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Synthesis and Properties of Luminophores Derived from Fluorinated Biphenyls

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Abstract—A procedure was developed for the synthesis of dimethyl 2-fluoro- and 2,2′-difluorobiphenyl-4,4′-dicarboxylates. The latter were converted into fluorinated 4,4′-bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]- and 4,4′-bis[5-(4-octyloxyphenyl)-1,3,4-oxadiazol-2-yl]biphenyls which showed strong luminescence in the crystalline state and in solution; their spectral properties were examined.

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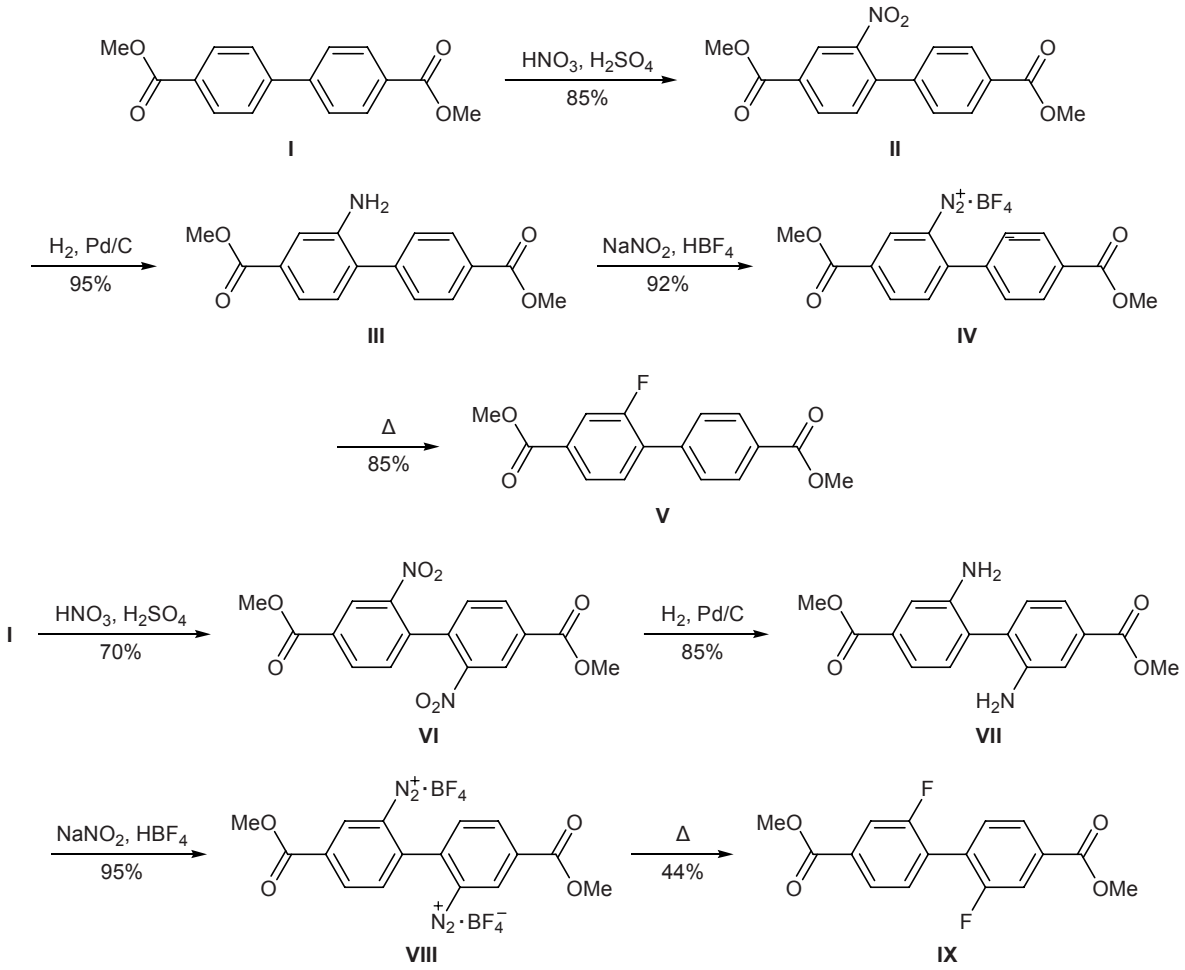
Polyconjugated biphenyl derivatives may be regarded as short-chain analogs of polyphenylenevinylenes that attract interest as active materials for light-emitting diodes. Most studies on the synthesis of such electroluminescent materials were performed on unsubstituted biphenyls [1, 2]. These compounds are generally characterized by poor solubility in most organic solvents and are very prone to undergo crystallization which hampers their use in practice. Therefore, it seems to be promising to design new short-chain analogs of polyphenylenevinylenes containing a modified biphenyl fragment and examine the effect of substitution in that fragment on physicochemical properties of such system. Among these, most interesting are compounds having an asymmetric structure, namely biphenyl-4,4′-dicarboxylic acid derivatives with electron-donating or electron-withdrawing substituents in one phenyl ring [3–5].

In the present article we report on the synthesis of 2-fluoro- and 2,2′-difluorobiphenyl-4,4′-dicarboxylic acids and a series of luminescent dyes based thereon. It is known that introduction of a fluorine atom into organic molecules leads to compounds with strongly different properties due to high electronegativity of the fluorine atom and its small size. Direct regioselective fluorination of aromatic systems is very difficult to accomplish; as a rule, mixtures of isomeric products are formed, which are difficult to separate. One of the most convenient regioselective methods for the introduction of fluorine atoms is based on the Balz–Schieman reaction of diazonium salts [6].

In our study, the key intermediate compounds for the synthesis of mono- and difluoro-substituted biphenyl-4,4′-dicarboxylic acid derivatives **V** and **IX** were the corresponding dimethyl 2-amino- and 2,2′-diaminobiphenyl-4,4′-dicarboxylates **III** and **VII** (Scheme 1). The latter were prepared in two steps, by nitration of dimethyl biphenyl-4,4′-dicarboxylate (**I**) and subsequent reduction of nitro compounds **II** and **VI**. The optimal nitration procedure was treatment of a solution of **I** in concentrated sulfuric acid with a mixture of concentrated sulfuric acid and 58% nitric acid at a volume ratio of 1 : (0.8–1.0). The synthesis of mononitro derivative **II** required careful temperature control. The temperature of the reaction mixture should not exceed 20°C. Rise in the temperature to 30°C leads to preferential formation of dinitro derivative **VI** even using an equimolar amount of nitric acid.

Dinitro derivatives **VI** was obtained in 70% yield using 2 equiv of nitric acid, the temperature of the reaction mixture ranging from 25 to 30°C. Here, the reaction temperature should also be controlled carefully; above 35°C, the reaction was accompanied by complete hydrolysis of the ester groups. The reduction of nitro compounds **II** and **VI** to the corresponding amines **III** and **VII** with hydrogen was performed in tetrahydrofuran in the presence of Pd/C as catalyst either under atmospheric pressure or at a hydrogen pressure of 10 atm (in a high-pressure reactor). In the reduction of mononitro derivative **II**, the yield of amine **III** was almost quantitative (93–95%). The reduction of dinitro compound **VI** under atmospheric

Scheme 1.

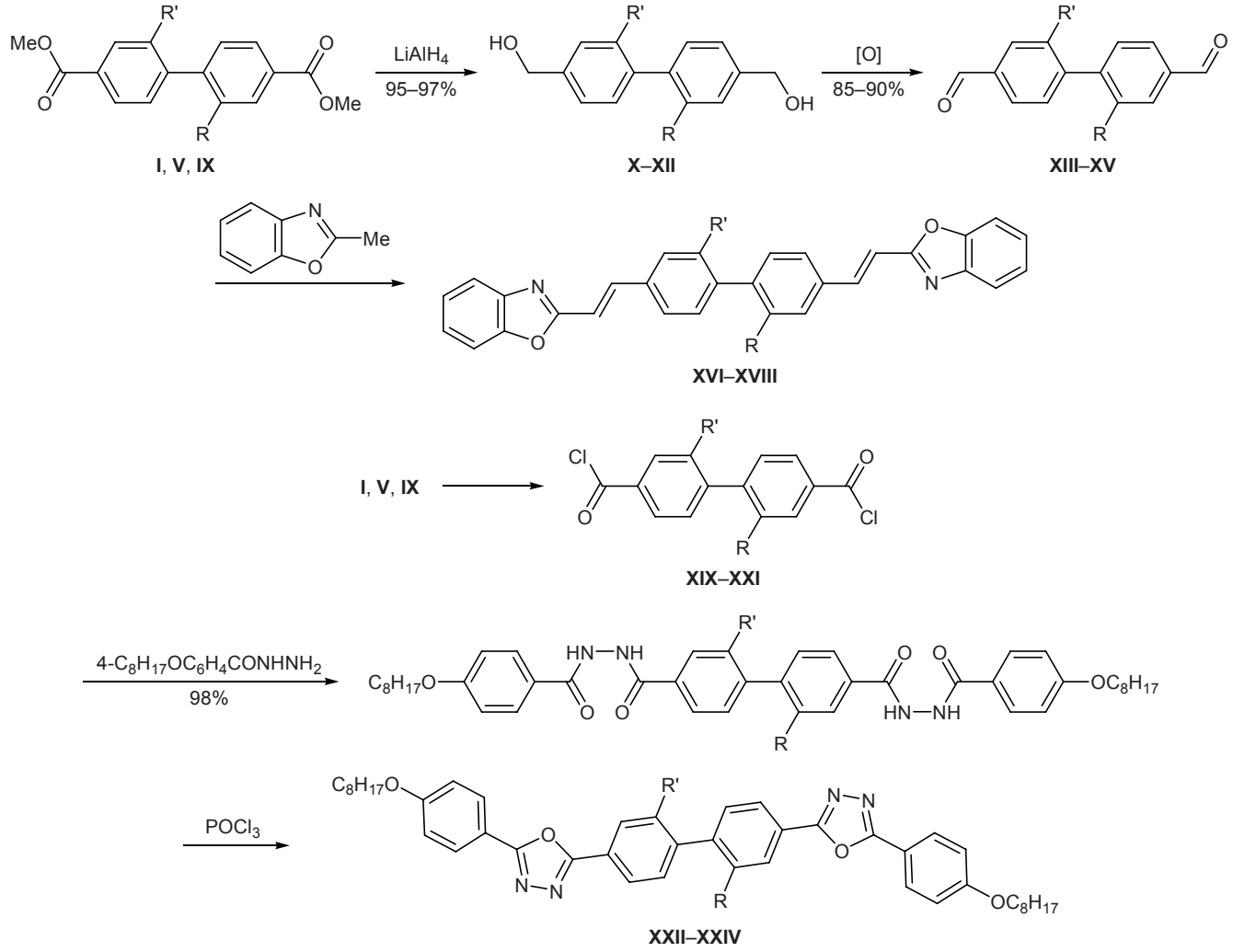


pressure was accompanied by side processes, and the maximal yield of amine **VII** (85%) was attained when the hydrogenation was carried out under pressure. Diazomiun salts **IV** and **VIII** were obtained by nitrosation of the corresponding amine hydrochlorides with a solution of sodium nitrite in 15% hydrochloric acid, followed by treatment with a 40% solution of tetrafluoroboric acid. Diazonium tetrafluoroborates **IV** and **VIII** were thoroughly dried over phosphorus(V) oxide prior to thermal decomposition [7]. Introduction of fluorine atoms into the biphenyl fragment of molecule **I** resulted in lowering of the melting point by 60°C, the effect being the strongest for monofluoro derivative **V** with distorted molecular symmetry. Unlike initial diester **I**, fluorinated biphenyls **V** and **IX** are readily soluble in most organic solvents.

Due to the presence of two carboxy groups fluorinated biphenyls **V** and **IX** are convenient starting compounds for the synthesis of extended poly-π-conjugated systems as potential electroluminescent materials. In the recent time, extensive studies are performed on poly-*p*-phenylene analogs having an electron-withdrawing heterocyclic fragment in the side and/or principal conjugation chain; this fragment is responsible for electron-transport properties of the molecule. Such compounds can be used as electron-active components of organic light-emitting diodes [8–10]. It is known that oxazole and oxadiazole heterocycles are strong electron withdrawers and that dyes based thereon are very stable [11]. Using fluorinated biphenyls **V** and **IX** as starting compounds we synthesized a series of new short-chain analogs of poly-*p*-phenylenes and poly-*p*-phenylenevinylenes containing 1,3,4-oxadiazole and 1,3-benzoxazole fragments in the principal conjugation chain. For the sake of comparison, we also synthesized analogous fluorine-free derivatives from unsubstituted biphenyldicarboxylate **I** (Scheme 1).

Dialdehydes **XIII**–**XV** were obtained in two steps. Diesters **I**, **V**, and **IX** were initially reduced to the corresponding 4,4′-bis(hydroxymethyl)biphenyls **X**–**XII**,

Scheme 2.



I, **X**, **XIII**, **XVI**, **XIX**, **XXII**, R = R′ = H; **V**, **XI**, **XIV**, **XVII**, **XX**, **XXIII**, R = F, R′ = H; **IX**, **XII**, **XV**, **XVIII**, **XXI**, **XXIV**, R = R′ = F.

and the latter were oxidized to dialdehydes. The reduction of diesters **I**, **V**, and **IX** was carried out using lithium tetrahydridoaluminate in tetrahydrofuran. The reaction with unsubstituted dimethyl biphenyl-4,4′-dicarboxylate required prolonged heating of the reaction mixture, while fluoro-substituted compounds were reduced in 20–30 min at room temperature to give 98% of diols **XI** and **XII**. The oxidation of **X**–**XII** with pyridinium chlorochromate in methylene chloride gave dialdehydes **XIII**–**XV** in 85–90% yield. The subsequent condensation of dialdehydes **XIII**–**XV** with 2-methyl-1,3-benzoxazole was characterized by high stereoselectivity. The reactions were carried out in dimethyl sulfoxide in the presence of sodium methoxide as a base, and the products were exclusively *trans*,*trans* isomers **XVI**–**XVIII** (yield up to 85%).

As noted above, the presence of carboxy groups in positions *4* and *4′* of biphenyl molecule ensures its easy further functionalization with a view to obtain rigid extended rod-like polyconjugated systems. For this purpose, diesters **I**, **V**, and **IX** were converted into carboxylic acid chlorides **XIX**–**XXI** which were treated with *p*-octyloxybenzohydrazide to obtain the corresponding intermediate bis-hydrazides. Cyclization of the latter gave 1,3,4-oxadiazole derivatives **XXII**–**XXIV** (Scheme 2). As a rule, structurally related linear molecules having no substituent in the side or principal chain are very poorly soluble, which prevents them from being used as electron-active materials in light-emitting diodes. To obtain readily soluble derivatives the hydrazide component contained an octyloxy group. The corresponding bis-hydrazides were formed in

almost quantitative yield and were subjected to subsequent cyclization without additional purification. The cyclization was performed by heating with various dehydrating agents. The best results were obtained by heating bis-hydrazides in phosphoryl chloride. The yields of oxadiazoles **XXII**–**XXIV** reached 82% (calculated on the initial esters **I**, **V**, and **IX**).

All benzoxazolylethenyl derivatives **XVI**–**XVIII** showed strong luminescence both in the crystalline state and in solution. Their fluorescence maxima in solution range from λ 430 to 440 nm, and introduction of fluorine atoms almost does not change the position of the fluorescence maxima. A different pattern was observed for solid-state fluorescence. Crystalline compound **XVI** displayed strong luminescence with its maximum at λ 547 nm upon UV excitation at λ 365 nm [12]. Introduction of fluorine atoms into position *2* of the biphenyl fragment (compounds **XVII** and **XVIII**) leads to short-wave shift of the fluorescence maximum (λ_{fl} 470–480 nm). The strongest effect was observed for monofluoro derivative **XVII** (λ = 473 nm) with distorted molecular symmetry. Better solubility of fluorinated compounds **XVII** and **XVIII** as compared to unsubstituted benzoxazole derivative **XVI** should also be noted.

The fluorescence maxima of oxadiazoles **XXII**–**XXIV** in which the electron-withdrawing group is directly attached to the biphenyl fragment are located at shorter wavelengths (λ 400–410 nm) for both solid samples and their solutions. Introduction of fluorine atoms almost does not affect the position of the solid-state and solution fluorescence maxima; only a slight red shift of the emission band is observed (Δλ = 5–7 nm; λ_{fl} 401 and 407 nm for **XXII** and **XXIII**, respectively.

EXPERIMENTAL

The IR spectra were measured in the range from 400 to 4000 cm^{-1} on a Specord M-80 spectrometer from samples pelleted with KBr. The ^1H and ^{13}C NMR spectra were recorded on Bruker Biospin Avance-500 (500 and 125 MHz for ^1H and ^{13}C, respectively), Tesla BS-587A (80 MHz), and Tesla BS-567A (100 MHz) instruments using tetramethylsilane as internal reference. The electron-impact mass spectra were obtained at an energy of ionizing electrons of 70 eV. The solvents and reagents used were purified and dehydrated by standard methods. The progress of reactions was monitored by TLC on plastic plates coated with silica gel 60 F_{254} (Merck). The melting points were determined on a Kofler hot stage.

Dimethyl 2-nitrobiphenyl-4,4′-dicarboxylate (II). A solution of 20 g (74 mmol) of dimethyl biphenyl-4,4′-dicarboxylate (**I**) in 200 ml of concentrated sulfuric acid was cooled to 15°C, and a mixture of 12 ml (149 mmol) of 58% nitric acid and 15 ml of concentrated sulfuric acid was added dropwise over a period of 40 min under stirring, maintaining the temperature at 15–20°C. The mixture was then stirred for 1 h at 15–20°C, diluted with 100 ml of water, and extracted with ethyl acetate. The extract was washed with water and a solution of sodium hydrogen carbonate, dried over anhydrous sodium sulfate, and evaporated, and the residue was recrystallized from isopropyl alcohol. Yield 19.8 g (85%), mp 98–99°C. IR spectrum, ν, cm^{-1}: 3450, 3100, 2960, 1720, 1610, 1530, 1440, 1360, 1310, 1290, 1240, 1120, 1020, 870, 760, 710. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.69 s (3H, OMe), 3.94 s (3H, OMe), 7.55 d (2H, 2′-H, 6′-H, J = 9 Hz), 7.73 d (1H, 6-H, J = 8 Hz), 8.03 d (2H, 3′-H, 5′-H, J = 9 Hz), 8.27 d.d (1H, 5-H, J_1 = 1.5, J_2 = 8 Hz), 9.97 d (1H, 3-H, J = 1.5 Hz). Found, %: C 60.56; H 4.06; N 4.32. $C_{16}H_{13}NO_6$. Calculated, %: C 60.95; H 4.16; N 4.44.

Dimethyl 2-aminobiphenyl-4,4′-dicarboxylate (III). A mixture of 15 g (0.05 mol) of compound **II**, 500 ml of THF, and 10 g of 5% Pd/C was hydrogenated for 5 days under vigorous stirring under atmospheric pressure. When hydrogen was no longer absorbed, the catalyst was filtered off, and the solvent was distilled off from the filtrate under reduced pressure. The residue was recrystallized from ethanol. Yield 13.25 g (93%), mp 176–177°C. IR spectrum, ν, cm^{-1}: 3470, 3380, 2960, 1700, 1620, 1600, 1440, 1400, 1250, 1130, 1000, 910, 760. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.39 s (2H, NH_2), 3.83 s (3H, OCH_3), 3.88 s (3H, OCH_3), 7.17–8.09 m (7H, H_{arom}). Found, %: C 67.29; H 5.32; N 4.98. $C_{16}H_{15}NO_4$. Calculated, %: C 67.36; H 5.30; N 4.91.

Dimethyl 2-fluorobiphenyl-4,4′-dicarboxylate (V). A suspension of dimethyl 2-aminobiphenyl-4,4′-dicarboxylate hydrochloride prepared from 6 g (21 mmol) of compound **III** and 20 ml of 15% hydrochloric acid was cooled to 0°C, and a solution of 2.2 g (0.32 mol) of sodium nitrite in 3 ml of water was added under vigorous stirring. The mixture was stirred for 10 min at 0°C, 2.8 g (0.31 mol) of HBF_4 was added, and the mixture was stirred for 1 h. The precipitate was filtered off, washed with water and ethanol, and thoroughly dried. The diazonium salt thus ob-

tained, 7.38 g (19 mmol), was placed into a flask connected to a gas-washing bottle filled with a 10% solution of sodium hydroxide, and the flask was heated with a stream of air heated to 300°C. When evolution of white smoke ceased, the melt was heated for an additional 1 min. The melt was cooled and dissolved in 200 ml of toluene, the hot solution was filtered through a layer of silica gel, and the sorbent was additionally washed with hot toluene (4×50 ml). The solvent was removed under reduced pressure, and the residue was recrystallized from 100 ml of isopropyl alcohol. Yield 4.65 g (85%), mp 142.5–143°C (from hexane). IR spectrum, ν, cm^{-1}: 3430, 3050, 2980, 1720, 1610, 1430, 1400, 1290, 1210, 1110, 770, 700. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.89 s (3H, OCH_3), 3.89 s (3H, OCH_3), 7.46 t (1H, J = 8 Hz), 7.58 d.d (2H, J_1 = 1.5, J_2 = 8.5 Hz), 7.76 d.d (1H, J_1 = 1.5, J_2 = 11 Hz), 7.84 d.d (1H, J_1 = 1.5, J_2 = 8 Hz), 8.06 d (2H, J = 8.5 Hz). Found, %: C 66.49; H 4.47; F 6.52. $C_{16}H_{13}FO_4$. Calculated, %: C 66.66; H 4.55; F 6.59.

Dimethyl 2,2′-dinitrobiphenyl-4,4′-dicarboxylate (VI). A solution of 20 g (74 mmol) of dimethyl biphenyl-4,4′-dicarboxylate in 200 ml of concentrated sulfuric acid was heated to 35°C, a mixture of 24.2 ml of 58% nitric acid and 25 ml of concentrated sulfuric acid was added dropwise under stirring over a period of 40 min, and the mixture was stirred for 1 h, maintaining the temperature at 35–40°C. The mixture was diluted with 100 ml of water and extracted with ethyl acetate, and the extract was washed with water and a saturated solution of sodium hydrogen carbonate and dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure, and the residue was recrystallized from isopropyl alcohol. Yield 18.76 g (70%), mp 155°C. IR spectrum, ν, cm^{-1}: 2960, 2930, 2850, 2730, 1700, 1600, 1590, 1560, 1430, 1380, 1310, 1290, 1270, 1240, 1210, 1170, 1150, 1000, 840, 810, 700, 730. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.80 s (6H, OCH_3), 7.67 d (2H, 6-H, 6′-H, J = 8 Hz), 8.36 d.d (2H, 5-H, 5′-H, J_1 = 1.6, J_2 = 8 Hz), 8.66 d (2H, 3-H, 3′-H, J = 1.4 Hz). Mass spectrum, m/z (I_{rel}, %): 360 $[M]^+$ (15), 330 $[M - 2CH_3]^+$ (15), 329 $[M - 2CH_3 - H]^+$ (78), 314 $[M - OCH_3 - CH_3]^+$ (100). Found, %: C 53.41; H 3.31; N 7.85. $C_{16}H_{12}N_2O_8$. Calculated, %: C 53.34; H 3.36; N 7.78.

Dimethyl 2,2′-diaminobiphenyl-4,4′-dicarboxylate (VII). A mixture of 5 g (14 mmol) of compound **VI**, 100 ml of acetic acid, and 10 g of 5% Pd/C in a high-pressure reactor was hydrogenated at 30°C and a hydrogen pressure of 3–10 atm until hydrogen was no longer absorbed. The catalyst was separated by filtration, and the solvent was distilled off from the filtrate under reduced pressure. The crude product was dissolved in 50 ml of toluene on heating, the solution was passed through a layer of silica gel, the solvent was distilled off, and the residue was recrystallized from ethanol. Yield 3.4 g (84%), mp 170–171°C. IR spectrum, ν, cm^{-1}: 3450, 3370, 3900, 1700, 1620, 1560, 1510, 1490, 1440, 1420, 1310, 1240, 1200, 1120, 1000, 980, 890, 765. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.5 s (4H, NH_2), 3.9 s (6H, OCH_3), 7.1–7.53 m (6H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 300 $[M]^+$ (100), 299 $[M - 1]^+$, (55), 285 $[M - NH_2 + H]^+$ (10), 268 $[M - 2NH_2]^+$, 253 $[C_{15}H_9O_4]^+$ (21), 241 (11), 182 (12). Found, %: C 63.90; H 5.43; N 9.21. $C_{16}H_{16}N_2O_4$. Calculated, %: C 63.99; H 5.37; N 9.33. M 300.31.

Dimethyl 2,2′-difluorobiphenyl-4,4′-dicarboxylate (IX). A suspension of 500 mg of finely powdered compound **VII** in 5 ml of 20% hydrochloric acid was cooled to 0°C, and a solution of 0.3 g of sodium nitrite in 3 ml of water was added dropwise under stirring, maintaining the temperature at 0 to 5°C. The precipitate was filtered off, washed with water and alcohol, and dried under reduced pressure. The diazonium salt thus obtained, 700 mg, was heated in a round-bottom flask to initiate exothermic reaction. The residue was extracted with hot toluene, the solvent was distilled off from the extract, and the crude product was purified by column chromatography on silica gel using methylene chloride as eluent. Yield 210 mg (41%), mp 139.5°C. IR spectrum, ν, cm^{-1}: 1720, 1560, 1490, 1430, 1400, 1300, 1250, 1200, 1130, 1100, 980, 900, 850, 800, 760. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.96 s (6H, OCH_3), 7.48–7.51 m (2H, H_{arom}), 7.84–7.86 m (2H, H_{arom}), 7.92 d.d (2H, H_{arom}, J_1 = 8, J_2 = 1.5 Hz). Found, %: C 62.93; H 4.03; F 12.34. $C_{16}H_{12}F_2O_4$. Calculated, %: C 62.75; H 3.95; F 12.41.

Biphenyl-4,4′-diyldimethanol (X). Dimethyl biphenyl-4,4′-dicarboxylate (**I**), 27 g (0.1 mol), was added in portions under continuous stirring to a suspension of 4.2 g (0.11 mol) of lithium tetrahydridoaluminate in 150 ml of anhydrous tetrahydrofuran. The mixture was heated for 2 h under reflux, cooled to room temperature, and carefully treated first with water and then with a 10% solution of sulfuric acid. The organic phase was separated by decanting, and the aqueous phase was extracted with ethyl acetate (3×50 ml). The extracts were combined with the organic phase and dried over anhydrous sodium sulfate, the solvent was distilled under reduced pressure, and the residue was recrystallized from ethanol. Yield 90%,

mp 191–192°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.54 d (4H, CH_2O, J = 5 Hz), 5.22 t (2H, OH, J = 5 Hz), 7.39 d (4H, 2-H, 2′-H, 6-H, 6′-H, J = 8 Hz), 7.61 d (4H, 3-H, 3′-H, 5-H, 5′-H, J = 8 Hz). Found, %: C 78.27; H 6.46. $C_{14}H_{14}O_2$. Calculated, %: C 78.48; H 6.59.

2-Fluorobiphenyl-4,4′-diyldimethanol (XI). A solution of 576 mg (2 mmol) of diester **V** in 10 ml of THF was added under vigorous stirring to a suspension of 400 mg (10 mmol) of lithium tetrahydridoaluminate in 40 ml of THF. The mixture was stirred for 30 min at room temperature, and excess $LiAlH_4$ was quenched by treatment with 10 ml of ethyl acetate. The mixture was then treated with a 15% solution of sodium hydroxide until a dense precipitate of aluminum oxide was formed. The precipitate was filtered off and washed with hot THF (2 × 15 ml). The filtrate was evaporated, the residue was dissolved in THF, and the solution was passed through a layer of silica gel. Yield 452 mg (99%), mp 132–133°C (from aqueous ethanol, 1:1). IR spectrum, ν, cm^{-1}: 3250, 3050, 2930, 1490, 1430, 1400, 1360, 1290, 1270, 1210, 1130, 1040, 1020, 810. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.53 d (4H, J = 11 Hz), 5.10 t (1H, J = 11 Hz), 5.22 t (1H, J = 11 Hz), 7.16 m (2H, H_{arom}), 7.38 m (2H, H_{arom}), 7.45 d.d, (2H, J_1 = 8, J_2 = 1.5 Hz). Found, %: C 72.54; H 5.51; F 8.31. $C_{14}H_{13}FO_2$. Calculated, %: C 72.40; H 5.64; F 8.18.

2,2′-Difluorobiphenyl-4,4′-diyldimethanol (XII). Lithium tetrahydridoaluminate, 0.2 g (5.21 mmol), was added to a solution of 1 g (3.26 mmol) of compound **IX**, and the solution was stirred for 6 h on heating under reflux. The mixture was treated with 1 ml of a 10% solution of sodium hydroxide, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, and the residue was recrystallized from ethanol. Yield 0.80 g (98%). IR spectrum, ν, cm^{-1}: 3110, 2940, 1620, 1560, 1500, 1410, 1270, 1240, 1130, 1050, 830. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.55 d (4H, C**H**$_2$, J = 5 Hz), 5.33 t (2H, OH, J = 5 Hz), 7.17–7.21 m (4H, H_{arom}), 7.32 m (2H, H_{arom}). Found, %: C 67.39; H 4.82; F 15.27. $C_{14}H_{12}F_2O_2$. Calculated, %: C 67.20; H 4.83; F 15.18

Biphenyl-4,4′-dicarbaldehyde (XIII). Compound **X**, 2.14 g (0.01 mol), was dissolved in 60 ml of dichloroethane, 15.8 ml of pyridinium chlorochromate in dioxane was added under vigorous stirring, and the mixture was stirred for 3 h at room temperature. The mixture was then diluted with 50 ml of dioxane, the solution was separated from the precipitate by decanting and was passed through a layer of silica gel. The residue (a dark brown material containing the oxidant) was dissolved in a 10% solution of sodium hydroxide, and the solution was extracted with toluene. The extracts were combined with the organic phase, washed with water until neutral reaction, and dried over $MgSO_4$. The solvent was distilled off, and the residue was recrystallized from ethanol. Yield 82%, mp 139–141°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.78 d (4H, 2-H, 2′-H, 6-H, 6′-H, J = 8 Hz), 8.00 d (4H, 3-H, 3′-H, 5-H, 5′-H, J = 8 Hz), 10.08 s (2H, CHO). Found, %: C 80.21; H 4.66. $C_{14}H_{10}O_2$. Calculated, %: C 79.98; H 4.79.

2-Fluorobiphenyl-4,4′-dicarbaldehyde (XIV). A solution of 2.6 g (12 mmol) of pyridinium chlorochromate in dioxane was added under continuous stirring to a solution of 684 mg (3 mmol) of compound **XI** in a mixture of 25 ml of methylene chloride and 10 ml of dioxane. The mixture was stirred for 20 h at room temperature, the progress of the reaction being monitored by TLC. Excess oxidant was decomposed by treatment with 10 ml of isopropyl alcohol, the mixture was stirred for 20 min and filtered through a layer of silica gel, the filtrate was evaporated, the residue was dissolved in 50 ml of methylene chloride, and the mixture was filtered through a layer of silica gel. The solvent was distilled under reduced pressure, and the residue was recrystallized from ethanol. Yield 605 mg (90%), mp >130°C (decomp.). IR spectrum, ν, cm^{-1}: 3060, 2840, 2750, 1690, 1600, 1580, 1560, 1490, 1440, 1410, 1390, 1300, 1270, 1250, 1210, 1180, 1150, 1130, 1010, 970, 890, 840, 820, 790, 760, 740, 720, 660. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.67 t (1H, 6-H, J = 7.5 Hz), 7.72 d (1H, 3-H, J = 10 Hz), 7.77 d (2H, 6′-H, 2′-H, J = 7.5 Hz), 7.8 d (1H, 5-H, J = 8 Hz), 8.0 d (1H, 5′-H, 3′-H, J = 7.5 Hz), 10.05 s (1H, CHO), 10.1 s (1H, CHO). Found, %: C 73.87; H 4.12; F 8.45. $C_{14}H_9FO_2$. Calculated, %: C 73.68; H 3.97; F 8.32.

2,2′-Difluorobiphenyl-4,4′-dicarbaldehyde (XV). A solution of 2.2 g (10 mmol) of pyridinium chlorochromate in 10 ml of dioxane containing 1 ml of water was added dropwise to a solution of 0.83 g (3.32 mmol) of compound **XII** in 30 ml of methylene chloride. The mixture was stirred for 12 h (TLC) and passed through a layer of silica gel, the solvent was removed under reduced pressure, and the residue was recrystallized from alcohol. Yield 0.6 g (73%), mp 150°C (decomp.). IR spectrum, ν, cm^{-1}: 3100, 2910, 1670, 1600, 1550, 1410, 1370, 1260, 1240, 1210, 1140, 1110, 1000, 950, 880, 800, 760, 730.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.60–7.64 m (2H, H_{arom}), 7.70–7.74 m (2H, H_{arom}), 7.79–7.82 m (2H, H_{arom}), 10.07 s (2H, CHO). Found, %: C 68.37; H 4.82; F 15.51. $C_{14}H_8F_2O_2$. Calculated, %: C 68.30; H 3.15; F 15.43.

4,4′-Bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]biphenyl (XVI). A solution of sodium methoxide prepared from 540 mg of metallic sodium and 5 ml of methanol was added to a solution of 1.05 g (5 mmol) of dialdehyde **XIII** and 1.4 g (10 mmol) of 2-methyl-1,3-benzoxazole in 50 ml of DMSO. The mixture was heated to 55–60°C, stirred for 6 h at that temperature, and cooled to room temperature, and the precipitate was filtered off, washed with ethanol and acetone, dried, and recrystallized from DMSO. Yield 1.85 g (84%), mp 317°C. IR spectrum, ν, cm^{-1}: 3060, 3040, 1640, 1530, 1450, 1410, 1350, 1310, 1290, 1280, 1240, 1190, 1160, 1150, 1010, 970, 940, 870, 840, 810, 740, 730. ^{1}H NMR spectrum (CF_3COOD), δ, ppm: 7.53 d (2H, CH=CH, *J* = 16 Hz), 7.89–7.97 m (8H), 8.04–8.09 m (10H), 8.65 d (2H, CH=CH, *J* = 16 Hz). ^{13}C NMR spectrum (CF_3CO_2D), δ_C, ppm: 96.78, 105.04, 107.24, 120.51, 120.84, 121.67, 122.35, 123.04, 125.38, 137.87, 141.57, 145.33, 156.43. Found, %: C 81.71; H 4.64; N 6.17. $C_{30}H_{20}N_2O_2$. Calculated, %: C 81.80; H 4.58; N 6.36.

4,4′-Bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-2-fluorobiphenyl (XVII) was synthesized in a similar way from 1.13 g (5 mmol) of dialdehyde **XIV** and 1.4 g (10 mmol) of 2-methyl-1,3-benzoxazole. Yield 1.8 g (78%), mp 298–299°C (from DMSO). IR spectrum, ν, cm^{-1}: 3060, 1640, 1600, 1570, 1530, 1450, 1430, 1400, 1350, 1290, 1240, 1180, 1160, 1010, 970, 930, 860, 840, 810, 740. ^{1}H NMR spectrum (CF_3CO_2D), δ, ppm: 7.17 d (2H, CH=CH, *J* = 16 Hz), 7.18 d (2H, CH=CH, *J* = 16 Hz), 7.42 d (1H, 3-H, *J* = 11 Hz), 7.49–7.64 m (10H, H_{arom}), 7.67–7.71 m (4H, H_{arom}), 8.21 d (2H, CH=CH, *J* = 16 Hz), 8.27 d (2H, CH=CH, *J* = 16 Hz). Found, %: C 78.82; H 4.06; F 4.25; N 6.01. $C_{30}H_{19}FN_2O_2$. Calculated, %: C 78.59; H 4.18; F 4.14; N 6.11.

4,4′-Bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-2,2′-difluorobiphenyl (XVIII). A mixture of 0.15 g (0.6 mmol) of compound **XV** and 0.2 g (1.5 mmol) of 2-methylbenzoxazole in 10 ml of DMSO was added to a solution of sodium methoxide prepared from 3 ml of methanol and 50 mg of metallic sodium. The mixture was stirred for 1 h, and the precipitate was filtered off and recrystallized from DMSO. Yield 0.23 g (72%), mp 276°C. IR spectrum, ν, cm^{-1}: 3060, 1630, 1540, 1520, 1480, 1470, 1450, 1405, 1340, 1310, 1270, 1240, 1225, 1170, 1140, 1010, 970, 960, 940, 930, 870, 860, 850, 810, 790, 730, 720. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.37–7.40 m (4H, H_{arom}), 7.41 d (2H, CH=CH, *J* = 17 Hz), 7.54–7.57 m (2H, H_{arom}), 7.69–7.71 m (2H, H_{arom}), 7.72–7.74 m (2H, H_{arom}), 7.74–7.75 m (2H, H_{arom}), 7.80–7.83 m (2H, H_{arom}), 7.86 d (2H, CH=CH, *J* = 17 Hz). Found, %: C 75.46; H 3.77; F 8.12; N 5.69. $C_{30}H_{18}F_2N_2O_2$. Calculated, %: C 75.62; H 3.81; F 7.97; N 5.88.

Biphenyl-4,4′-dicarbonyl dichlorides XIX–XXI (*general procedure*). A mixture of 3.3 mmol of dimethyl biphenyl-4,4′-dicarboxylate **I**, **V**, or **X**, 25 mmol of sodium hydroxide, and 50 ml of 90% ethanol was heated for 1 h under reflux. The mixture was cooled to room temperature, 50 ml of 10% hydrochloric acid was added, and the precipitate was filtered off and dried in a vacuum desiccator over phosphoric anhydride. The crude product was mixed with 10 ml of thionyl chloride, one drop of DMF was added, and the mixture was heated for 1 h under reflux. Excess thionyl chloride was removed under reduced pressure, and the dry residue was brought into further transformations without additional purification.

1,3,4-Oxadiazole derivatives XXII–XXIV (*general procedure*). A solution of 2.65 mmol of dichloride **XIX**–**XXI** in 20 ml of anhydrous THF was added under continuous stirring to a solution of 5.5 mmol of *p*-octyloxybenzohydrazide and 20 mmol of triethylamine in 30 ml of anhydrous THF, and the mixture was stirred for 24 h at room temperature. The precipitate was filtered off, washed with ethanol and acetone, and dried. The product was mixed with 30 ml of phosphoryl chloride, and the mixture was heated for 48 h under reflux (TLC). The mixture was cooled and poured under vigorous stirring into 200 ml of a mixture of crushed ice with water, and the precipitate was filtered off, washed with water, dried, and recrystallized from DMSO.

4,4′-Bis[5-(4-octyloxyphenyl)-1,3,4-oxadiazol-2-yl]biphenyl (XXII). Yield 83%, mp 256°C. IR spectrum, ν, cm^{-1}: 3070, 2930, 2860, 1620, 1590, 1550, 1500, 1490, 1470, 1420, 1410, 1310, 1260, 1180, 1100, 1070, 1050, 1030, 1010, 970, 840, 830, 740, 730, 700, 650. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.9 t (6H, CH_3, *J* = 7 Hz), 1.3–1.38 m (16H, CH_2), 1.49 m (4H, CH_2), 1.83 m (4H, CH_2), 4.05 t (4H, OCH_2, *J* = 6.5 Hz), 7.04 d (4H, H_{arom}, *J* = 9 Hz), 7.82 d (4H, H_{arom}, *J* = 8 Hz), 8.09 d (4H, H_{arom}, *J* = 9 Hz), 8.24 d (4H, H_{arom}, *J* = 8 Hz). ^{13}C NMR spectrum

($CDCl_3$), δ_C, ppm: 14.12, 22.66, 26.01, 29.14, 29.24, 29.35, 31.81, 68.31, 115.01, 116.07, 123.69, 127.42, 127.72, 128.73, 142.78, 162.06, 163.79, 164.76. Found, %: C 75.77; H 7.13; N 7.82. $C_{44}H_{50}N_4O_4$. Calculated, %: C 75.62; H 7.21; N 8.02.

2-Fluoro-4,4′-bis[5-(4-octyloxyphenyl)-1,3,4-oxadiazol-2-yl]biphenyl (XXIII). Yield 82%, mp 246–247°C. IR spectrum, ν, cm^{-1}: 3060, 2940, 2860, 1610, 1580, 1550, 1490, 1470, 1420, 1400, 1300, 1250, 1180, 1100, 1070, 1050, 1030, 1000, 980, 970, 880, 840, 690, 670, 650. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.9 t (6H, CH_3, J = 7 Hz), 1.3–1.4 m (16H, CH_2), 1.45–1.5 m (4H, CH_2), 1.8–1.85 m (4H, CH_2), 4.04 t (4H, OCH_2, J = 6.5 Hz), 7.04 d (4H, H_{arom}, J = 8.5 Hz), 7.67 t (1H, 6-H, J = 8.5 Hz), 7.78 d (2H, 2′-H, 6′-H, J = 7 Hz), 7.94 d.d (1H, 3-H, J_1 = 10.5, J_2 = 1.5 Hz), 8.03 d.d (1H, 5-H, J_1 = 8, J_2 = 1.5 Hz), 8.08 d (2H, H_{arom}, J = 8.5 Hz), 8.09 d (2H, H_{arom}, J = 8.5 Hz), 8.24 d (2H, 3′-H, 5′-H, J = 8.5 Hz). Found, %: C 73.64; H 6.94; F 2.59; N 7.71. $C_{44}H_{49}FN_4O_4$. Calculated, %: C 73.72; H 6.89; F 2.65; N 7.82.

2,2′-Difluoro-4,4′-bis[5-(4-octyloxyphenyl)-1,3,4-oxadiazol-2-yl]biphenyl (XXIV). Yield 33%, mp 185°C. IR spectrum, ν, cm^{-1}: 3100, 2930, 2860, 1610, 1580, 1550, 1490, 1470, 1420, 1300, 1240, 1170, 1130, 1090, 1070, 1040, 1030, 990, 970, 960, 860, 830, 730, 710, 640. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (6H, CH_3, J = 7 Hz), 1.31–1.40 m (16H, CH_2), 1.47–1.51 m (4H, CH_2), 1.81–1.87 m (4H, CH_2), 4.06 t (2H, CH_2, J = 7 Hz), 7.02–7.05 m (4H, H_{arom}), 7.60–7.65 m (2H, H_{arom}), 7.95–7.97 m (2H, H_{arom}), 8.05 d.d (2H, J_1 = 8, J_2 = 1.5 Hz), 8.07–8.09 m (4H, H_{arom}). Found, %: C 72.14; H 6.49; F 5.21; N 7.68. $C_{44}H_{48}F_2N_4O_4$. Calculated, %: C 71.91; H 6.58; F 5.17; N 7.62.

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