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Synthesis of New Polyconjugated Compounds Based on 9,10-Diphenylphenanthrene

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Abstract—A procedure was developed for the synthesis of dimethyl 9,10-diphenylphenanthrene-2,7-dicarboxylate, and the latter was used as starting compound for the preparation of 9,10-diphenyl-2,7-bis(2-phenylethenyl)phenanthrene derivatives and 2,7-bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-9,10-diphenylphenanthrene, which showed strong luminescence in the solid state and in solution. Spectral properties of the products were studied.

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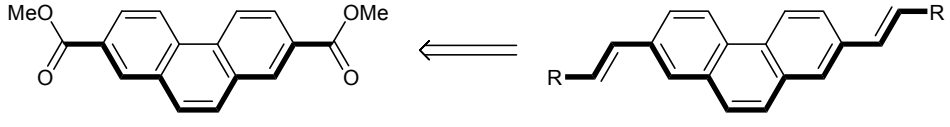
Fused polycyclic aromatic compounds attract strong interest as chromophore building blocks in the synthesis of electroluminescent dyes and organic semiconductors [1]. Substituted phenanthrenes **I** having functional groups in positions *2* and *7* (Scheme 1) possess the most extended conjugation chain, and they can be used in the synthesis of new polyvinylene and other polyconjugated aromatic systems like **II**. However, direct functionalization of phenanthrene and its homologs is not always regioselective, so that this approach is inappropriate. A promising approach to targeted structures may be that based on palladium-catalyzed reaction of aryl iodides with alkynes, which ensures one-step preparation of polycyclic aromatic compounds with required functionalities [2, 3].

In the present communication we report on the synthesis of dimethyl 9,10-diphenylphenanthrene-2,7-dicarboxylate (**VI**) and a series of luminescent dyes based thereon. The presence of methoxycarbonyl groups in positions *2* and *7* of molecule **VI** makes it possible to readily append side chains in the opposite directions and obtain derivatives possessing extended π-conjugation systems, which are potential electroactive materials.

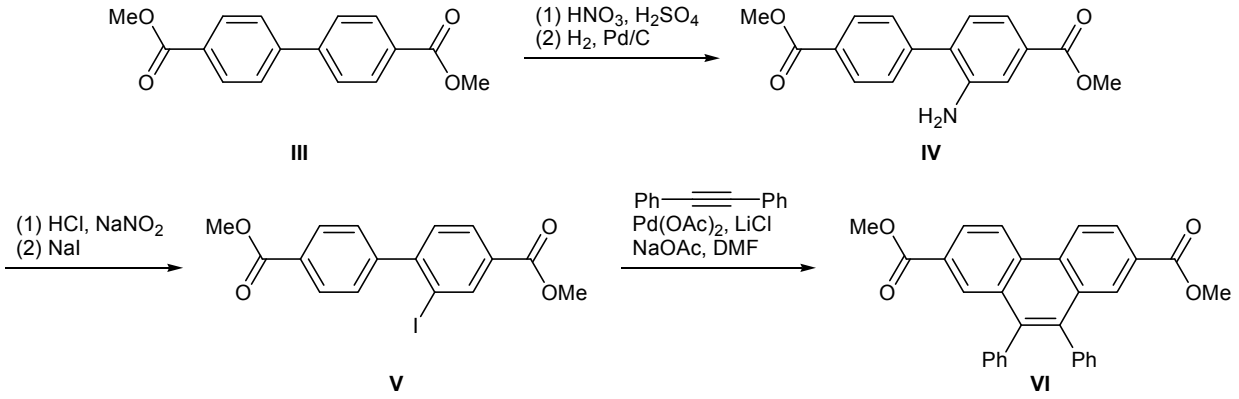
Mandal et al. [2] previously reported on the formation of 9,10-diphenylphenanthrene-2,7-dicarboxylates in a very poor yield (no less than 9%) in the reactions of 2,2′-diiodobiphenyl-4,4′-dicarboxylic acid esters with diphenylacetylene in the presence of palladium acetate [2]. An alternative version of the synthesis of substituted 9,10-diphenylphenanthrenes from 2-iodobiphenyls was proposed in [3]. However, coupling with diphenylacetylene was studied only for biphenyls having only one electron-donating substituent in the iodine-free aromatic ring. We tried to apply analogous approach to the synthesis of dimethyl 9,10-diphenylphenanthrene-2,7-dicarboxylate (**VI**). As starting compound we used the corresponding iodo derivative, dimethyl 2-iodobiphenyl-4,4′-dicarboxylate (**V**) which was synthesized according to Scheme 2. Nitration of dimethyl biphenyl-4,4′-dicarboxylate (**III**), followed by hydrogenation of the 2-nitro derivative over Pd/C gave amine **IV** [4] which was subjected to diazotization and treatment with sodium iodide. Iodide **V** was

Scheme 1.



I **II**

Scheme 2.

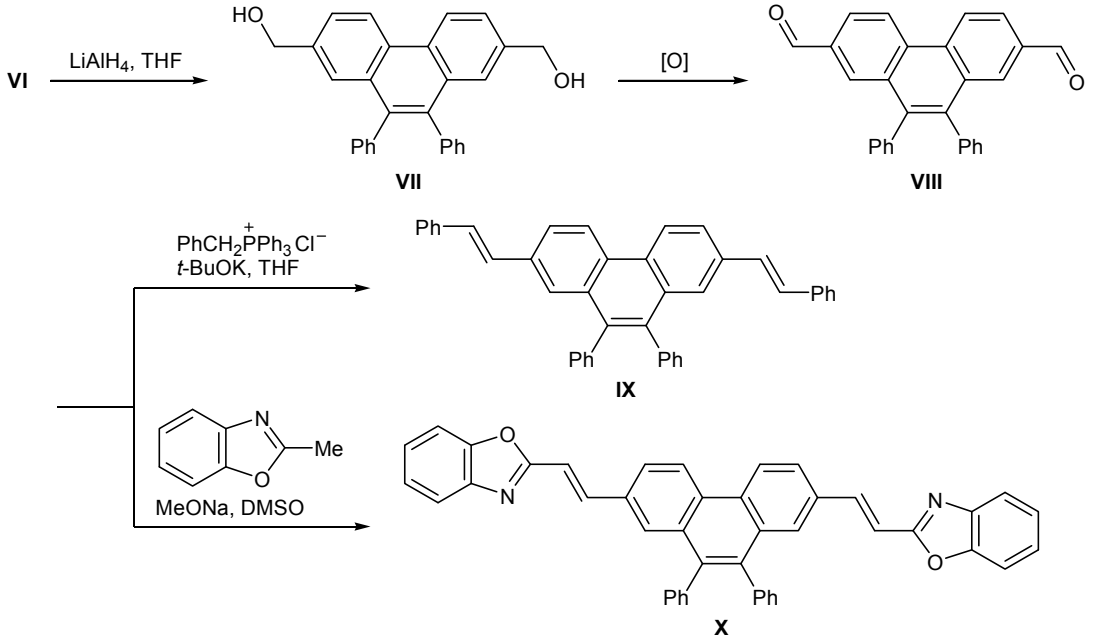


thus synthesized in 60% yield. Substituted phenanthrene **VI** was obtained in 42% yield by heating a solution of iodo diester **V**, diphenylacetylene, and palladium(II) acetate in anhydrous *N*,*N*-dimethylformamide at 100°C over a period of 140 h.

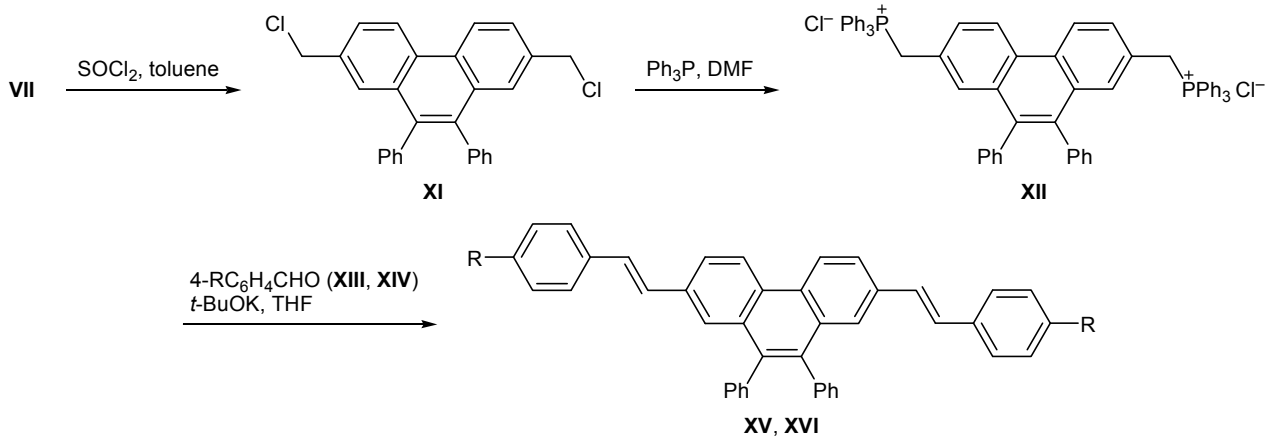
As noted above, the presence of ester groups in positions *2* and *7* of molecule **VI** ensures its facile functionalization to obtain rigid linear polyconjugated systems. *p*-Phenylenevinylene analogs conjugated with aromatic or heterocyclic fragments in the main or side chain attract much attention as promising luminescent materials for the preparation of organic light-emitting diodes [5–7]. Taking the above into account, we made an attempt to obtain on the basis of dimethyl 9,10-diphenylphenanthrene-2,7-dicarboxylate (**VI**) a series of new short-chain poly-*p*-phenylenevinylene analogs possessing both electron-withdrawing and electron-donating groups in the main conjugation chain (Scheme 3).

The reduction of diester **VI** with lithium tetrahydridoaluminate in tetrahydrofuran gave diol **VII** which was oxidized to the corresponding dialdehyde **VIII** with pyridinium chlorochromate in dioxane (yield 77%). Compound **VIII** was then brought into Knoevenagel and Wittig condensations to obtain poly-π-conjugated systems containing electron-withdrawing and electron-donating fragments. The condensation of dialdehyde **VIII** with 2-methylbenzoxazole in the presence of sodium methoxide afforded compound **X**. Dialdehyde **VIII** also reacted with benzyl(triphenyl)phosphonium chloride according to Wittig to produce symmetrically substituted phenanthrene **IX** in good yield (Scheme 3). These reactions were characterized by

Scheme 3.



Scheme 4.



XIII, **XV**, R = CN; **XIV**, **XVI**, R = NPh_2.

high stereoselectivity, and the major products were the corresponding *trans*,*trans* isomers.

This scheme of synthesis ensures preparation of a relatively limited series of ethenyl derivatives, depending on the accessibility of benzyl(triphenyl)phosphonium salts, which is determined in turn by the nature of substituents in the benzene ring. In order to obtain difficultly accessible compounds, especially those containing several triarylamine fragments in the conjugation chain, we followed an alternative transformation sequence: the corresponding ylide was generated from bis-triphenylphosphonium salt **XII** derived from phenanthrene **XI**, and subsequent coupling with monosubstituted benzaldehydes **XIII** and **XV** gave target products **XIV** and **XVI**, respectively (Scheme 4). Dichloride **XI** was synthesized by treatment of diol **VII** with thionyl chloride, and compound **XI** reacted with triphenylphosphine, yielding bis-phosphonium salt **XII**. Compounds **XV** and **XVI** were formed exclusively as *trans*,*trans* isomers.

The structure of the isolated compounds was confirmed by ^{1}H NMR, IR, and mass spectra. The ^{1}H NMR spectra of **VI**–**XI** and **XV**–**XVI** contained signals from six protons in the phenanthrene core with the expected multiplicities. The steric configuration of compounds **IX**, **X**, **XV**, and **XVI** was determined on the basis of the ^{1}H NMR data. Signals from protons at the exocyclic double bonds in compound **IX** resonated in the ^{1}H NMR spectrum as two doublets at δ 7.45 ppm with a vicinal coupling constant of 16.5 Hz which is typical of their *trans* orientation.

All compounds **IX**, **X**, **XV**, and **XVI**, both in the crystalline state and in solution, showed strong luminescence in the blue region of the spectrum. As follows from the data given in table, additional electron-withdrawing substituents in the main conjugation chain of compounds **X** and **XV** do not affect their spectral parameters to an appreciable extent, and these compounds differ only slightly from 2,7-bis(phenylethenyl) derivative **IX**. By contrast, the presence of an electron-donor fragment in molecule **XVI** is responsible for a strong red shift of fluorescence maximum of this compound, while extension of the conjugation induces more than threefold increase in its molar absorption coefficient, as well as strong increase in the photoluminescence quantum yield as compared to compound **IX**.

Electronic absorption spectra and photoluminescence of phenanthrene derivatives **VI**, **IX**, **X**, **XV**, and **XVI**

Compound no.	Absorption, λ_{max}, nm	ε, l mol^{-1} cm^{-1}	Fluorescence, λ_{max}, nm
VI	289.5	36000	420
IX	305, 366.5	46000, 59800	428, 447[a]
X	306.5, 385	42500, 87000	442, 481[a]
XV	298.5, 382	41500, 74400	449, 479[a]
XVI	298.5, 409.5	163900, 195200	480, 485[a]

[a] In the solid state.

EXPERIMENTAL

The melting points were determined on a Kofler melting point apparatus equipped with a Hanna HI 93530 electronic thermometer. The ^{1}H NMR spectra were recorded on a Bruker Biospin Avance 500 spectrometer (500 MHz). The IR spectra were measured in the range from 400 to 4000 cm^{-1} on a Specord M-80 instrument from samples prepared as KBr pellets. The electronic absorption and fluorescence spectra were recorded from solutions in DMF or microcrystalline samples on a Solar CM2203 spectrofluorimeter (excitation wavelength 365 nm). The mass spectra (atmospheric pressure chemical ionization) were obtained on an Accela-LCQ Fleet mass chromatograph. The solvents and reagents used were purified and dehydrated by standard methods to a pure or analytical grade. The progress of reactions was monitored by TLC on aluminum plates coated with silica gel 60 F_{254} (Merck).

Dimethyl 2-iodobiphenyl-4,4′-dicarboxylate (V). A solution of 1.42 g (5 mmol) of dimethyl 2-aminobiphenyl-4,4′-dicarboxylate (**IV**) [4] in 5 ml of 15% hydrochloric acid was cooled to 0–4°C, and a solution of 0.4 g (5.8 mol) of sodium nitrite in 3 ml of water was added dropwise under vigorous stirring. The mixture was stirred for 10 min at 0–4°C, a solution of 0.9 g (6 mmol) of sodium iodide in 3 ml of water was added, and the mixture was heated to 60°C and kept for 10 min at that temperature. The mixture was cooled to room temperature, diluted with 50 ml of water, and extracted with ethyl acetate (3×75 ml). The combined extracts were washed in succession with a 10% solution of $NaHSO_3$, water, a saturated solution of $NaHCO_3$, and water again and dried over anhydrous Na_2SO_4. The solvent was distilled off under reduced pressure, and the crude product was purified by column chromatography on silica gel using toluene as eluent, followed by recrystallization from ethanol. Yield 1.2 g (60%), mp 112–113°C. IR spectrum, ν, cm^{-1}: 3450, 2970, 1730, 1440, 1290, 1250, 1140, 970, 850, 770, 720. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.89 s (6H, OCH_3), 7.29 d (1H, 6-H, J = 8 Hz), 7.36 d (2H, 6′-H, 2′-H, J = 8.5 Hz), 7.99 d.d (1H, 5-H, J = 8, 1.5 Hz), 8.06 d (2H, 5′-H, 3′-H, J = 8.5 Hz), 8.56 d (1H, 3-H, J = 1.5 Hz). Found, %: C 48.65; H 3.24; I 32.10. $C_{16}H_{13}IO_4$. Calculated, %: C 48.51; H 3.31; I 32.03.

Dimethyl 9,10-diphenylphenanthrene-2,7-dicarboxylate (VI). A mixture of 1.3 g (3.2 mmol) of iodobiphenyl **V**, 0.138 g (3.2 mmol) of LiCl, 0.65 g (3.5 mmol) of diphenylacetylene, 0.04 g (5 mol %) of palladium(II) acetate, and 0.5 g (6.4 mmol) of sodium acetate in 50 ml of DMF was stirred for 72 h at 95–105°C. The mixture was cooled to room temperature and diluted with water (100 ml), and the precipitate was filtered off, washed with hexane, and recrystallized from *o*-xylene. Yield 0.61 g (42%), mp 309–310°C. IR spectrum, ν, cm^{-1}: 3440, 3100, 3050, 2970, 1730, 1570, 1440, 1390, 1340, 1300, 1260, 1210, 1130, 1020, 970, 830, 770, 710. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.81 s (6H, OCH_3), 7.20–7.40 m (10H, H_{arom}), 8.09 d (2H, 1-H, 8-H, J = 1.5 Hz), 8.22 d.d (2H, 3-H, 6-H, J = 9, 1.5 Hz), 9.13 d (2H, 4-H, 5-H, J = 9 Hz). Found, %: C 80.55; H 5.07. $C_{30}H_{22}O_4$. Calculated, %: C 80.70; H 4.97.

(9,10-Diphenylphenanthrene-2,7-diyl)dimethanol (VII). A solution of 2.3 g (5.1 mmol) of diester **VI** in 10 ml of tetrahydrofuran was added to a suspension of 0.2 g (5.1 mmol) of lithium tetrahydridoaluminate in 5 ml of THF. The mixture was heated for 4 h under reflux, cooled to room temperature, and treated with 2 ml of a 10% solution of sodium hydroxide. The precipitate was filtered off and washed with 50 ml of THF, the filtrate was evaporated under reduced pressure, and the residue was recrystallized from isopropyl alcohol. Yield 1.7 g (85%), mp 235–235.5°C. IR spectrum, ν, cm^{-1}: 3300, 3070, 2860, 1490, 1450, 1410, 1300, 1180, 1070, 1050, 1010, 805, 700. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.57 d (4H, CH_2OH, J = 5.5 Hz), 5.18 t (2H, OH, J = 5.5 Hz), 7.1– 7.3 m (10H, H_{arom}), 7.39 d (2H, 1-H, 8-H, J = 1.5 Hz), 7.65 d.d (2H, 3-H, 6-H, J = 9, 1.5 Hz), 8.83 d (2H, 4-H, 5-H, J = 9 Hz). Found, %: C 86.28; H 5.75. $C_{28}H_{22}O_2$. Calculated, %: C 86.13; H 5.68.

9,10-Diphenylphenanthrene-2,7-dicarbaldehyde (VIII). Diol **VII**, 0.39 g (1 mmol), was dissolved in 5 ml of dioxane, 0.63 g of pyridinium chlorochromate in 10 ml of dioxane was added under vigorous stirring, and the mixture was stirred for 3 h at room temperature. The mixture was then diluted with 5 ml of dioxane, the solution was separated by decanting and passed through a layer of silica gel, the precipitate (a dark brown material) was dissolved in a 10% solution of sodium hydroxide, and the alkaline solution was extracted with toluene. The extract was combined with the organic phase, washed with water until neutral reaction, and dried over $MgSO_4$. The solvent was distilled off under reduced pressure, and the residue was recrystallized from ethanol. Yield 0.3 g (77%), mp 265°C. IR spectrum, ν, cm^{-1}: 3070, 2850, 1690, 1610, 1580, 1450, 1435, 1380, 1300, 1230, 1200, 1150, 1090, 1040, 920, 830, 710. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.10–7.30 m (10H, H_{arom}), 8.03 d

(2H, 1-H, 8-H, J = 1.5 Hz), 8.14 d.d (2H, 3-H, 6-H, J = 9, 1.5 Hz), 8.90 d (2H, 4-H, 5-H, J = 9 Hz), 9.96 s (2H, CHO). Found, %: C 87.22; H 4.62. $C_{28}H_{18}O_2$. Calculated, %: C 87.02; H 4.69.

9,10-Diphenyl-2,7-bis[(*E*)-2-phenylethenyl]-phenanthrene (IX). Potassium *tert*-butoxide, 0.07 g (0.6 mmol), was added under nitrogen to 0.2 g (0.5 mmol) of benzyl(triphenyl)phosphonium chloride, a solution of 0.1 g (0.25 mmol) of dialdehyde **VIII** in 5 ml of THF was added dropwise over a period of 5 min, and the mixture was stirred for 4 h at 40°C. The mixture was then treated with water (50 ml) and extracted with chloroform (3×75 ml). The extracts were washed with water, a saturated solution of sodium chloride, and water again, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using toluene as eluent. Yield 0.1 g (82%), mp 322–323°C. IR spectrum, ν, cm^{-1}: 3070, 3030, 2240, 1610, 1510, 1480, 1450, 1420, 1190, 970, 870, 840, 710. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.10–7.30 m (20H, H_{arom}), 7.42 d (2H, 1-H, 8-H, J = 1.5 Hz), 7.45 d (2H, CH=CH, J = 16.5 Hz), 7.45 d (2H, CH=CH, J = 16.5 Hz), 7.87 d.d (2H, 3-H, 6-H, J = 9, 1.5 Hz), 8.69 d (2H, 4-H, 5-H, J = 9 Hz). Mass spectrum: m/z 535 $[M + 1]^+$.

2-{(*E*)-7-[(*E*)-2-(1,3-Benzoxazol-2-yl)ethenyl]-9,10-diphenylphenanthren-2-ylethenyl}-1,3-benzoxazole (X). Anhydrous dimethyl sulfoxide, 60 ml, 2-methylbenzoxazole, 0.15 g (1.1 mmol), and dialdehyde **VIII**, 0.15 g (0.4 mmol), were added in succession to a solution of sodium methoxide prepared from 0.05 g (2.1 mmol) of metallic sodium and 3 ml of anhydrous methanol. The mixture was heated to 40°C and stirred for 4 h at that temperature. After cooling, the precipitate was filtered off and washed with dimethyl sulfoxide (3×5 ml). The product was recrystallized from DMSO. Yield 0.16 g (60%), mp >360°C. IR spectrum, ν, cm^{-1}: 3070, 3040, 1640, 1540, 1460, 1360, 1250, 1190, 1170, 1020, 970, 950, 830, 810, 750, 710. ^{1}H NMR spectrum (CF_3COOD), δ, ppm: 6.60–6.80 m (10H, H_{arom}), 6.84 d (2H, CH=CH, J = 16 Hz), 7.10–7.30 m (8H, benzoxazole), 7.52 d (2H, 1-H, 8-H, J = 1.5 Hz), 7.62 d.d (2H, 3-H, 6-H, J = 9, 1.5 Hz), 7.89 d (2H, CH=CH, J = 16 Hz), 8.48 d (2H, 4-H, 5-H, J = 9 Hz). Mass spectrum: m/z 617 $[M + 1]^+$.

2,7-Bis(chloromethyl)-9,10-diphenylphenanthrene (XI). Thionyl chloride, 2 ml (25 mmol), was added to solution of 1.6 g (4.1 mmol) of diol **VII** in 100 ml of toluene, and the mixture was heated to the boiling point and kept boiling for 10 min. After cooling to room temperature, the mixture was poured into 50 ml of water, and the organic phase was separated, washed in succession with water, a saturated solution of $NaHCO_3$, and water again, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using toluene as eluent. The product was additionally recrystallized from isopropyl alcohol. Yield 1.7 g (95%), mp 65–67°C. IR spectrum, ν, cm^{-1}: 3070, 3040, 2930, 1610, 1490, 1450, 1410, 1260, 1090, 1040, 1010, 810, 710. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.58 s (4H, CH_2Cl), 7.10–7.30 m (10H, H_{arom}), 7.45 d (2H, 1-H, 8-H, J = 1.5 Hz), 7.67 d.d (2H, 3-H, 6-H, J = 8.5, 1.5 Hz), 8.73 d (2H, 4-H, 5-H, J = 8.5 Hz). Found, %: C 78.47; H 4.79; Cl 16.50. $C_{28}H_{20}Cl_2$. Calculated, %: C 78.69; H 4.72; Cl 16.59.

(9,10-Diphenylphenanthrene-2,7-diyldimethylene)bis(triphenylphosphonium) dichloride (XII). Compound **XI**, 1.9 g (4.5 mmol), and triphenylphosphine, 2.33 g (12 mmol), were dissolved under argon in 50 ml of DMF. The mixture was heated for 5 h under reflux, 2/3 of the solvent was removed under reduced pressure, and 70 ml of toluene was added to the residue. The precipitate was filtered off and dried under reduced pressure. Yield 2.15 g (51%), decomposition point 250°C. IR spectrum, ν, cm^{-1}: 3450, 2950, 2850, 1440, 1120, 750, 720, 680, 500.

4-{(*E*)-7-[(*E*)-2-(4-Cyanophenyl)ethenyl]-9,10-diphenylphenanthren-2-ylethenyl}benzonitrile (XV). A solution of 0.10 g (0.92 mmol) of potassium *tert*-butoxide in 10 ml of THF was added under nitrogen to 0.44 g (0.46 mmol) of Wittig salt **XII**, the mixture was stirred for 10 min at room temperature, a solution of 0.12 g (0.92 mmol) of aldehyde **XIII** in 5 ml of THF was added dropwise over a period of 5 min. and the mixture was stirred for 4 h at 40°C, treated with water (50 ml), and extracted with chloroform (3×75 ml). The extracts were washed with water, a saturated solution of NaCl, and water again, dried over Na_2SO_4, and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using toluene as eluent. Yield 0.2 g (77%), mp >360°C. IR spectrum, ν, cm^{-1}: 3070, 3030, 2240, 1640, 1610, 1510, 1480, 1450, 1420, 1190, 970, 870, 840, 710. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.10–7.30 m (10H, H_{arom}), 7.37 d (2H, CH=CH, J = 16.5 Hz), 7.45 d (2H, CH=CH, J = 16.5 Hz), 7.45 d (2H, 1-H, 8-H, J = 1.5 Hz), 7.76 d (4H, H_{arom}, J = 9.5 Hz), 7.80 d (4H, H_{arom}, J = 9.5 Hz), 8.13 d.d (2H,

3-H, 6-H, J = 8.5, 1.5 Hz), 8.99 d (2H, 4-H, 5-H, J = 8.5 Hz). Mass spectrum: m/z 584 $[M]^-$.

4-[(*E*)-2-{7-(*E*)-2-[4-(Diphenylamino)phenyl]-ethenyl-9,10-diphenylphenanthren-2-yl}ethenyl]-*N*,*N*-diphenylaniline (XVI). A solution of 0.10 g (0.92 mmol) of potassium *tert*-butoxide in 10 ml of THF was added under nitrogen to 0.44 g (0.46 mmol) of Wittig salt **XII**, the mixture was stirred for 10 min at room temperature, a solution of 0.25 g (0.92 mmol) of aldehyde **XIV** in 5 ml of THF was added dropwise, and the mixture was stirred for 4 h at 40°C, treated with 50 ml of water, and extracted with chloroform (3×75 ml). The combined extracts were washed with water, a saturated solution of NaCl, and water again, dried over Na_2SO_4, and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using hexane–toluene (1:1) as eluent. Yield 0.2 g (81%), mp 112–113°C. IR spectrum, ν, cm^{-1}: 3070, 3040, 1600, 1500, 1450, 1340, 1320, 1270, 1190, 1090, 1040, 970, 830, 760, 710. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.00–7.30 m (30H, H_{arom}), 7.31 d (2H, CH=CH, J = 16 Hz), 7.40 d (2H, 1-H, 8-H, J = 1.5 Hz), 7.45 d (2H, CH=CH, J = 16 Hz), 7.56 d (4H, H_{arom}, J = 9.5 Hz), 7.72 d (4H, H_{arom}, J = 9.5 Hz), 7.97 d.d (2H, 3-H, 6-H, J = 8.5, 1.5 Hz), 8.68 d (2H, 4-H, 5-H, J = 8.5 Hz). Mass spectrum: m/z 869 $[M + 1]^+$.

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