO_2S$: C 78.18, H 5.95, N 2.85, S 6.52 Found: C 78.42, H 5.79, N 2.74, S 6.72; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 0.99 (t, 3H, J = 7.5 Hz, CH_3), 1.48 (m, 2H, CH_2), 1.71 (m, 2H, CH_2), 3.33 (m, 2H, N-CH_2), 5.99 (t, 1H, J = 5.5, -NH), 7.20 (s, 1H, 2-H thioph.), 7.30-7.43 (m, 8H, arom.), 7.56 (d, 2H, J = 16.5 Hz, *trans*-**CH**=CH), 7.55-7.67 (m, 5H, arom.), 7.92 (m, 1H, J^{ortho} = 8 Hz, J^{meta} = 1Hz, 8-H thioph.), 8.17 (d, 1H, J^{ortho} = 8 Hz, 9-H thioph.), 8.26 (d, 1H, J^{meta} = 1 Hz, 6-H thioph.); ^{13}C NMR (DMSO-d6, 125.75 MHz), δ: 13.8,

19.8, 30.4, 42.8, 106.5, 113.1, 115.7, 118.9, 124.2, 126.30, 126.7, 127.2, 128.1, 128.7, 129.6, 130.6, 130.8, 132.1, 136.6, 137.0, 137.3, 139.3, 140.4, 146.0; IR (KBr, ν cm^{-1}): 3390, 3040, 2970, 2940, 2875, 1600, 1575, 1500, 1455, 1415, 1300, 1220, 1160, 1065, 970, 915, 880, 835, 760, 720, 700, 640; FLU (toluene, λ_{max}, nm, λ_{EX} = 387.0 nm) 473.0.

1-Dimethylamino-3, 7-bis [(*E*)-2-phenylethenyl]-5*H*-dibenzo [*b*,*d*]thiophene-5,5-dione (19). According to the procedure for obtaining of **17**: triphenylbenzylphosphonium bromide (0.9 g, 2 mmol), t-BuOK (0.25 g, 2.2 mmol), the crude product **16 (**0.3 g). After purification **19** (246 mg, 11% calculated from diester **11**) was obtained as a yellow solid. MP=240-242°C (toluene). Elemental Anal. Calcd for $C_{30}H_{25}NO_2S$: C 77.72, H 5.44, N 3.02, S 6.92. Found: C 77,96, H 5.32, N 2.88, S 7.15; ^{1}H NMR (DMSO-d6, 500 MHz), δ: 3.26 (s, 6H, $N(CH_3)_2$), 7.72-7.85 (m, 8H, arom.), 8.01 (d, 2H, J = 16Hz, *trans*-**CH**=CH), 8.01-8.10 (m, 5H, arom.), 8.36 (s, 1H, 4-H dibenzothioph.), 8.38 (dd, 1H, J^{ortho} = 8 Hz, J^{meta} = 1.5 Hz, 8-H dibenzothioph.), 8.66 (d, 1H, J^{ortho} = 8 Hz, 9-H dibenzothioph.), 8,70 (d, 1H, J^{meta} = 1.5 Hz ,6-H dibenzothioph.); ^{13}C NMR (DMSO-d6, 125.75 MHz), δ: 21.0, 30.6, 43.9, 112.7, 118.8, 121.0, 122.9, 125.2, 125.6, 126.3, 126.5, 126.8, 128.1, 128.2, 128.9, 131.1, 131.4, 132.4, 136.5, 136.6, 137.5, 138.5, 139.7, 140.6, 151.7; IR (KBr, ν cm^{-1}): 3075, 3090, 2960, 2880, 2855, 2810, 1630, 1600, 1485, 1460, 1410, 1305, 1215, 1165, 1070, 1015, 975, 945, 900, 845, 765, 730, 705, 640; FLU (toluene, λ_{max}, nm, λ_{EX} = 406.0 nm) 472.0.

Dibutyl 2, 2'-dihydroxy [1, 1'-biphenyl]-4, 4'-dicarboxylate (21a). A mixture of well ground NaOH (10 g, 0.25 mol) and the diacid **8** (1 g, 3 mmol) was heated at 210°C under intensive stirring for 20 min. Then the cooled fuse was dissolved in 100 ml of water and was acidified with 10% hydrochloric acid. Precipitated crystals were filtered off, washed with water and air-dried. The crude product was boiled in mixture of 30 ml of butanol and 0.5 ml of H_2SO_4 with regular removing of nascent water until TLC indicated no starting material. The reaction mixture was diluted with $CHCl_3$, was washed with 100 ml of 5% $NaHCO_3$ and brine. Concentration of the solution in vacuum afforded a brown solid, which was placed in the Soxhlet apparatus and was extracted with petroleum ether to remove 2-hydroxy derivative **21b**. The solid residue was recrystallazed from toluene to yield **21a** (0.6 g, 52%) as white crystals. The extract was concentrated in vacuum and the residue was purified by column chromatography on silica gel (toluene) to give **21b** (0.3 g, 27%) as a white solid.

Dibutyl 2, 2'-dihydroxy [1, 1'-biphenyl]-4, 4'-dicarboxylate (21a). MP=170-172°C; Elemental Anal. Calcd for $C_{22}H_{26}O_6$: C 68.38, H 6.78 Found: C 68.00, H 6.65; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 0.94 (t, 6H, J = 7.4 Hz, CH_3), 1.40-1.47 (m, 4H, CH_2), 1.66-1.72 (m, 4H, CH_2), 4.27 (t, 4H, J = 6.5 Hz, -OCH_2), 7.29 (d, 2H, J^{ortho} = 8 Hz, 6-, 6'-H), 7.42 (dd, 2H, J^{ortho} = 8 Hz, J^{meta} = 1 Hz, 5-, 5'-H), 7.52 (br s, 2H, 3-, 3'-H), 9.80 (s, 2H, OH); IR (KBr, ν cm^{-1}): 3450, 2980, 2960, 2900, 1730, 1630, 1600, 1490, 1450, 1440, 1420, 1320, 1260, 1240, 1150, 1130, 1090, 1050, 1040, 990, 920, 870, 840, 790, 640.

Dibutyl 2-hydroxy [1,1'-biphenyl]-4,4'-dicarboxylate (21b). MP = 93-95°C; Elemental Anal. Calcd for $C_{22}H_{26}O_5$: C 71.33, H 7.07 Found: C 70.97, H 6.99; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 0.94 (t, 6H, J = 7.4 Hz, CH_3), 1.40-1.47 (m, 4H, CH_2), 1.66-1.73 (m, 4H, CH_2), 4.27 (t, 4H, J =

6.5 Hz, -OCH_2), 4.29 (t, 4H, J = 6.5 Hz, -OCH_2), 7.45 (d, 1H, J^{ortho} = 8 Hz, 5- or 6-H), 7.49 (d, 1H, J^{ortho} = 8 Hz, 5- or 6-H), 7.60 (br s, 1H, 3-H), 7.74 (d, 2H, J^{ortho} = 8.2 Hz, 3'-, 5'-H), 8.00 (d, 2H, J^{ortho} = 8.2 Hz, 2'-, 6'-H), 10.22 (s, 1H, OH); IR (KBr, ν cm^{-1}): 3430, 2990, 2960, 2910, 1740, 1710, 1630, 1610, 1500, 1450, 1430, 1380, 1320, 1290, 1260, 1170, 1150, 1140, 1100, 1070, 1070, 1040, 1020, 970, 930, 900, 850, 820, 800, 770, 740, 650.

2-Hexyloxy-4, 4'-bis [hydroxymethyl]-1,1'-biphenyl (23). To dry methanol (1l) saturated with HCl, 26.5 g (0.103 mol) of well-milled powder of 2-hydroxy [1,1'-biphenyl]-4,4'-dicarboxylic acid **20** was added. The resulting suspension was stirred under reflux for 12 h. After cooling, a precipitate was filtered off, washed with cold methanol. The crude product was dissolved in 180 ml of DMSO and 13.8 g (0.1 mol) of K_2CO_3 was added. The reaction mixture was heated at 75°C, 16.5 g (0.1 mol) of 1-bromohexane was added and the resulting solution was stirred for 10 h at 75°C, then was poured into 0.5 l of 5% hydrochloric acid, and extracted with ethyl acetate. The organic layer was washed with water and dried over Na_2SO_4. After removal of solvent, the residue was recrystallized from ethanol. The obtained crystals were dissolved in 150 ml of THF and added dropwise to the suspension of 3.8 g (0.1 mol) $LiAlH_4$ in 100 ml of THF under stirring. The reaction mixture was refluxed for 2 h, excess of $LiAlH_4$ was quenched with addition of 15 ml of 15 % water solution of NaOH, and an inorganic solid was separated by filtration and washed with THF. Solvent was removed under reduced pressure, the residue was dissolved in ethyl acetate, washed with water and dried over Na_2SO_4. After removal of solvent, the residue was crystallized from toluene to afford 26.73 g (83%) of white crystals. MP = 60-61°C; Elemental Anal. Calcd for $C_{20}H_{26}O_3$: C 76.40, H 8.33 Found: C 76.04, H 8.21; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.85 (t, J= 7 Hz, 3H, -CH_3), 1.4- 1.48 (m, 6H, -$(CH_2)_3$-), 1.58- 1.86 (m, 2H, -CH_2-), 1.81 (s. 2H, -OH,), 3.95 (t, 2H, J= 7 Hz, -O-CH_2-), 4.69 (s, 2H, -CH_2-), 4.70 (s, 2H, -CH_2-), 7.00 (d, 1H, J^{meta} = 1.5 Hz, 3 biphenyl), 7.10 (dd, 1H, J^{ortho} = 7.5 Hz, J^{meta} = 1.5 Hz, 5 biphenyl), 7.29 (d, 1H, J= 7.5 Hz, 6 biphenyl), 7.41 (d, 2H, J^{ortho} = 8.5 Hz, 3',5' biphenyl), 7.50 (d, 1H, J^{ortho} = 8.5 Hz, 2',6' biphenyl); IR (KBr, ν cm^{-1}): 3350, 2950, 2880, 1610, 1580, 1490, 1470, 1430, 1400, 1270, 1175, 1140, 1010, 960, 820, 810; EIMS (m/z): 315($[M+1]^+$, 10), 314($[M]^+$, 44), 312($[M-2H]^+$, 100), 311($[M-3H]^+$, 71), 228($[C_{14}H_{12}O_3]^+$,93), 226(61), 225(86), 209(50), 197(52), 153(43), 57(43), 43(42), 18(14).

2, 2'-Dihexyloxy-4, 4'-bis [hydroxymethyl]-1, 1'-biphenyl (24). To a solution of dibutyl 2, 2'-dihydroxy [1, 1'-biphenyl]-4, 4'-dicarboxylate **21a** (0.6 g, 1.5 mmol) and 1-bromohexane (0.6 g, 3.6 mmol) in 40 ml of DMSO, anhydrous K_2CO_3 (0.5 g, 3.6 mmol) was added and the resulting mixture was heated at 60°C and stirred for 12 h. Then the reaction mixture was diluted with water and extracted with chloroform. The combined organic solution was dried over Na_2SO_4, and then concentrated in vacuum. The residue brown oil was added as a solution in 10 ml of dry THF to a suspension of $LiAlH_4$ (0.37 g, 10 mmol) in 30 ml of THF and the reaction mixture was stirred at RT for 12 h. Excess of $LiAlH_4$ was quenched with 5% solution of NaOH in water and inorganic solids were filtered off and washed with hot THF. After concentration of the filtrate in vacuum the residue was purified by column chromatography on silica gel (toluene) to yield **24** (0.7 g, 80%) as colorless oil. Elemental Anal. Calcd for $C_{26}H_{38}O_4$: C 75.32, H 9.24 Found: C

74.97, H 9.12; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 0.86 (t, 6H, J = 7 Hz, CH_3), 1.20-1.32 (m, 12H, CH_2), 1.55-1.61 (m, 4H, CH_2), 3.88 (t, 4H, J = 6.5 Hz, -OCH_2-), 4.70 (d, 4H, J = 5.5, -C**H$_2$**OH), 4.93 (t, 2H, J = 5.5 Hz, OH), 6.82 (dd, 2H, J^{ortho} = 8 Hz, J^{meta} = 1 Hz, 5-, 5'-H), 6.90 (br s, 2H, 3-, 3'-H), 7.04 (d, 2H, J^{ortho} = 8 Hz, 6-, 6'-H); IR (KBr, ν cm^{-1}): 2975, 2950, 2880, 1620, 1590, 1570, 1510, 1470, 1420, 1290, 1260, 1200, 1150, 1070, 1040, 1025, 970, 940, 865, 840, 790.

4,4'-Bis[bromomethyl]-2-(hexyloxy)biphenyl. To a cooled at 0°C solution of 4 g (13 mmol) 4,4`-bis(dihydroxymethyl)-2-(hexyloxy)biphenyl **(24)** in CCl_4, 3 g (10 mmol) of PBr_3 was added dropwise under stirring. The reaction mixture was stirred for 5 h at RT, and then it was poured into 100 ml of water, and extracted with CCl_4. The combined organic solution was washed with water and dried over Na_2SO_4. After removal of solvent, the residue was purified by column chromatography on silica gel (eluent: toluene) to give white solid (4.89 g, 86%), which was recrystallized from hexane. MP = 40°C; Elemental Anal. Calcd for $C_{20}H_{24}Br_2O$: C 54.57, H 5.50 Found: C 54.21, H 5.36; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.90 (t, J = 7 Hz, 3H, -CH_3), 1.2-1.9 (m, 8H, -$(CH_2)_4$-), 3.96 (t, 2H, J = 7 Hz, -OCH_2-), 4.50 (s, 2H, -CH_2-), 4.53 (s, 2H, CH_2-Br), 6.99 (d, 1H, J^{meta} = 1.5 Hz, 3-H), 7.02 (dd, 1H, J^{ortho} = 7.5 Hz, J^{meta} = 1.5 Hz, 5-H), 7.27 (d, 1H, J^{ortho} = 7.5 Hz, 6-H), 7.39 (d, 2H, J^{ortho} = 8.5 Hz, 3'-,5'-H), 7.48 (d, 1H, J^{ortho} = 8.5 Hz, 2'-,6'-H); IR (KBr, ν cm^{-1}): 3450, 2930, 2860, 1610, 1500, 1440, 1400, 1280, 1210, 1180, 1070, 820, 650, 600, 550.

4, 4'-bis [(triphenylphosphonio)methyl]-2-(hexyloxy)biphenyl dibromide (25). A mixture of 2 g (4,5 mmol) 4,4'-bis(bromomethyl)-2-(hexyloxy)biphenyl, 3.33 g (12 mmol) of triphenylphosphine, and 50 ml of DMF was heated at 150ºC for 5-6 h. Then a half volume of DMF was removed in vacuum and 70 ml of toluene was added. The precipitated white crystals were filtered off, washed with cold toluene (2×10 ml), and vacuum dried at room temperature to afford 4.18 g (95%) of a white powder. MP = 250°C (dec.); IR (KBr, ν cm^{-1}): 3450, 2950, 2850, 1440, 1120, 750, 720, 680, 500.

2-Hexyloxy-1, 1'-biphenyl-4,4'-dicarbaldehyde (26). To a stirred solution of 2-hexyloxy-4,4'-bis[hydroxymethyl]-1,1'-biphenyl **23 (**14 g, 0.041 mol) in CH_2Cl_2, 26.4 g (0.123 mol) of PCC in 80 ml of dioxane was added dropwise during 1.5 h. Inorganic solids were separated off, the filtrate was concentrated in vacuum and the residue was purified by column chromatography on silica gel to give 2-(hexyloxy)-1,1'-biphenyl-4,4'-dicarbaldehyde **26** (12.02 g, 85 %) as a white solid. Recrystallization from hexane gave yellow crystals. MP = 40-41°C; Elemental Anal. Calcd for $C_{20}H_{22}O_3$: C 77.39, H 7.14 Found: C 76.99, H 7.04; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.85 (t, J= 7 Hz, 3H, -CH_3), 1.1- 1.8 (m, 8H, -$(CH_2)_4$-), 4.05 (t, 2H, J= 7 Hz, -O-CH_2-), 7.38 (d, 1H, J^{meta} = 1.5 Hz, 3 biphenyl), 7.43 (dd, 1H, J^{ortho} = 7.5 Hz, J^{meta} = 1.5 Hz, 5 biphenyl), 7.56 (d, 1H, J= 7.5 Hz, 6 biphenyl), 7.83 (d, 2H, J^{ortho} = 8.5 Hz, 3',5' biphenyl), 7.87 (d, 1H, J^{ortho} = 8.5 Hz, 2',6' biphenyl), 10.05 (s, 2H, CHO); IR (KBr, ν cm^{-1}): 2960, 2940, 2860, 1700, 1600, 1570, 1560, 1430, 1380, 1310, 11290, 1270, 1210, 1170, 1150, 1140, 1050, 1000, 840, 810, 760; EIMS (m/z) : 311($[M+1]^+$, 16), 310($[M]^+$, 100).

2, 2'-Bis (hexyloxy) [1,1'-biphenyl]-4,4'-dicarbaldehyde (27). To a solution of **24** (2.7 g, 6.5 mmol) in 70 ml of $CHCl_3$, 5 g PCC in 50 ml of dioxane was added and the resulting mixture was stirred at RT for 10 h. The reaction mixture was filtered through a layer of silica gel and purified by flash chromatography to afford **27** as colorless oil. Yield 2.2 g (82%). Elemental Anal. Calcd for $C_{26}H_{34}O_4$: C 76.06, H 8.35 Found: C 75.74, H 8.23; ^{1}H NMR ($CDCl_3$, 500MHz), δ: 0.82 (t, 6H, J = 7 Hz), 1.22–1.30 (m, 12H, -C**H**$_2$-), 1.58 – 163 (m, 4H, -C**H**$_2$-), 4.00 (t, 4H, J = 6.5 Hz, -OC**H**$_2$-), 7.37 (d, 2H, J = 7.5 Hz, 6,6'-H), 7.45 (d, 2H, J = 1 Hz, 3,3'-H), 7.51 (dd, 2H, J = 1, Hz, J = 7.5 Hz, 5,5'-H), 9.98 (s, 2H, C**H**O); IR (KBr, ν cm^{-1}): 3460, 3000, 2970, 2895, 1730, 1690, 1610, 1570, 1485, 1435, 1400, 1280, 1260, 1230, 1185, 1155, 1055, 1025, 920, 890, 850, 760, 680.

4, 4'-Bis [(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-2-(hexyloxy)biphenyl (28). A sodium methylate solution, obtained from 0.32 g of sodium (14 mmol) and 15 ml of MeOH was added dropwise under stirring to a solution of aldehyde **26** (1.86 g, 6 mmol) and 2-methyl-1,3-benzoxazole (2.1 g, 15 mmol) in 25 ml of DMSO. The reaction mixture was heated at 50-60°C and stirred for 3 h, then cooled at RT and a formed precipitate was filtered off, washed with MeOH and dried in vacuum. Recrystallization from ethanol gave **28** (2.6 g, 80%) as yellow crystals. MP = 155-156°C; Elemental Anal. Calcd for $C_{36}H_{32}N_2O_3$: C 79.97, H 5.97, N 5.18 Found: C 80.32, H 5.73, N 5.33; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.900 (t, 3H, J = 6.4 Hz, -CH_3), 1.30- 1.50 (m, 6H, -$(CH_2)_3$-), 1.80 (m, 2H, -CH_2-) 4.11 (t, 2H, J= 6.4 Hz, -OCH_2-), 7.11 (d, 1H J = 16 Hz, *trans*-CH=CH), 7.12 (d, 1H J = 16 Hz, *trans*-CH=CH), 7.19 (s, 1H, arom.), 7.27 (d, 1H, J= 7.2 Hz, arom.), 7.33- 7.36 (m, 4H, arom.), 7.41 (d, 1H, J= 8 Гц, arom.), 7.53- 7.55 (m, 2H, arom.), 7.63-7.67 (m, 4H, arom.), 7.72-7.74 (m, 2H, arom.), 7.79 (d, 1H, J = 16.0 Hz, *trans*-CH=CH), 7.83 (d, 1H, J = 16.0 Hz, *trans*-CH=CH); IR (KBr, ν cm^{-1}): 2950, 2870, 1640, 1600, 1540, 1460, 1430, 1410, 1360, 1270, 1250, 1190, 1160, 1020, 980, 940, 850, 830, 760; FLU ($CHCl_3$, λ_{max}, nm, λ_{EX} = 365.0 nm) 449.0, film - 475.

4, 4'-Bis [(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-2,2'-(dihexyloxy)biphenyl (29). To a solution of dialdehyde **(27) (**200 mg, 0.5 mmol) and 2-methyl-1, 3-benzoxazole (230 mg, 1.7 mmol) in 15.0 ml of DMSO, *t*-BuOK (120 mg, 1 mmol) was added. The reaction mixture was heated at 40-50°C for 16 h under stirring, then was diluted with brine and extracted with toluene. Organic phases were combined and solvents removed by the rotary evaporator. The residue was purified by column chromatography on silica gel (toluene) to give **29** (260 mg, 80%) as yellow solid. The recrystallization from toluene afforded yellow crystals. MP = 128-130°C; Elemental Anal. Calcd for $C_{42}H_{44}N_2O_4$: C 78.72, H 6.92, N 4.37 Found: C 78.43, H 6.99, N 4.15; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 0.85 (t, 6H, J =7 Hz, CH_3), 1.21-1.35 (m, 12H, -CH_2-), 1.63 (m, 4H, -$(CH_2)_2$-), 4.01 (t, 4H, J = 6.5 Hz, -OCH_2), 7.22-7.27 (m, 6H, arom.), 7.31-7.36 (m, 6H, arom.), 7.59 (dd, 2H, J^{ortho} = 7Hz, J^{meta} = 1.5Hz, 6,6'-H), 7.67 (dd, 2H, J^{ortho} = 7Hz, J^{meta} = 2 Hz, 5,5'-H), 7.79 (d, 2H, J = 16Hz, *trans*-CH=C**H**-); ^{13}C NMR ($CDCl_3$, 125.75 MHz), δ: 13.96, 14.11, 22.58, 22.68, 25.64, 29.09, 31.45, 31.87, 68.49, 110.30, 110.49, 113.67, 119.82, 124.51, 125.19, 129.38, 131.94, 135.61, 139.58, 142.21, 150.43, 156.89; IR (KBr, ν cm^{-1}): 3070, 2970, 2870, 1645, 1605,

1540, 1495, 1455, 1420, 1395, 1355, 1250, 1275, 1250, 1190, 1160, 1040, 1020, 985, 950, 870, 830, 810, 765; FLU ($CHCl_3$, λ_{max}, nm, λ_{EX} = 365.0 nm) 455.0; film - 443.

General procedure for the Wittig condensation

To the suspension of 1 g (1 mmol) 4,4'-bis[(triphenylphosphonio)methyl]-2-(hexyloxy)biphenyl dibromide **(25)** in 20 ml of dry THF, *t*-BuOK (0.28 g, 2.5 mmol) was added and the reaction mixture was stirred until complete dissolution of phosphonium salt happened with formation of the dark-red solution . Then a solution of 2 mmol corresponding aldehyde in 10 ml of THF was slowly added and the resulting mixture was stirred for an additional 2 h. After 2 h, the reaction mixture was poured into 100 ml of water and extracted with chloroform. The combined organic phase was washed with water and then dried over Na_2SO_4. After removal of solvent, the residue was purified by column chromatography on silica gel (eluent: chloroform) and recrystallized from hexane.

2-Hexyloxy-4, 4'-bis [2-phenylethenyl]-1,1'-biphenyl (30a). Yield 0.44 g (95%). MP = 152-153°C; Elemental Anal. Calcd for $C_{34}H_{34}O$: C 89.04, H 7.47 Found: C 88.69, H 7.61; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.85 (t, 3H, J = 7 Hz, -CH_3), 1.2- 1.9 (m, 8H, -$(CH_2)_4$-), 4.05 (t, 2H, J = 7 Hz, -O-CH_2-), 7.1- 7.6 (m, 21H, arom.); ^{13}C NMR ($CDCl_3$, 125.75 MHz), δ: 14.01, 22.58, 25.78, 29.14, 31.45, 68.50, 110.30, 119.30, 126.03, 126.31, 126.47, 127.52, 127.66, 128.38, 128.47, 128.52, 128.67, 128.69, 129.76, 137.24, 137.44, 137.85, 137.65, 137.80; (KBr, ν cm^{-1}): 2950, 2930, 2850, 1600, 1500, 1450, 1400, 1270, 1230, 1180, 1140, 1070, 1030, 1000, 960, 810, 750, 680; UV ($CHCl_3$, λ_{max}, nm (ε, l/(mol*cm))): 340.0 (16300); FLU ($CHCl_3$, λ_{max}, nm, λ_{EX} = 365.0 nm) 428.0.

2-Hexyloxy-4, 4'-bis [2-(4-cyanophenyl)ethenyl]-1,1'-biphenyl (30b). Yield 0.3 g (61%). MP = 170-171°C; Elemental Anal. Calcd for $C_{36}H_{32}N_2O$: C 85.01, H 6.34, N 5.51 Found: C 84.48, H 7.52, N 5.66; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.86 (t, 3H, J = 7 Hz, -CH_3), 1.3-1.8 (m, 8H, -$(CH_2)_4$-), 4.10 (t, 2H, J = 7 Hz, -OCH_2-), 7.3- 8.0 (m, 19H, aromatic H); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ: 14.99, 22.26, 29.08, 31.41, 68.54, 110.55, 119.06, 119.74, 126.49, 126.81, 126.86, 129.77, 129.91, 130.48, 130.89, 132.09, 132.13, 132.50, 136.98, 138.43, 141.69, 141.89, 156.39; IR (KBr, ν cm^{-1}): 2960, 2940, 2860, 1610, 1510, 1450, 1400, 1270, 1230, 1180, 1140, 1070, 1030, 1000, 960, 810, 750, 680; UV ($CHCl_3$, λ_{max}, nm (ε, l/(mol*cm))): 359.0 (27000); FLU ($CHCl_3$, λ_{max}, nm, λ_{EX} = 365.0 nm) 443.0.

2-Hexyloxy-4, 4'-bis [2-(4-fluorophenyl)ethenyl]-1,1'-biphenyl (30c). Yield 0.31 g (63%). MP = 104-105°C; Elemental Anal. Calcd for $C_{34}H_{32}F_2O$: C 86.56, H 6.52 Found: C 86.87, H 6.68; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.89 (t, 3H, J = 7 Hz, -CH_3), 1.3- 1.8 (m, 8H, -$(CH_2)_4$-), 4.03 (t, 2H, J = 7 Hz, -O-CH_2-), 7.3- 7.6 (m, 19H, arom.); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ: 14.0, 22.6, 25.8, 29.1, 31.4, 68.5, 110.2, 115.6, 119.2, 125.9, 127.2, 127.5, 127.9, 128.3, 129.8, 130.8, 135.5, 137.6, 156.3; IR (KBr, ν cm^{-1}): 2960, 2940, 2860, 1600, 1520, 1440, 1400, 1270, 1240, 1160, 1140, 1010, 970, 850, 840, 760, 730, 700, 540; UV ($CHCl_3$, λ_{max}, nm (ε, l/(mol*cm))): 395.0 (23000); FLU ($CHCl_3$, λ_{max}, nm, λ_{EX} = 365.0 nm) 405.0.

2-Hexyloxy-4, 4'-bis {(E)-2-[4-(diphenylamino)phenyl]ethenyl}-1,1'-biphenyl (30d). Yield 0.6 g (75%). MP = 171–172°C; Elemental Anal. Calcd for $C_{58}H_{52}N_2O$: C 87.84, H 6.61, N 3.53 Found: C 87.58, H 6.79, N 3.62; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.89 (t, 3H, J = 7 Hz, -CH_3), 1.3- 1.8 (m, 8H, -$(CH_2)_4$-), 4.03 (t, 2H, J = 7 Hz, -OCH_2-), 7.00 (d, 2H, J =16 Hz, *trans*-C<u>H</u>=CH-), 7.0–7.2 (m, 18H), 7.15 (dd, 1H, J^{ortho} = 8 Hz, J^{meta} = 1.5 Hz, 5-H biphenyl), 7.26 (d, 2H, J^{ortho} = 16 Hz, *trans*-CH=C<u>H</u>-), 7.2-7.3 (m, 7H), 7.34 (d, 1H, J^{ortho} = 8 Hz, 6-H biphenyl), 7.40 (d, 4H, J^{ortho} = 9 Hz –C_6H_4-N), 7.56 (d, 2H, J^{ortho} = 9 Hz, 3'-, 5'-H biphenyl), 7.61 (d, 2H, J^{ortho} = 9 Hz, 2'-, 6'-H biphenyl); ^{13}C NMR ($CDCl_3$, 125.75 MHz), δ: 14.2, 22.7, 25.9, 29.3, 31.6, 68.6, 110.3, 119.2, 123.1, 123.2, 123.7, 123.8, 124.6, 124.7, 126.0, 126.5, 126.9, 127.0, 127.48, 127.53, 128.0, 128.4, 129.4, 129.9, 130.9, 131.5, 131.8, 136.2, 137.5, 138.3, 147.4, 147.5, 147.6, 147.7, 156.5; IR (KBr, ν cm^{-1}): 2940, 2860, 1580, 1480, 1320, 1270, 1180, 970, 830, 750, 700; UV ($CHCl_3$, λ_{max}, nm (ε, l/(mol*cm))): 382.0 (45000); FLU ($CHCl_3$, λ_{max}, nm, λ_{EX} = 365.0 nm) 452.0.

2-[(2-ethylhexyl)oxy]-4,4'-bis{(E)-2-[4-(diphenylamino)phenyl]ethenyl}-1,1'-biphenyl (30e). To a suspension of 4,4'-bis[(triphenylphosphonio)methyl]-2-(ethylhexyloxy)biphenyl dibromide (prepared according to the procedure as for compound **25**) (1 g, 1 mmol) in 20 mL of dry THF, *t*-BuOK (0.28 g, 2.5 mmol) was added and the reaction mixture was stirred until complete dissolution phosphonium salt happened. Then a solution of 0.55 g 4-(diphenylamino)benzaldehyde (2 mmol) in 10 mL of THF was slowly added dropwise. After 2 h stirring, the reaction mixture was poured into 100 ml of water and extracted with chloroform. The combined organic solution was washed with brine, dried over Na_2SO_4 and then evaporated in vacuum. The residue was chromatographed on silica gel (chloroform) to yield **30e** (0.78g, 95%) as white-yellow solid. After recryistallization from hexane. MP = 76–77°C; Elemental Anal. Calcd for $C_{60}H_{56}N_2O$: C 87.77, H 6.87, N 3.41 Found: C 88.06, H 6.99, N 3.54; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.87 (t, J = 7.0 Hz, 3H, -CH_3), 0.89 (t, 3H, J = 7.0 Hz, -CH_3), 1.2-1.5 (m, 8H, -$(CH_2)_4$-), 1.70 (m, 1H, -OCH_2-C<u>H</u>=), 3.93 (d, 2H, J = 5,5 Hz, -O-C<u>H</u>$_2$-), 7.04 (d, 2H, J = 16 Hz -C<u>H</u>=CH-), 7.0 – 7.2 (m, 18H), 7.18 (dd, 1H, J^{ortho} = 8 Hz, J^{meta} = 1.5 Hz, 5 biphenyl), 7.29 (d, 2H, J = 16 Hz -CH=C<u>H</u>-), 7.2-7.3 (m, 7H), 7.37 (d, 1H, J^{ortho} = 8 Hz, 6 biphenyl), 7.43 (d, 4H, J^{ortho} = 9 Hz), 7.53 (d, 2H, J^{ortho} = 9 Hz, 3', 5' biphenyl), 7.58 (d, 2H, J^{ortho} = 9 Hz, 2', 6' biphenyl); IR (KBr, ν cm^{-1}): 2930, 2870, 1590, 1500, 1340, 1280, 1180, 970, 830, 760, 700. UV ($CHCl_3$, λ_{max}, nm (ε, l/(mol*cm))): 382.0 (40000); FLU ($CHCl_3$, λ_{max}, nm, λ_{EX} = 365.0 nm) 452.0.

2-Nitrobiphenyl-4, 4'-dicarboxylic acid dimethyl ester (31). To a solution of 20 g (74 mmol) of biphenyl-4, 4'-dicarboxylic acid dimethyl ester (**1**) in 200 ml of conc. sulfuric acid was added 12 ml (74.0 mmol) of 56% HNO_3 in 15 ml of conc. H_2SO_4 dropwise at 15°C under intense stirring. The reaction mixture was maintained at 15-20°C for additional 1 h and then was carefully poured on a crushed ice. The precipitated solids were separated by filtration, washed with water, recrystallized from isopropanol and air-dried. Yield 20.2 g (86%) of the colorless crystals. MP = 163-164°C; Elemental Anal. Calcd for $C_{16}H_{13}NO_6$: C 60.95, H 4.16, N 4.44 Found: C 60.56, H 4.06, N 4.32; ^{1}H NMR (DMSO-d^6, 100 MHz), δ: 3.88 (s, 3H, –CH_3), 3.93 (s,

3H, –CH_3), 7.53 (d, 2H, J^{ortho} = 8.6 Hz, 3',5'/2',6'-Ar), 7.73 (d, 1H, J^{ortho} = 7.9 Hz, 6-Ar(NO_2)), 8.04 (d, 2H, J^{ortho} = 8.6 Hz, 3',5'/2',6'-Ar), 8.28 (dd, 1H, J^{ortho} = 8.0 Hz, J^{meta} = 1.7 Hz, 5-Ar(NO_2)), 8.48 (d, 1H, J^{meta} = 1.5 Hz, 3-Ar(NO_2)); IR (KBr, ν cm^{-1}): 3107, 3093, 3027, 2980, 2900, 2863, 1733, 1620, 1543, 1443, 1373, 1323, 1293, 1253, 1217, 1200, 1173, 1147, 1133, 1123, 1040, 1023, 993, 980, 973, 940, 907, 890, 873, 837, 793, 787, 770, 720.

9*H*-Carbazole-2, 7-dicarboxylic acid dimethyl ester (32). A solution of 1.0 g (3.2 mmol) of 2-azidobiphenyl-4, 4'-dicarboxylic acid dimethyl ester in 15 ml of xylene was heated at reflux for 40 h. When TLC indicated no starting material, the reaction mixture was cooled to RT, precipitate collected, recrystallized from xylene and air-dried. Yield 0.8 g (88%), colorless crystals. MP = 273-274°C; Elemental Anal. Calcd for $C_{16}H_{13}NO_4$: C 67.84, H 4.63, N 4.94 Found: C 67.57, H 4.57, N 4.86; ^{1}H NMR (DMSO-d_6 : CCl_4 (1:1), 500 MHz), δ: 3.93 (s, 6H, –CH_3), 7.80 (dd, 2H, J^{ortho} = 8.5 Hz, J^{meta} = 1.3 Hz, 3,6-carbazolyl), 8.15 (s, 2H, 1,8-carbazolyl), 8.19 (d, 2H, J^{ortho} = 8.3 Hz, 4,5-carbazolyl), 11,64 (s, 1H, –NH–); IR (KBr, ν cm^{-1}): 3367, 3083, 2993, 2837, 2700, 2633, 2587, 2513, 1920, 1860, 1677, 1630, 1610, 1573, 1507, 1460, 1413, 1293, 1243, 1217, 1127, 1100, 1003, 943, 890, 880, 847, 827, 757, 723, 687, 657; UV (EtOH, λ_{max}, nm): 252.0, 276.5, 306.5, 320.0.

9(N)-Phenylcarbazole-2, 7-dicarboxylic acid dimethyl ester (33). To a solution of 285 mg (1 mmol) of 9H-carbazole-2,7-dicarboxylic acid dimethyl ester **(3)** and 55 mg (0.2 mmol) of dibenzo-18-crown-6 in 30 ml of dry bromobenzene, K_2CO_3 (350 mg, 2.5 mmol) and CuI (290 mg, 1.5 mmol) was added and the reaction mixture was heated at reflux for 8 h. After reaction finished (by TLC), inorganic solids were filtered off, the filtrate diluted with chloroform, washed with 5% aq. hydrochloric acid and brine. The combined organic solution was concentrated in vacuum. The obtained beige crystals were recrystallized from benzene and air-dried. Yield 336 mg (92%) colorless crystals. MP = 210-211°C; Elemental Anal. Calcd for $C_{22}H_{17}NO_4$: C 73.53, H 4.77, N 3.90 Found: C 73.19, H 4.66, N 3.87; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 3.85 (s, 6H, –CH_3), 7.67 (m, 1H, J^{ortho} = 8.0 Hz, 4-Ph), 7.68 (dd, 2H, J^{ortho} = 8.0 Hz, J^{meta} = 1.0 Hz, 2-Ph), 7.76 (t, 2H, J^{ortho} = 7.8 Hz, 3-Ph), 7.89 (s, 2H, 1,8-carbazolyl), 7.92 (dd, 2H, J^{ortho} = 8.3 Hz, J^{meta} = 1.3 Hz, 3,6-carbazolyl), 8.47 (d, 2H, J^{ortho} = 8.0 Hz, 4,5-carbazolyl); IR (KBr, ν cm^{-1}): 3428, 3110, 3063, 3040, 3034, 2966, 2931, 2859, 1728, 1634, 1603, 1578, 1509, 1481, 1450, 1438, 1348, 1303, 1294, 1253, 1241, 1225, 1107, 1009, 894, 828, 763, 737, 716; UV (EtOH, λ_{max}, nm): 253.5, 278.5, 305.0, 318.0.

2,7-Bis(hydroxymethyl)-9(N)-phenylcarbazole. To a solution of 300 mg (0,8 mmol) of 9(N)-phenylcarbazole-2,7-dicarboxylic acid dimethyl ester **(33)** in 50 ml of dry THF, 190 mg (5 mmol) of $LiAlH_4$ was added and the mixture was refluxed for 2 h under stirring. When TLC indicated the reaction was finished, the reaction mixture was treated with 10 ml of ethyl acetate followed by 50% aq. solution of potassium hydroxide until aluminum hydroxide precipitated, which was filtered off and washed several times with hot THF. The organic phase was combined and solvent removed on the rotary evaporator. The crude product was recrystallized from ethanol. Yield 201 mg (80%), light yellow powder. MP = 211-213°C; Elemental Anal. Calcd for $C_{20}H_{17}NO_2$: C 79.19, H 5.65, N 4.62 Found: C 78.89, H 5.18, N 4.56; ^{1}H NMR (DMSO-d_6, 500

MHz), δ: 4.62 (d, 4H, J = 5.5 Hz, –CH_2–), 5.25 (t, 2H, J = 5.8 Hz, –OH), 7.20 (dd, 2H, J^{ortho} = 8.0 Hz, J^{meta} = 0.5 Hz, 3,6-carbazolyl), 7.33 (d, 2H, J^{meta} = 0.5 Hz, 1,8-carbazolyl), 7.56 (m, 1H, J^{ortho} = 8.0 Hz, J^{meta} = 1.3 Hz, 4-Ph), 7.59 (dd, 2H, J^{ortho} = 8.5 Hz, J^{meta} = 1.0 Hz, 2-Ph), 7,71 (t, 2H, J^{ortho} = 7.8 Hz, 3-Ph), 8.13 (d, 2H, J^{ortho} = 8.0 Hz, 4,5-carbazolyl); IR (KBr, ν cm^{-1}): 3343, 3227, 3110, 3079, 3043, 3023, 1603, 1580, 1503, 1450, 1436, 1373, 1340, 1303, 1240, 1210, 1177, 1140, 1043, 1010, 873, 813, 800, 713.

2,7-Diformyl-9(N)-phenylcarbazole (34). To a suspension of 150 mg (0.5 mmol) of 2, 7-bis(hydroxymethyl)-9(N)-phenylcarbazole in 30 ml of dry dichloromethane, PCC in dioxane (500 mg of PCC and minimal amount of dioxane) was added at RT with intense stirring. The reaction was continued for 8 h and then 10 ml of isopropanol was added. Inorganic solids were separated by flash chromatography, solvents removed in vacuum, the obtained brown solid was purified by column chromatography on silica gel (dichloromethane). Yield 107 mg (73%), bright yellow solid. MP ~196°C (subl.); Elemental Anal. Calcd for $C_{20}H_{13}NO_2$: C 80.25, H 4.38, N 4.68 Found: C 79.89, H 4.17, N 4.61; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 7.65 (m, 1H, J^{ortho} = 7.3 Hz, J^{meta} = 1.6 Hz, 4-Ph), 7.73 (dd, 2H, J^{ortho} = 8.5 Hz, J^{meta} = 1.5 Hz, 2-Ph), 7.77 (t, 2H, J^{ortho} = 7.5 Hz, 3-Ph), 7.88 (dd, 2H, J^{ortho} = 8.0 Hz, J^{meta} = 1.0 Hz, 3,6-carbazolyl), 7.94 (s, 2H, 1,8-carbazolyl), 8.57 (d, 2H, J^{ortho} = 8.0 Hz, 4,5-carbazolyl), 10.11 (s, 2H, –CHO); IR (KBr, ν cm^{-1}): 3083, 3043, 2973, 2943, 2853, 2777, 2760, 2710, 1687, 1623, 1597, 1507, 1473, 1447, 1433, 1407, 1350, 1297, 1277, 1240, 1200, 1170, 1147, 1100, 1087, 1043, 1017, 883, 813, 773, 710; UV (EtOH, λ_{max}, nm): 255.5, 295.0, 335.5.

9(N)-Phenylcarbazole-2, 7-dicarboxylic acid dihydrazide (35). To a solution of 285 mg (1 mmol) of 9(N)-phenylcarbazole-2, 7-dicarboxylic acid dimethyl ester **(33)** in 50 ml of ethanol, 10 ml (ca. 303 mmol) of hydrazine hydrate was added and the resulting mixture was refluxed for 3 h. During that time a bulky precipitate was formed, which was separated from mother liquor, washed with ethanol and water, recrystallized from ethanol and air-dried. Yield 358 mg (99%). MP ~265°C (subl.); Elemental Anal. Calcd for $C_{20}H_{17}N_5O_2$: C 66.84, H 4.77, N 19.49 Found: C 66.53, H 4.68, N 19.40; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 4.56 (s, 4H, –NH_2), 7.61 (м, 1H, J^{ortho} = 7.3 Hz, J^{meta} = 1.4 Hz, 4-Ph), 7.68 (dd, 2H, J^{ortho} = 9.0 Hz, J^{meta} = 2.0 Hz, 2-Ph), 7.74 (t, 2H, J^{ortho} = 7.8 Hz, 3-Ph), 7.79 (dd, 2H, J^{ortho} = 8.0 Hz, J^{meta} = 1.25 Hz, 3,6-carbazolyl), 7.86 (s, 2H, 1,8-carbazolyl), 8.36 (d, 2H, J^{ortho} = 8.0 Hz, 4,5-carbazolyl), 9.93 (s, 2H, –NH–); IR (KBr, ν cm^{-1}): 3440, 3410, 3334, 3298, 3082, 2950, 2872, 1650, 1623, 1607, 1573, 1553, 1537, 1520, 1507, 1467, 1440, 1360, 1327, 1273, 1247, 1177, 1113, 1047, 1020, 953, 903, 867, 833, 773, 717.

2-Aminobiphenyl-4,4'-dicarboxylic acid dimethyl ester (36). To a solution of 14.6 g (46 mmol) of 2-nitrobiphenyl-4,4'-dicarboxylic acid dimethyl ester **(31)** in 500 ml of dry THF, 10 g of 10% Pd/C was added and the reaction mixture was stirred up under hydrogen atmosphere at RT for 10 days. When the absorption of hydrogen was ceased, the catalyst was filtered off and solvents removed by the rotary evaporator. The resulting yellow paste was recrystallized from ethanol and dried under reduced pressure. Yield 12 g (91%) of light yellow to white solid. MP = 160.0–160.5°C; Elemental Anal. Calcd for $C_{16}H_{15}NO_4$: C 67.36, H 5.30, N 4.91 Found: C 67.04,

H 5.22, N 4.83; ^{1}H NMR (DMSO-d_6, 100 MHz), δ: 3.84 (s, 3H, –CH_3), 3.88 (s, 3H, –CH_3), 5.16 (s, 2H, –NH_2), 7.16 (s, 1H, 3-Ar(NH_2)), 7.20 (d, 1H, J^{meta} = 1.3 Hz, 6-Ar(NH_2)), 7.45 (d, 1H, J^{meta} = 1.0 Hz, 5-Ar(NH_2)), 7.59 (d, 2H, J^{ortho} = 8.5 Hz, 3',5'/2',6'-Ar), 8.03 (d, 2H, J^{ortho} = 8.5 Hz, 3',5'/2',6'-Ar); IR (KBr, ν cm^{-1}): 3475, 3380, 3225, 3100, 3070, 3047, 3015, 2960, 2900, 2845, 1943, 1913, 1807, 1780, 1720, 1630, 1610, 1570, 1560, 1530, 1490, 1440, 1403, 1367, 1340, 1313, 1303, 1283, 1267, 1250, 1190, 1157, 1123, 1113, 1073, 1020, 1003, 970, 953, 910, 867, 840, 827, 793, 773, 760, 727, 700.

2-Azidobiphenyl-4,4'-dicarboxylic acid dimethyl ester (37). To a 2.9 g (10.1 mmol) of 2-aminobiphenyl-4,4'-dicarboxylic acid dimethyl ester **36**, the mixture of 40 ml of hydrochloric acid and 20 ml of water was added and the resulted solution was stirred at RT for 1 h. The obtained suspension then was cooled to 0°C and the solution of 0.7 g (10.2 mmol) of $NaNO_2$ in minimal amount of water was added dropwise within 1 h at 0-5°C and constant stirring. After the reaction mixture was stirred at 0°C for additional 1 h, the solution of 0.65 g (10 mmol) of NaN_3 in minimal amount of water was added dropwise under intense stirring, and the reaction continued at RT for another 2 h. The precipitated solid was filtered off, washed with water and dried under reduced pressure in the dark. Yield 3.1 g (99%), light-yellow or white powder. MP = 107-108°C (dec.); Elemental Anal. Calcd for $C_{16}H_{13}N_3O_4$: C 61.73, H 4.21, N 13.50 Found: C 61.45, H 4.13, N 13.39; ^{1}H NMR (DMSO-d_6, 100 MHz), δ: 3.93 (s, 3H, –CH_3), 3.95 (s, 3H, –CH_3), 7.43 (s, 1H, Ar(–N_3)), 7.47 (s, 1H, Ar(–N_3)), 7.56 (s, 1H, Ar(–N_3)), 7.87 (d, 2H, J^{ortho} = 8.4 Hz, 3',5'/2',6'-Ar), 8.09 (d, 2H, J^{ortho} = 8.2 Hz, 3',5'/2',6'-Ar); IR (KBr, ν cm^{-1}): 3100, 3077, 3050, 3013, 2960, 2857, 2160, 2120, 1950, 1723, 1713, 1607, 1573, 1560, 1557, 1517, 1493, 1437, 1417, 1397, 1377, 1337, 1290, 1283, 1270, 1260, 1250, 1203, 1197, 1160, 1123, 1027, 1010, 993, 977, 963, 890, 873, 850, 833, 807, 780, 757, 733, 707, 683, 653.

Dimethyl 2-iodobiphenyl-4, 4'-dicarboxylate (38). Dimethyl 2-aminobiphenyl-4,4'-dicarboxylate **(36)** 1.42 g (5 mmol) was suspended in 5 ml of 15% hydrochloric acid, the suspension was cooled at 0°C and a solution of $NaNO_2$ (0.4 g, 5.8 mol) in 3 ml of water was added dropwise. The mixture was stirred at 0°C for 10 min, then 0.9 g (6 mmol) NaI was added and the resulting solution was heated to 60°C for 10 min. The reaction mixture was poured into 50 ml of water and extracted with ethyl acetate. The combined organic solution was washed with 10% solution of sodium sulfite and then was dried over Na_2SO_4. After removal of solvent, a residue was purified by column chromatography on silica gel (toluene) to give **38** (1.2 g, 60%) as colorless solid. Recrystallization from ethanol afforded white needle-like crystals. MP = 112-113°C; Elemental Anal. Calcd for $C_{16}H_{13}IO_4$: C 48.51, H 3.31 Found: C 48.01, H 3.30; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 3.89 (s, 6H,–CH_3), 7.29 (d, 1H, J^{ortho} = 8.0 Hz, 6 biphenyl), 7.36 (d, 2H, J^{ortho} = 8.5 Hz, 2', 6' or 3', 5' biphenyl), 7.99 (dd, 1H, J^{ortho} = 8.0 Hz, J^{meta} = 1.5 Hz, 5 biphenyl), 8.06 (d, 2H, J^{ortho} = 8.5 Hz, 3', 5' or 2', 6' biphenyl), 8.56 (d, 1H, J^{meta} = 1.5 Hz, 3 biphenyl); IR (KBr, ν cm^{-1}): 2970, 1730, 1440, 1290, 1250, 1140, 970, 850, 770, 720.

2, 7-Bis [2-(benzoxazol-2-yl)-(E)-ethenyl]-9(N)-phenylcarbazole (39). A solution of 100 mg (0.3 mmol) of 2,7-diformyl-9(N)-phenylcarbazole **(34)** in 15 ml of dry DMSO was treated with 110 mg (0.8 mmol) of 2-methyl-1,3-benzoxazole in the presence of 111 mg (1 mmol) *t*-BuOK.

Reaction mixture was heated at 40-50°C for 16 h under stirring, and then was diluted with brine and extracted with chloroform. Organic phases were combined and solvents removed in vacuum. The residue was purified by column chromatography on silica gel (chloroform) and dried under reduced pressure. Recrystallization from benzene gave **39 (**138 mg, 78%), as bright green-yellow crystals. MP = 306– 309°C (dec.); Elemental Anal. Calcd for $C_{36}H_{23}N_3O_2$: C 81.65, H 4.38, N 7.93 Found: C 81.84, H 4.13, N 7.71; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 7.32–7.45 (m, 4H, 5',5",6',6"–oxazolyl), 7.63 (m, 1H, J^{ortho} = 6.5 Hz, J^{meta} = 1.3 Hz, 4-Ph), 7.65–7.80 (m, 8H, 4',4",7',7"-oxazolyl + 2,3-Ph), 7.77 (d, 2H, J = 16.0 Hz, =CH–), 7.86 (dd, 2H, J^{ortho} = 8.0 Hz, J^{meta} = 1.0 Hz, 3,6-carbazolyl), 8.00 (d, 2H, J = 16.0 Hz, =CH–), 8.31 (s, 2H, 1,8-carbazolyl), 8.37 (d, 2H, J^{ortho} = 8.0 Hz, 4,5-carbazolyl); IR (KBr, ν cm^{-1}): 3072, 3039, 2971, 2941, 2872, 1639, 1600, 1571, 1534, 1505, 1456, 1430, 1354, 1321, 1305, 1292, 1250, 1233, 1207, 1184, 1171, 1154, 1118, 1085, 1039, 1017, 975, 944, 905, 885, 869, 846, 833, 807, 770, 754, 708; UV (DMF, λ_{max}, nm (ε, l/(mol*cm))): 386.0 (71300), 408.5 (shoulder, 56000); FLU (DMF, λ_{max}, nm, λ_{EX} = 365.0 nm) 457.5.

2, 7-Bis [5-(4-bromophenyl)-1,3,4-oxadiazol-2-yl]-N-phenylcarbazole (40). A solution of 9(N)-phenylcarbazole-2,7-dicarboxylic acid dihydrazide **35** (300 mg, 0,8 mmol) in 30 ml of dry pyridine was treated with 4-bromobenzoyl chloride (455 mg, 2,1 mmol) at 60°C for 16 h under stirring. Then the reaction mixture was diluted with water, a precipitate was collected and washed with water. The obtained substance was recrystallized from benzene and dried under reduced pressure.

The crude product was placed in 30 ml of $POCl_3$ and heated at reflux for 8 h. The reaction mixture was poured on crushed ice, the precipitated product was filtered off, washed with the sat. solution of sodium bicarbonate and water. The crude product was placed into the Soxhlet apparatus to remove the contaminants with cyclohexane, and then a residue was purified by column chromatography on silica gel (dichloromethane) and, finally, recrystallized from dimethyl sulfoxide. Yield (2 steps) 262 mg (46%). MP ~ 350°C (subl.); Elemental Anal. Calcd for $C_{34}H_{19}Br_2N_5O_2$: C 59.24, H 2.78, Br 23.18, N 10.16 Found: C 58.91, H 2.54, Br 23.26, N 10.28; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 7.71 (m, 1H, J^{ortho} = 6.5 Hz, J^{meta} = 1.3 Hz, 4-Ph), 7.79 (dd, 1H, J^{ortho} = 7.0 Hz, J^{meta} = 1.3 Hz, 2-Ph), 7.80–7.88 (m, 6H, 3'-(Br)Ph + 3-Ph), 8.00–8.08 (m, 4H, 2'-(Br)Ph), 8.14 (dd, 2H, J^{ortho} = 8.0 Hz, J^{meta} = 1.0 Hz, 3,6-carbazolyl), 8.47 (s, 2H, 1,8-carbazolyl), 8.62 (d, 2H, J^{ortho} = 8.0 Hz, 4,5-carbazolyl); IR (KBr, ν cm^{-1}): 3100, 3083, 2937, 2870, 1687, 1603, 1580, 1547, 1477, 1413, 1400, 1370, 1360, 1347, 1310, 1283, 1273, 1247, 1237, 1193, 1183, 1130, 1120, 1086, 1017, 973, 847, 747, 720; UV (DMF, λ_{max}, nm (ε, l/(mol*cm))): 340.0 (87300); FLU (DMF, λ_{max}, nm, λ_{EX} = 365.0 nm) 428.5.

2,7-Bis{5-[4-(octyloxy)phenyl]-1,3,4-oxadiazol-2-yl}-9,10-diphenylphenanthrene (41). To a solution of 0.21 g (0.47 mmol) dimethyl 9, 10-diphenylphenanthrene-2, 7-dicarboxylate **(5)** in 25 ml of THF, 10 ml of 10% ethanol solution of NaOH was added. The mixture was refluxed for 3 h. After cooling at RT, 5 ml of 20% hydrochloric acid was added to give a precipitate. The precipitate was filtered off and, after drying in a vacuum desiccator, was dissolved in 5 ml of $SOCl_2$. A drop of DMF was added and the mixture was refluxed for 2 h. After the removal of

excess of a $SOCl_2$ in vacuum, the residue was dissolved in 25 ml of THF and added dropwise to a solution of 0.26 g (1 mmol) 4-(octyloxy)benzohydrazide and 0.1 g (1 mmol) triethylamine in 5 ml of THF. The reaction mixture was stirred for 3 h at room temperature and then was poured into 50 ml of water. The precipitate was collected by filtration and washed with water. After drying, white powder was dissolve in 5 ml of $POCl_3$ and the mixture was refluxed for 5 h. The reaction mixture was poured on 100 ml of crushed ice and extracted with chloroform. The combined organic phase was washed with water and then dried over Na_2SO_4. After removal of solvents, the residue was purified by column chromatography on silica gel (toluene/ ethyl acetate = 2: 1) to give **41** (270 mg, 66%) as a colorless solid. Recrystallization from hexane afforded white crystals. MP = 163-165°C; Elemental Anal. Calcd for $C_{58}H_{58}N_4O_4$: C 79.60, H 6.68, N 6.40 Found: C79.27, H 6.56, N 6.32; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.90 (t, 6H, J^{ortho} = 7.0 Hz, $-CH_3$), 1.2–1.7 (m, 24H,-$(CH_2)_6$-), 3.98 (t, 4H, J= 7.0 Hz, -O-CH_2-), 6.9–8.9 (m, 24H, arom.); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ: 14.1, 22.7, 25.9, 29.3, 29.7, 31.8, 68.8, 114.9, 117.7, 122.9, 123.5, 124.6, 126.3, 126.6, 127.7, 127.9, 128.1, 129.3, 129.5, 130.8, 136.4, 157.4, 164.5; IR (KBr, ν cm^{-1}): 3450, 2930, 2860, 1710, 1610, 1490, 1300, 1250, 1170, 1070, 1030, 1000, 840, 740, 700; UV ($CHCl_3$, λ_{max}, nm (ε, l/(mol*cm))): 288.0 (26400); 335 (28800), FLU ($CHCl_3$, λ_{max}, nm, λ_{EX} = 365.0 nm) 404.5, 423.5.

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