Synthesis of Pyrene-Anthracene Conjugated Molecular Rods

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Abstract: Fully conjugated pyrene-anthracene-based molecular rods were synthesized by the Horner-Wadsworth–Emmons reaction utilizing potassium *tert*-butoxide in dry THF. The synthesized rods, which have butylene groups as solubility spacers in the main chain, exhibited good solubility in polar solvents. The solutions of the synthesized pyrene-containing molecular rods exhibited a blue shift in the UV-vis from the absorption maximum due to the presence of the pyrene group in comparison with the dialdehydes. The chemical structure and purity of the synthesized rods were confirmed by ^{1}H and ^{13}C NMR, FAB+, MALDI-TOF, electrospray mass spectra and elemental analysis.

Keywords: Molecular rods, Horner-Wadsworth–Emmons, anthracene, pyrene.

The presence of charge-transfer reaction centers in macromolecules depends on factors as the composition, the separation in the interchromophore, the overall dynamical and supramolecular reorganization, and the electronic coupling [1]. The synthesis of artificial charge-transfer model systems in which the introduction of simple molecular changes is used to control and tune the magnitude of the electron-transfer parameters became a theme of great interest in the last years. The molecular chains or bridges inside the molecule provide endless opportunities, since they determine the

cal entities in molecular and supramolecular electronic and photonic devices [7]. In this context, the combination of anthracene and styrene with pyrene compounds could lead to systems with good response in the electron-transfer processes [8].

In the present work, we describe the synthesis of a new series of compounds in which pyrene is linked to a vinyl anthracene and oligo(phenylvinylene)anthracene. These conjugated block oligomers with well defined structure and do-
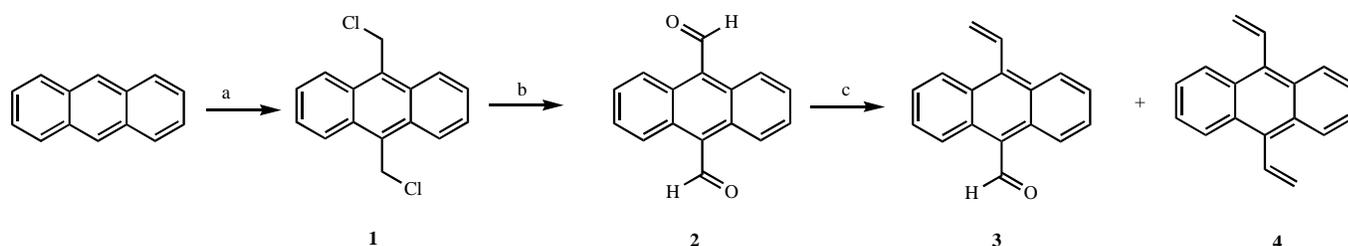
Scheme 1. a) 1,4-dixane, HCl, NaCl/H$_2$SO$_4$; b) DMSO, N$_2$, EtOH, 2-nitropropane, Na; c) CH$_3$(Ph)$_3$PBr, *n*-BuLi, THF, N$_2$.

structural features and the size of the electronic coupling between the donor and acceptor fragments [2]. The modification of the spacer gives the possibility to introduce a systematic alteration of separation, orientation, and overlap without affecting the electronic nature of the donor–acceptor pair, for which the coupling is proportional to the overlap of their electronic clouds [3]. The electron-transfer processes depend on molecular size and structure, as well as the temperature and the free-energy difference between the donor and acceptor in donor–bridge–acceptor systems. Currently, monodisperse and soluble π-conjugated systems with a well-defined length and composition are receiving a growing interest for the design of molecular wires [4] and rods [5], since they can be used as tunable building blocks [6] for nanoscale chemi-

nor-bridge array were synthesized by Heck and Horner–Wadsworth–Emmons reactions using aromatic mono vinyl aldehydes, dialdehydes and diphosphonates as monomers.

RESULTS AND DISCUSSION

The synthesis of the monovinyl and divinylanthracene **3** and **4** was started from a chloromethylation of the anthracene to obtain the 9,10-bis(chloromethyl) anthracene **1**. Treatment of **1** with sodium, 2-nitropropane in DMSO and ethanol gives the anthracene-9,10-dicarbaldehyde **2** in good yield (83 %). Compound **2** was treated with CH$_3$(Ph)$_3$PBr, *n*-BuLi in dry THF to obtain compounds **3** and **4** (Scheme 1).

The following signals were observed in the ^{1}H NMR spectrum of compound **3**: two doublets at δ 5.48 and at δ 5.97 for the vinylic protons, which coupling constant *J*= 18 Hz; one multiplet at 7.25 due to the =CH group; three signals at δ7.40, 7.53, 8.22 and 8.80 due to the aryl group, and, finally, the signal at δ11.30 assigned to the carboxylic group.

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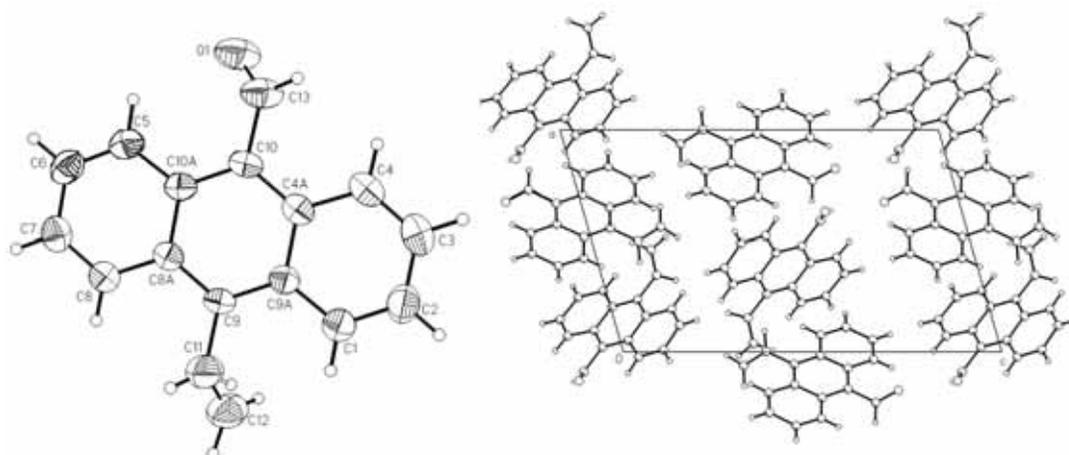
Fig. (1). Crystal structure and crystal packing of the 10-vinylanthracene-9-carbaldehyde **3**. Selected bond lengths [Å]: O(1)-C(13)=1.162, C(10)-C(13)=1.471, C(9)-C(11)= 1.477, C(11-C(12)=1.206. Selected angles (°): C(10A)-C(10)-C(13)=121.3, C(4A)-C(10)-C(13)=117.9, C(8A)-C(9)-C(11)=118.7, O(1)-C(13)-C(10)=128.1, C(12)-C(11)-C(9)=118.7.
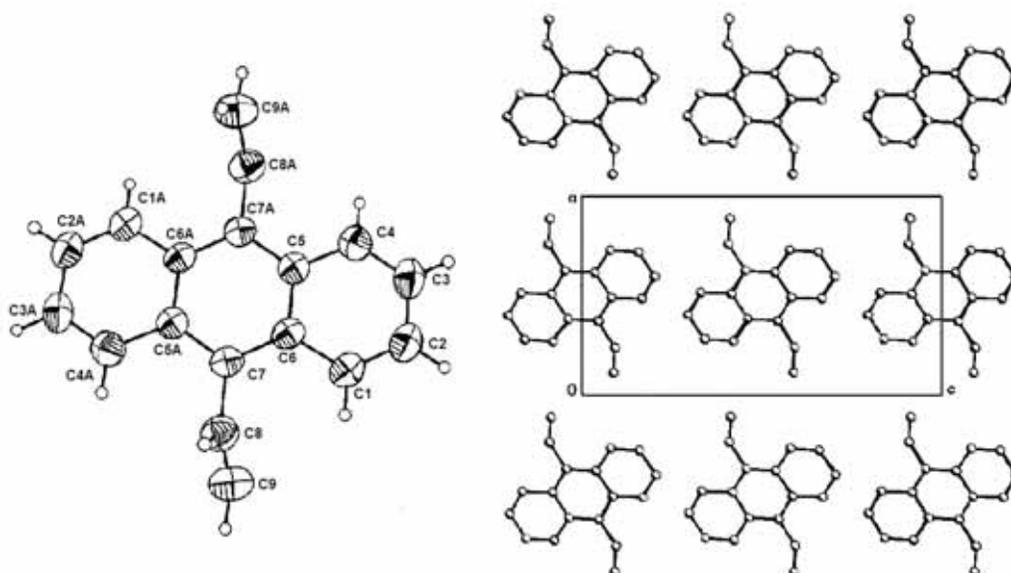

Fig. (2). Crystal structure and crystal packing of the 9,10-divinylanthracene **4**. Selected bond lengths [Å]: C(8)-C(9)=1.284, C(7)-C(8)=1.477. Selected angles (°): C(5)-C(7)-C(8)=119.87, C(9)-C(8)-C(7)=126.35.

The mono and divinyl anthracenes **3** and **4** were crystallized in dichloromethane and the structures were confirmed by X-ray crystallographic studies (Figs. **1** and **2**).

In the second step, the synthesis of the counterpart for the oligoanthracenevinylene (OAV) preparation started with the alkylation of the hydroquinone with 1-bromobutane under classical Williamson conditions (NaOH, ethanol, reflux) to yield the 1,4-dibutoxybenzene **5** in 94 % yield. Halogenation of **5** with bromine in CCl_4 afforded 1,4-dibromo-2,5-dibutoxybenzene **6** in 85 % yield (Scheme **2**).

As **6** has two bromine groups a Mizoroki-Heck cross coupling reaction was carried out with two equivalents of 10-
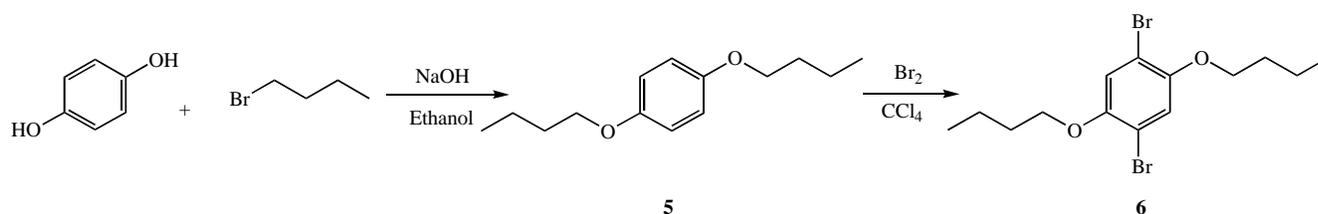
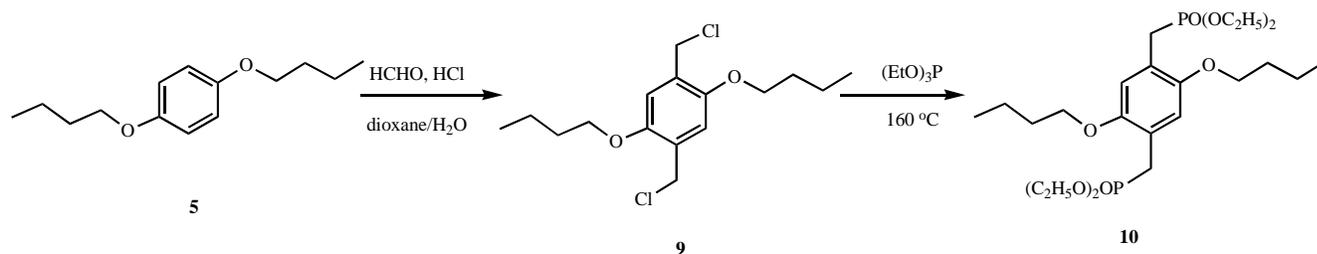**Scheme 2.** Synthesis of 1,4-dibromo-2,5-dibutoxybenzene **6**.
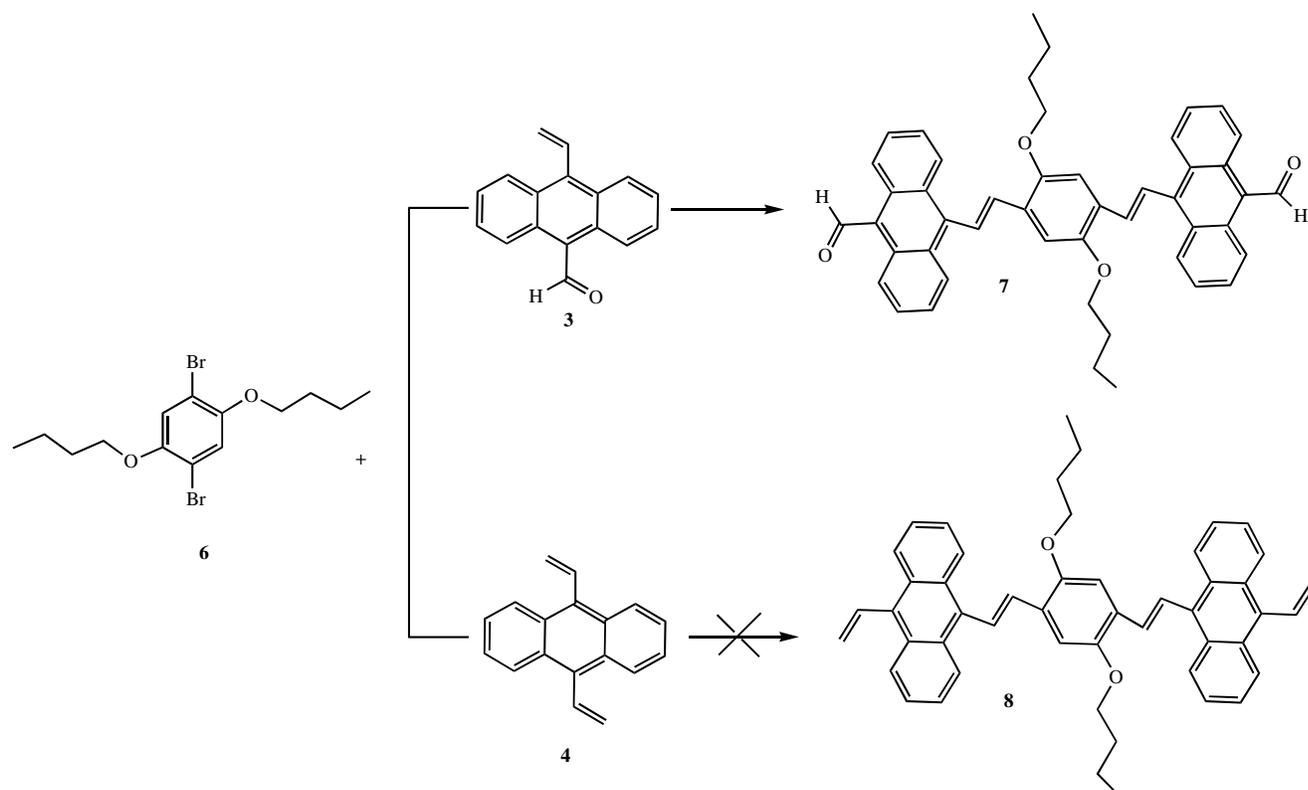
Scheme 3. Synthesis of the dihaldehydes **7** and **8**.

vinylanthracene-9-carbaldehyde **3** and 9,10-divinylanthracene **4**. For this Pd(OAc)$_2$ was used as catalyst in presence of tri-*o*-tolylphosphine (TOP) in DMF-Et$_3$N (1:1) at 110 °C (Scheme **3**). Under these conditions, the bridge compound **7** was obtained in low yield (5 %), and compound **8** was not observed. This could be due to the fact that the central step in the mechanism of the Heck reaction is the *syn*-addition of the palladium-organic species to the double bond. In the case of 9, 10- divinylanthracene **4**, due to its stereochemistry, the necessary proximity of the insertion compound cannot be achieved. As a result, no addition to the vinylic double bond was observed.

To avoid the problem, the Horner–Wadsworth–Emmons reaction [9, 10] was used. For this, the 1,4 dibutoxy benzene **5** was converted to the benzyl choride **9**. Then, **9** was converted to **10** *via* a Michaelis-Arbuzov reaction [11-13] in high yield (Scheme **4**).
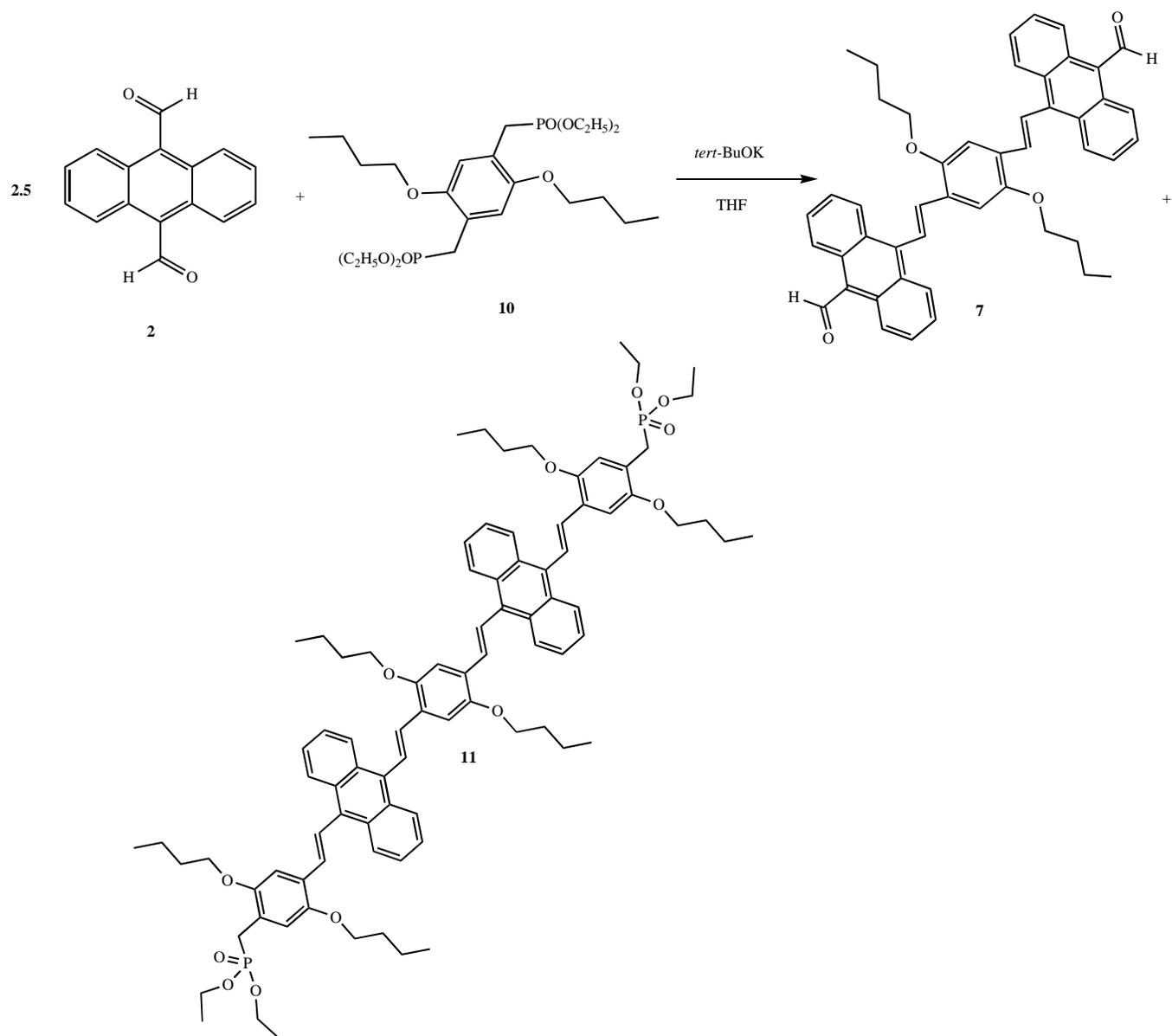
The Horner–Wadsworth–Emmons reaction was carried out between the anthracene-9,10-dicarbaldehyde **2** and **10** using potassium *tert*-butoxide in dry THF for 5 h (Scheme **5**).
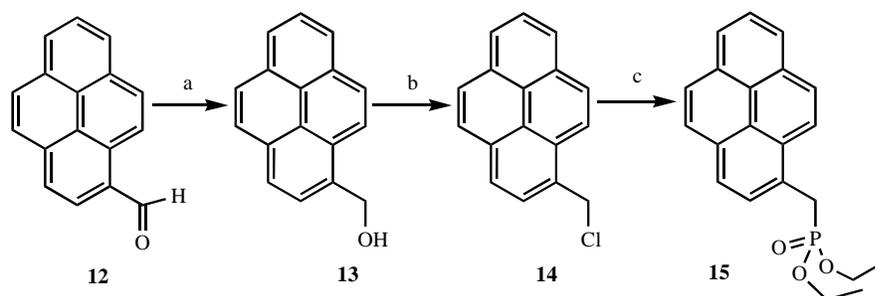
Compounds **7** and **11** were characterized by ^{1}H NMR spectroscopy. In the spectrum of **7** the following signals were observed: one triplet at δ_H 0.96 assigned to the CH$_3$ groups, two multiplets at δ_H 1.44 and at δ_H 1.72 due to the CH$_2$ groups, one triplet at δ_H 4.30 for the CH$_2$-O, two doublets at δ_H 7.54 and at δ_H 7.69 with a coupling constants J=16.8 and J=17.1 Hz for the vinylic protons, the characteristic signals at δ_H 8.06, δ_H 8.98 for the anthracene, and finally one singlet at δ_H 11.54 due to the carbonyl group HC=O. For compound **11,** the most important signal was one doublet due to the ethyl group joined with the phosphonate at δ_H 3.33 with coupling constant J_{H-P}= 21.9 Hz. In the ^{31}P NMR spectrum of compound **11** one singlet was observed at 27.57 ppm.

The donor **15** was synthesized from the commercially available 1-pyrenecarboxaldehyde **12** *via* the reduction of the aldehyde **12** to obtain the pyren-1-ylmethanol **13** and its chloration with SOCl$_2$ and pyridine to obtain the compound **14** (Scheme **6**) and finally, treatment of **14** with triethyl phosphate yielded the compound **15**.


Scheme 4. Synthesis of the tetraethyl (2,5-dibutoxy-1,4-phenylene)bis(methylene) diphosphonate **10**.

Scheme 5. Synthesis of the dialdehydes **7** and **11**.

Scheme 6. Synthesis of the pyrene derivatives a) LiAlH$_4$, THF, 0°C, N$_2$; b) SOCl$_2$, Py, CH$_2$Cl$_2$; c) P(OC$_2$H$_5$)$_3$, *tert*-BuOK, THF.

The following signals were observed in the ^{1}H NMR spectrum of compound **13**: one singlet at δ_H 1.95 for the OH proton, one singlet at δ_H 5.31 due to the CH$_2$ group and for the pyrene group (multiplets at δ_H 7.93- 8.29). The formation of the 1-(chloromethyl)pyrene **14** and the diethyl pyren-1-ylmethylphosphonate **15** was confirmed by X-ray diffraction studies as shown in Figs. (**3** and **4**).

To obtain the donor-bridge system of first and second generation, we used the same methodology reported above between the dialdehyde **3**, or **11** and the diethyl pyren-1-ylmethylphosphonate **15** (Scheme **7**).

In the ^{1}H NMR spectrum of the first generation aldehyde **16** two doublets were observed at δ_H 7.57 and at δ_H 7.72 due
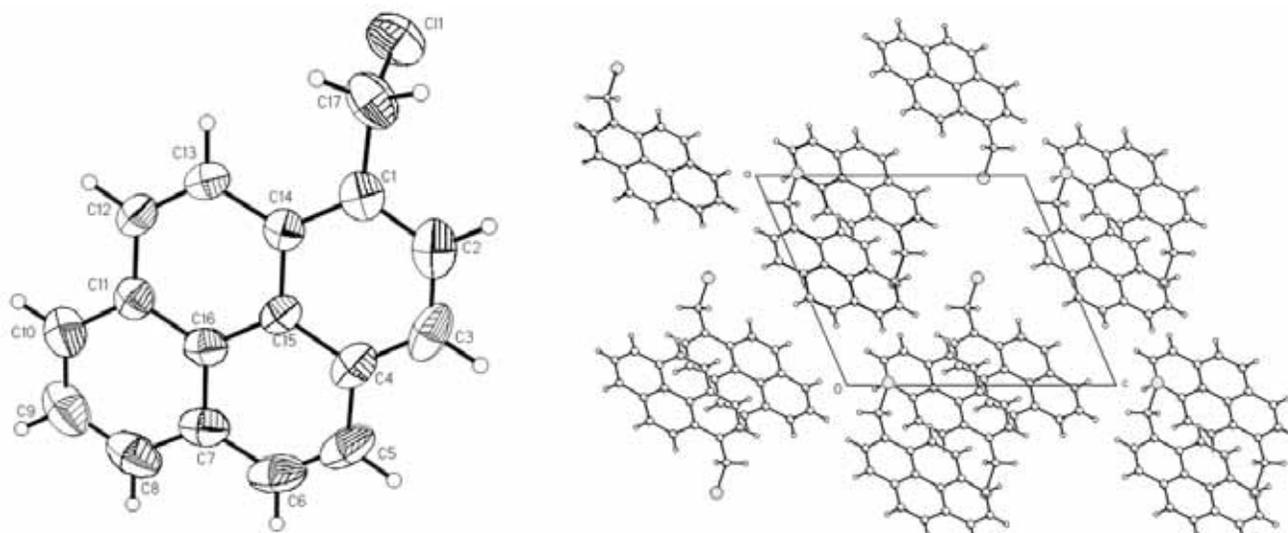
Fig. (3). Crystal structure and crystal packing of the 1-(chloromethyl)pyrene **14**. Selected bond lengths [Å]: Cl(1)-C(17)=1.801, C(1)-C(17)=1.491. Selected angles (°): C(2)-C(1)-C(17)=118.5, C(14)-C(1)-C(17)=122.1, C(1)-C(17)-Cl(1)=110.88.
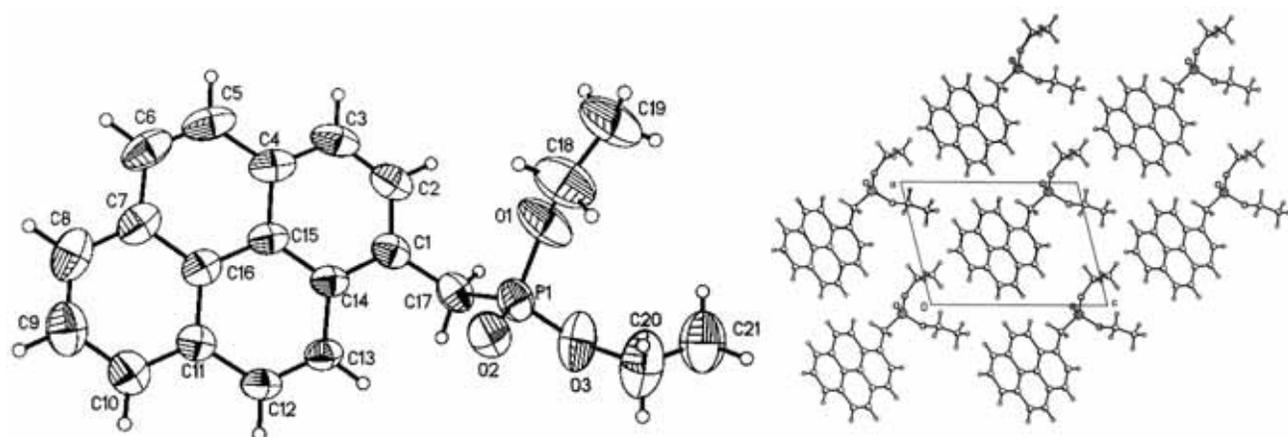
Fig. (4). Crystal structure and crystal packing of diethyl pyren-1-ylmethylphosphonate **15**. Selected bond lengths [Å]: Cl(1)-C(17)=1.801, C(1)-C(17)=1.491. Selected angles (°): O(2)-P(1)-O(1)=115.16, O(2)-P(1)-O(3)=114.04, O(1)-P(1)-O(3)=104.98, O(2)-P(1)-C(17)=117.05, O(1)-P(1)-O(17)=103.20, C(1)-C(17)-P(1)=113.34, C(14)-C(1)-C(17)=122.0.

to the vinylic protons with coupling constants J= 15.0 and J = 14.7 Hz, respectively. Also the characteristic signals due to the pyrene moiety were observed at δ_H 7.58 to 8.05, and finally one singlet at δ_H 11.58 assigned to the aldehyde proton.

The ^{1}H NMR spectrum of compound **17** showed one triplet at δ_H 0.95 due to the methyl groups, two doublets at δ_H 1.53 and 1.83 assigned to the CH$_2$ groups of the aliphatic chain, one triplet at δ_H 4.17 due to the CH$_2$-O groups, six doublets at δ_H 7.25-8.44 due to the vinylic protons, with coupling constants J= 16.2 Hz, multiplets due to the anthracene and pyrene groups, and one singlet at δ_H 11.55 assigned to the proton of the aldehyde group. The structures of the aldehydes **16** and **17** were confirmed by FAB+ mass spectrometry.

Compound **11**, pyrene carboxaldehyde **12** and the anthracene dialdehyde **2** were used to obtain pyrene derivative **19** using the same Horner–Wadsworth–Emmons reaction upon the conditions described above (Scheme **8**).

In the ^{1}H NMR spectrum of the compound **18** one doublet was observed at δ 3.33 with a coupling constant of J =

21.9 Hz, due to the methylene group joined to the phosphonate fragment (CH$_2$-P). In addition, signals assigned to the anthracenyl group were observed: one singlet at δ 8.86, one doublet at δ 8.41 with a coupling constant J = 6.9 Hz double of doublets at δ 8.1 with coupling constants J = 6.4 Hz, and finally one multiplet at δ 7.4. In the ^{13}C NMR spectrum of compound **19** characteristic signals for the anthracene and the pyrene moietys were observed at δ 111.3-134.8.

Fig. (**5**) shows the UV-Vis spectra of CH$_2$Cl$_2$ solutions of the dialdehydes **2**, **7** (Fig. **5a**) and the corresponding pyrene containing systems **16**, **17** and **19** (Fig. **5b**). The absorption spectra of dialdehydes **2**, **7** showed two main peaks at 232-237 and 264-270 nm and broad band with maximum at 423 nm. The presence of one more anthracene and the styryl group in compounds **16**, **17** and **19** provoked an ipsochromic shift in the firs two t peaks, and the broad signal became bigger and its maximum was shifted to 427 nm. In the case of the pyrene-monoaldehyde **16**, the signals became broader and the most significant change is the appearance of two maxima observed at 334 and at 363 nm, attributed to the pyrene moiety. These maxima were red shifted passing from
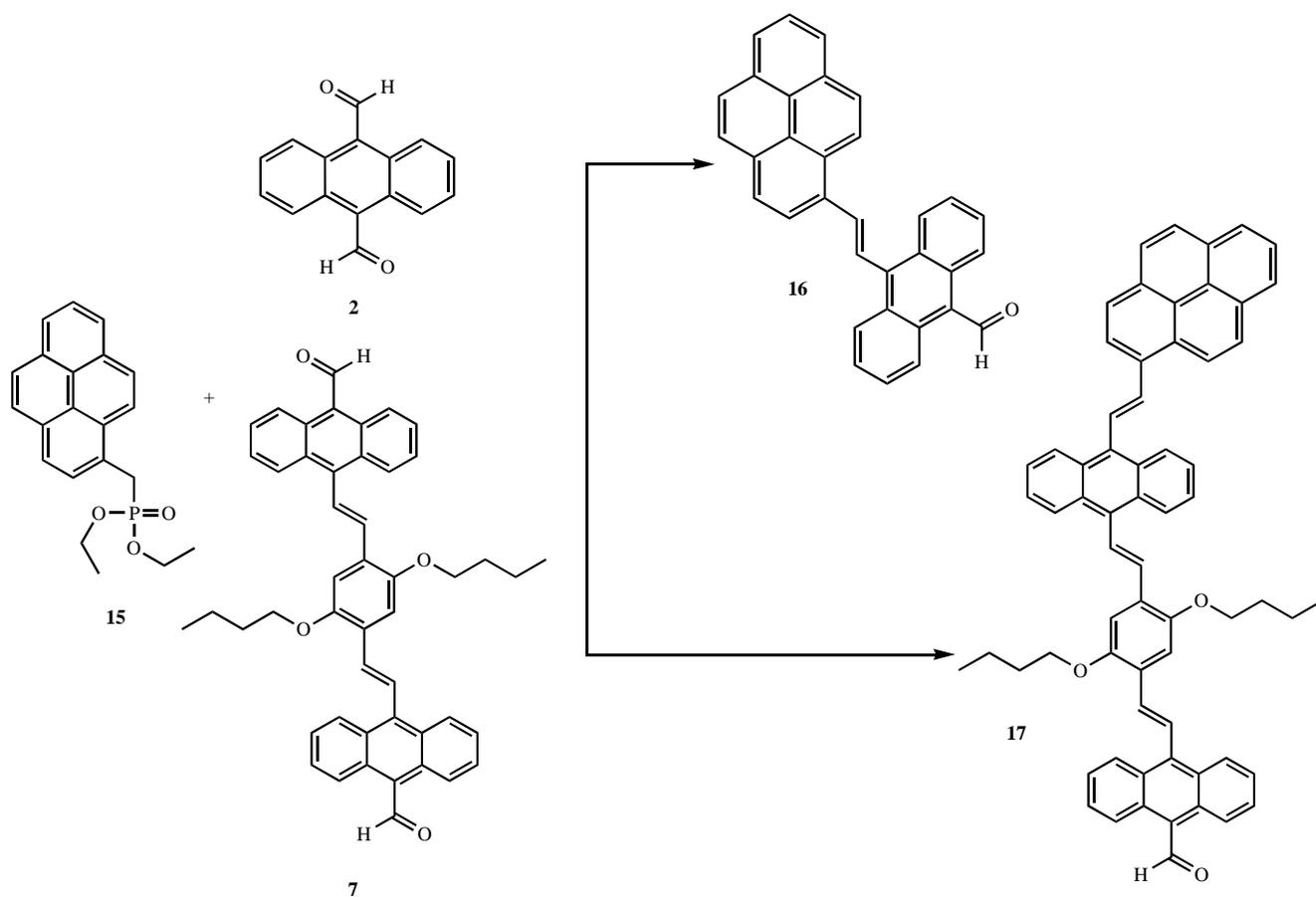
Scheme 7. Synthesis of the rods of first **16** and second **17** generation (*tert*-BuOK in dry THF).
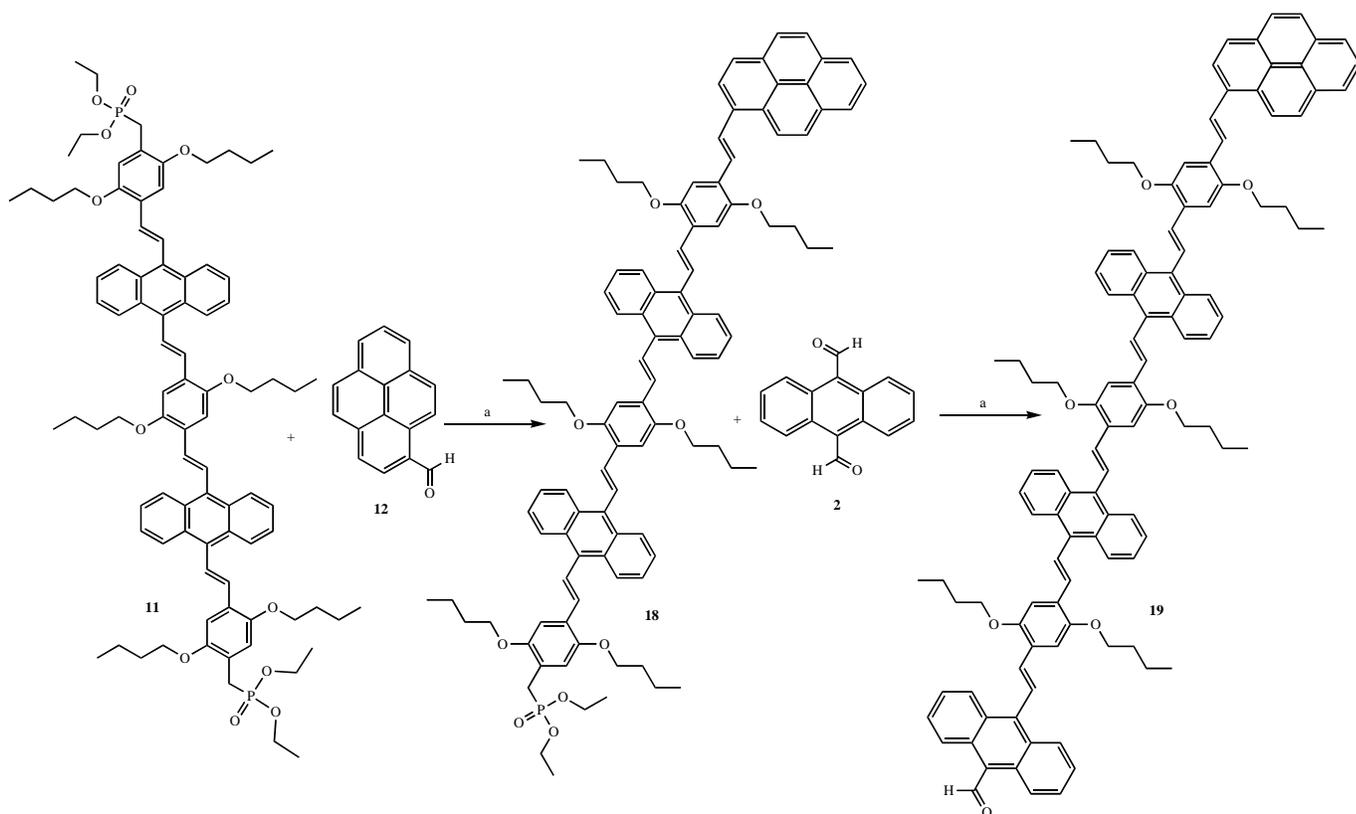
Scheme 8. Synthesis of the molecular antenna of third generation **19** a) *tert*-BuOK, dry THF.
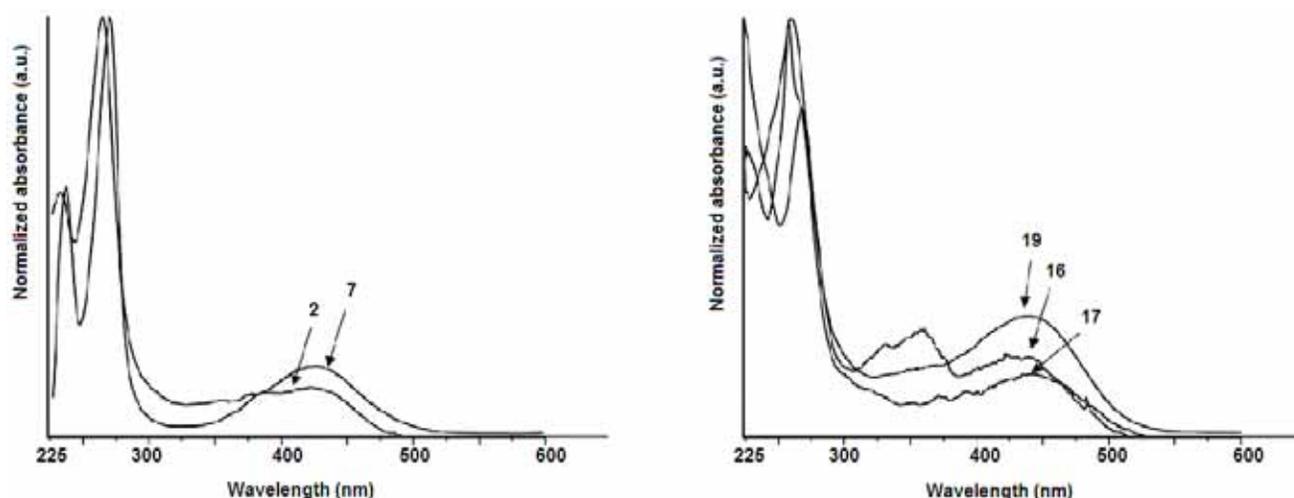
Fig. (5). UV-vis spectra of CH_2Cl_2 solutions of a) dialdehydes **2** and **7**; b) monoaldehydes **16**, **17** and **19**.

Table 1.   UV-vis Data of the Dialdehydes 2, 7 and Monoaldehydes 16, 17 and 19

Compound	λ_{max} (nm)	Band gap, eV
2	237, 270, 423	4.30
7	232, 264, 427	4.13
16	228, 270, 334, 363, 443	4.13
17	230, 261, 273, 374, 394, 445	4.12
19	224, 260, 348, 449	4.11

the first **16** to the second generation **17** which is in agreement with the higher conjugation of the dianthracenyl in comparison with the mono anthracenyl fragment. In the case of compound **17** the band attributed to the anthracene moiety was strongly diminished. Sharpness in the peaks at 400 to 500 nm is observed suggesting a higher molecular order in solution for the greater molecules. The fact that the optical absorption properties of the pyrene-anthracene and pyrene-anthracene-styrene-anthracene fragments are not affected by the nature of the aliphatic chain in the styrene are coincident with those of the corresponding conjugated model molecules suggests that each moiety in the rod acts as an isolated molecule.

CONCLUSIONS

Fully conjugated rods with anthrylene vinylene and phenylene vinylene repeated units were successfully synthesized by Horner–Wadsworth–Emmons reaction utilizing potassium *tert*-butoxide in dry THF. The synthesized rods which have butylene groups as solubility spacers in the main chain exhibited good solubility in polar solvents. The solutions of the synthesized pyrene- containing molecular rods exhibited a blue shift in the UV-vis from the absorption maximum due to presence of the pyrene group compared to the dialdehydes.

EXPERIMENTAL SECTION

Materials and Equipments

Solvents and reagents were purchased as reagent grade and used without further purification. Acetone was distilled

over calcium chloride. Tetrahydrofuran was distilled from sodium and benzophenone. Column chromatography was performed on Merck silica gel 60 Å (70-230 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Unity-300 MHz with tetra-methylsilane (TMS) as an internal reference. Infrared (IR) spectra were measured on a Nicolet FT-SSX spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, INC Knoxville. FAB+ mass spectra were taken on a JEOL JMS AX505 HA instrument. Electrospray mass spectra were taken on a Bruker Daltonic, Esquire 6000.

9,10-Bis(chloromethyl)anthracene (1)

1,4-dixane 40 ml of and hydrochloric acid 5 ml were saturated with hydrogen chloride gas, prepared form sodium chloride and sulfuric acid. Then anthracene 5g (28.08 mmol) was added. The mixture was stirred slowly and heated to 60°C overnight. The fine granular solid was filtered and dissolved in dichloromethane and washed with water. The solvent was removed in vacuum, and the residue was chromatographed on alumina (hexane–diethyl ether, 3:1) to give 9,10-bis(chloromethyl)anthracene (**1**) as a yellow powder, yield 4.8 g, 17.51 mmol (63%), m.p. 280-282 °C (lit [15] m.p. 253-255). FTIR (pellet, KBr, cm^{-1}): 3057, 1952, 1706, 1621, 1525, 1475, 1444, 1245, 1181, 1032, 764, 689, 620, 559. 405, 383, 364, 263, 232. ^{1}H NMR (200 MHz, DMSO-d6), δ(ppm): 5.86 (s, 4H, CH_2-Cl), 7.69 (m, 4H, Ar-H), 8.49 (m, 4H, Ar-H). ^{13}C NMR (DMSO-d6), δ(ppm): 124.7 (Ar), 126.7 (Ar), 129.2 (Ar), 130.6 (Ar), 132.6 (C_{ipso}). EM: m/z: 274 [M]$^+$ Calc. for $C_{16}H_{12}Cl_2$: C, 69.84; H, 4.40 (%). Found: C,69.83; H,4.38.

Anthracene-9,10-dicarbaldehyde (2)

A stirred suspension of 9,10-bis(chloromethyl)anthracene (**1**) 1 g (3.6 mmol) and anhydrous dimethyl sulfoxide 20 ml under nitrogen at room temperature were added slowly to a solution of sodium 0.2 g (8.6 mmol), ethanol 12 ml and 2-nitropropane 1.2 ml (13.6 mmol). The mixture was stirred for 12 h. Cold water was added, and the precipitate was filtered and dried. The product was purified by silica gel chromatography using hexane as an eluent to give 9,10-anthracenedicarboxaldehyde (**2**) as an orange powder, yield 0.7 g, 2.99 mmol (83%), m.p. 243-244 °C. FTIR (pellet, KBr, cm^{-1}): 3080, 2860, 1677, 1444, 1353, 1177, 1022, 889, 744, 562. UV-Vis (CH$_2$Cl$_2$, nm) λ_{max}: 437, 265. ^{1}H NMR (DMSO-d6, 200 MHz), δ(ppm) 7.67 (m, 4H, Ar-H), 8.69 (m, 4H, Ar-H), 11.44 (s, 2H, HC=O). ^{13}C NMR (DMSO-d6), δ(ppm): 124.1 (Ar), 128.3 (Ar), 130.2 (Ar), 131.6 (C$_{ipso}$), 194.2 (HC=O). EM: m/z: 234 [M]$^+$ Calc. for C$_{16}$H$_{10}$O$_2$: C, 82.04; H, 4.30 (%). Found: C, 82.03; H, 4.31 (%).

10-Vinylanthracene-9-carboxaldehyde (3)

9,10- anthracenedicarboxaldehyde (**2**) 2 g (8.53 mmol) was added to the suspension of methyltriphenilphosphonium bromide 3.04 g (8.53 mmol) and *n*-Buthyl lithium 3.28 ml (8.52 mmol) under nitrogen at 0°C in dry THF 40 ml. The solution was stirred overnight. After that, a few drops of water were added and the mixture was concentrated and purified by silica gel chromatography using a mixture of hexane-dichloromethane 90:10 as an eluent to give 10-vinylanthracene-9-carboxaldehyde (3) as orange crystals, yield 1.5 g, 6.48 mmol (76%), m.p. 93-95 °C. FTIR. (pellet, KBr, cm^{-1}): 3056, 2927, 1675, 1437, 1188, 1118, 721, 542. UV-vis (CHCl$_3$, nm) λ_{max}: 403, 382, 265. ^{1}H NMR (300 MHz, CDCl$_3$), δ_H (ppm): 5.48 (dd, 1H, =CH$_2$, J_{trans}= 18 Hz), 5.97 (dd, 1H, =CH$_2$, J_{cis}= 11.7 Hz), 7.25 (q, 1H, =CH, J_{trans}= 18 Hz, J_{cis}= 11.7 Hz), 7.40 (m, 2H, Ar-H), 7.53 (m, 2H, Ar-H), 8.22 (m, 2H, Ar-H), 8.80 (m, 2H, Ar-H), 11.30 (s, 1H, HC=O). ^{13}C NMR (CDCl$_3$), δ(ppm) 122.9 (=CH$_2$), 124.1 (C$_{ipso}$), 125.0 (Ar), 126.2 (Ar), 128.3 (Ar), 128.5 (Ar), 128.8 (C$_{ar}$), 133.1 (C$_{ar}$), 133.3 (C$_{ipso}$), 133.8 (=CH), 193.2 (C=O). EM: m/z: 232 [M]$^+$. Calc. for C$_{17}$H$_{12}$O: C, 87.90; H, 5.21 (%). Found: C, 87.92; H, 5.23 (%).

9, 10-Divinylanthracene (4)

Yield 0.19 g, 0.85 mmol (10%), yellow crystals, m.p 84-86 °C. FTIR. (pellet, KBr, cm^{-1}): 3056, 2927, 1675, 1437, 1188, 1118, 721, 542. UV-vis (CHCl$_3$, nm) λ_{max}: 403, 382, 265. ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm): 5.45 (dd, 1H, =CH$_2$, J_{trans}= 17.8 Hz), 5.98 (dd, 1H, =CH$_2$, J_{cis}= 11.4 Hz), 7.38-7.53 (m, 6H, H-Ar, =CH, J_{trans}= 16.4 Hz, J_{cis}= 10.2 Hz), 8.33 (dd, 4H, H-Ar, J_{cis}= 11.7 Hz). ^{13}C NMR (CDCl$_3$), δ(ppm): 123.0 (=CH$_2$), 125.8 (Ar), 126.3 (Ar), 128.9 (Car), 133.5 (C$_{ipso}$), 133.8 (=CH).). EM: m/z: 230 [M]$^+$. Calc. for C$_{18}$H$_{14}$: C, 93.87; H, 6.13 (%). Found: C, 93.85; H, 6.15 (%).

1,4-Dibutoxybenzene (5)

Ground NaOH (16.0 g, 285 mmol) was added to EtOH (250 mL), and the mixture was stirred for 20 min. Upon addition of hydroquinone (12.1 g, 110 mmol), the solution turned dark brown, it was stirred for another 30 min, and heated to reflux. After 15 min, (S)-2- methylbutyl-*p*-toluenesulfonate (58.64 g, 242 mmol) was added dropwise. The resulting suspension was stirred for another 16 h, cooled

to room temperature, and filtered. The solvent was evaporated, and the residue was purified by silica gel chromatography using hexane as an eluent to afford 1,4-dibutoxybenzene (**5**) as white flakes, yield 9.52 g, 42.8 mmol (94 %) m.p. 45-47 °C (lit. [14] m.p. 44.5-45.2). FTIR. (pellet, KBr, cm^{-1}): 2958, 2935, 1866, 1510, 1471, 1235, 1121, 1042, 828, 760. UV-vis (CHCl$_3$, nm) λ_{max}: 293, 242. ^{1}H NMR (200 MHz, CDCl$_3$), δ(ppm): 0.96 (t, 6H, CH$_3$, J= 6.9 Hz), 1.47 (m, 4H, CH$_2$), 1.73 (m, 4H, CH$_2$), 3.90 (t, 4H, CH$_2$, J= 6.7 Hz), 6.83 (s, 2H, Ar-H). ^{13}C NMR (CDCl$_3$), δ(ppm): 13.8 (CH$_3$), 19.2 (CH$_2$), 31.4 (CH$_2$), 68.3 (CH$_2$-O), 115.3 (Ar), 153.1 (Ar-O). EM: m/z: 222 [M]$^+$. Calc. for C$_{14}$H$_{22}$ O$_2$: C, 75.63; H, 9.97; Found: C, 75.65; H, 9.96 (%).

1,4-Dibromo-2,5-dibutoxybenzene (6)

To a solution of **5** (9.04 g, 20.24 mmol) in carbon tetrachloride (100 mL), were added to 2.6 mL of bromine. The reaction mixture was heated to 60 °C and stirred for 48 h. Then a solution 1N of NaOH was added to the reaction mixture. The organic phase was partially evaporated under vacuum and the residue was precipitated from hexane, to obtain 1,4-dibromo-2,5-dibutoxybenzene (**6**), as a white solid, yield 12.8 g, 33.86 mmol (90 %), m.p. 76-77 °C (lit. [16] m.p. 72 °C) FTIR (pellet, KBr, cm-1): 2959, 2934, 2871, 1506, 1470, 1229, 1032, 824. UV-vis (CHCl$_3$, nm) λ_{max}: 301, 242. ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm): 0.97 (t, 6H, CH$_3$, J= 6.6 Hz), 1.53 (m, 4H, CH$_2$), 1.78 (m, 4H, CH$_2$), 3.98 (t, 4H, CH$_2$, J= 6.4 Hz), 4.63 (s, 4H, CH$_2$-Cl), 6.91 (s, 2H, Ar-H). ^{13}C NMR (CDCl$_3$), δ (ppm): 13.8 (CH$_3$), 19.2 (CH$_2$), 31.4 (CH$_2$), 41.6 (CH$_2$-Cl), 68.2 (CH$_2$-O), 115.2 (Ar), 150.8 (Ar-O), 153.0 (Ar-O). EM: m/z: 318 [M]$^+$. Calc. for C$_{14}$H$_{20}$O$_2$ Br$_2$: C, 60.19; H, 7.58; Found C, 60.18; H, 7.57 (%).

1,4-Dibutoxy-2,5-bis(chloromethyl)benzene (9)

A solution of **5** (10.04 g, 40.1 mmol) in 1,4-dioxane (60 mL) was cooled to 0 °C, and aqueous HCl (35 mL) 37% was added. HCl gas was bubbled through the solution while 36% aqueous formaldehyde (20 mL) was added dropwise, the mixture was stirred at room temperature for 1.5 h and then it was heated to 60 °C and stirred for 16 h. The mixture was partially evaporated and methanol (150 mL) was added, the suspension was filtered. The solid was recrystallized from hexane to afford 1,4-dibutoxy-2,5-dichloromethylbencene (**9**) as a white powder, yield 12.8 g, 40.23 mmol (90.1 %), m.p 86-87°C. FTIR. (pellet, KBr, cm^{-1}): 2959, 2934, 2871, 1506, 1470, 1229, 1032, 824. UV-vis (CHCl$_3$, nm) λ_{max}: 301, 242. ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm): 0.97 (t, 6H, CH$_3$, J= 6.7 Hz), 1.53 (m, 4H, CH$_2$), 1.78 (m, 4H, CH$_2$), 3.98 (t, 4H, CH$_2$, J= 6.4 Hz), 4.63 (s, 4H, CH$_2$-Cl), 6.91 (s, 2H, Ar-H). ^{13}C NMR (CDCl$_3$), δ (ppm): 13.8 (CH$_3$), 19.2 (CH$_2$), 31.4 (CH$_2$), 41.6 (CH$_2$-Cl), 68.2 (CH$_2$-O), 115.2 (Ar), 150.8 (Ar-O), 153.0 (Ar-O). EM: m/z: 318 [M]$^+$. Calc. for C$_{16}$H$_{24}$ O$_2$Cl$_2$: C, 60.19; H, 7.58; Cl, 22.21 (%); Found: C, 60.18; H, 7.56 (%).

Tetraethyl (2,5-dibutoxy-1,4-phenylene)bis(methylene)diphosphonate (10)

Triethyl phosphite (8.1 ml, 47.23 mmol) and **9** (6.7 g, 20.98 mmol) were stirred at 160 °C for 4 h. The reaction mixture was cooled at room temperature and purified by silica gel chromatography using ethyl acetate as an eluent to afford 2,5-bis(buthyloxy)-1,4-bis(benzyl)phosphonate (**10**)

as a yellow pale oil, yield 0.3 g, 19.20 mmol (94.4%), FTIR. (pellet, KBr, cm-1): 2960, 2934, 2872, 1507, 1217, 1030, 965, 754. UV-vis (CHCl$_3$, nm) λmax: 296, 241. 1H NMR (200 MHz, CDCl$_3$), δ (ppm): 0.95 (m, 6H, CH$_3$), 1.24 (m, 12H, CH$_3$), 1.48 (m, 4H, CH$_2$), 1.73 (m, 4H, CH$_2$), 3.19 (s, 2H, CH$_2$-P), 3.26 (s, 2H, CH$_2$-P), 3.88 (m, 4H, CH$_2$-O), 4.01 (m, 8H, CH$_2$-O), 6.79 (s, 2H, Ar-H). 13C NMR (CDCl$_3$), δ (ppm): 13.5 (CH3), 16.0 (CH$_3$), 18.9 (CH$_2$), 25.4 (CH$_2$), 27.3 (CH$_2$), 31.2 (CH$_2$), 61.5 (CH$_2$-O), 67.9 (CH$_2$-O), 68.4 (CH$_2$-O), 115.1 (Ar), 121.0 (C$_{ipso}$), 150.2 (Ar-O), 153.0 (Ar-O). EM: m/z: 522 [M]+. Calc. for C$_{24}$H$_{44}$O$_8$P$_2$: C, 55.16; H, 8.49; P: 11.85 (%). Found: C, 55.14; H, 8.50 (%);

10,10'-(1E,1'E)-2,2'-(2,5-Dibutoxy-1,4-phenylene)bis(ethene-2,1-diyl)dianthracene-9-carboxaldehyde (11)

A solution of **10** (0.89 g, 1.7 mmol) and *tert*-BuOK (0.47 g, 4.18 mmol) in dry THF (5 mL), under nitrogen was added dropwise to aldehyde **2** (1 g, 4.26 mmol) dissolved in dry THF (10 mL). The reaction mixture was stirred for 5 h. The solution was poured on crushed ice, and 6 M HCl (6 mL) was added. The aqueous phase was extracted, and the organic layer was subsequently washed with an aqueous solution of 3 M HCl. The organic layer was dried over Na$_2$SO$_4$; the solvent was removed in vacuum, and the residue was purified by aluminum oxide chromatography using hexane/CH$_2$Cl$_2$ 2:1 as an eluent to afford 10,10'-(1E,1'E)-2,2'-(2,5-dibutoxy-1,4-phenylene)bis(ethene-2,1-diyl)dianthracene-9-carboxaldehyde (**11**) as an orange solid, yield 0.874 g, 1.28 mmol (30%), t, desc. 165 ^{o}C. FTIR. (pellet, KBr, cm^{-1}): 2959, 2932, 1724, 1674, 1450, 1285, 1123, 1073, 736. UV-vis (CHCl$_3$, nm) λ$_{max}$: 401, 373, 266, 241. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 0.93 (t, 6H, CH$_3$, *J*= 6.9 Hz), 1.55 (m, 4H, CH$_2$), 1.82 (m, 4H, CH$_2$), 4.16 (t, 4H, CH$_2$-O, *J*=6.6 Hz), 7.54 (m, 8H, =CH, Ar-H, *J*$_{trans}$=16.8 Hz), 7.69 (m, 6H, =CH, Ar-H, *J*$_{trans}$=17.1 Hz), 8.06 (dd, 4H, Ar-H, *J*=8.2, 8.0 Hz), 8.98 (dd, 4H, Ar-H, *J*=8.0 Hz), 11.54 (s, 2H, HC=O). ^{13}C NMR (CDCl$_3$), δ (ppm): 13.6 (CH$_3$), 19.1 (CH$_2$), 30.5 (CH$_2$), 65.5 (CH$_2$-O), 123.5 (=CH), 125.6 (=CH), 126.8 (C$_{ipso}$), 127.4 (C$_{ipso}$), 128.5 (Ar), 128.8 (C$_{Ar}$), 129.1 (C$_{Ar}$), 129.2 (Ar), 130.8 (=C), 192.9 (HC=O). FAB$^+$ Ms; (m/z): 682 [M]$^+$. Calc. for C$_{48}$H$_{42}$O$_4$: C, 84.43; H, 6.20 (%). Found: C, 84.43; H, 6.22 (%).

Tetraethyl (4,4'-(1E,1'E)-2,2'-(10,10'-(1E,1'E)-2,2'-(2,5-dibutoxy-1,4-phenylene)bis(ethene-2,1-diyl)bis (anthracene-10,9-diyl)) bis(ethene-2,1-diyl) bis(2,5-dibutoxy-4,1-phenylene))bis(methylene)diphosphonate (12) as a yellow solid, yield 0.57 g, 0.4 mmol (24 %), t, desc. 230oC. FTIR. (pellet, KBr, cm-1): 3043, 2956, 2931, 2868, 1499, 1384, 1203, 1029, 755. UV-vis (CHCl$_3$, nm) λ max: 447, 344, 265. 1H NMR (300 MHz, CDCl$_3$), δ(ppm): 0.94 (t, 9H, CH$_3$, J= 6.6 Hz), 1.02 (t, 9H, CH$_3$, J= 6.9 Hz), 1.32 (t, 12H, CH$_3$, J= 6.5 Hz), 1.52 (m, 12H, CH$_2$), 1.82 (m, 12H, CH$_2$), 3.33 (d, 4H, CH$_2$-P, J$_{H-P}$= 21.9 Hz), 4.09 (m, 20H, CH$_2$-O), 7.05 (s, 2H, H-Ar), 7.24 (d, 2H, =CH, J$_{trans}$= 16.8 Hz), 7.24 (s, 2H, H-Ar), 7.29 (s, 2H, H-Ar), 7.33 (d, 2H, =CH, J$_{trans}$= 16.5 Hz), 7.45 (d, 2H, =CH, J$_{trans}$= 16.2 Hz), 7.49 (m, 8H, H-Ar$_{ant}$, J= 6.2 Hz), 7.96 (d, 1H, =CH, J$_{trans}$= 16.5 Hz), 8.04 (d, 1H, =CH, J$_{trans}$= 16.8 Hz), 8.49 (m, 8H, H-Ar$_{ant}$, J= 8.4 Hz). 13C NMR (CDCl$_3$), δ(ppm): 13.85 (CH$_3$), 16.4 (CH$_3$), 19.4 (CH$_2$), 31.5 (P-CH$_2$), 31.6 (CH$_2$), 68.9 (O-CH$_2$), 69.2 (O-CH$_2$), 110.6 (HC$_{ar}$), 111.3 (HC$_{ar}$), 115.7 (HC$_{ar}$), 121.1 (C$_{ar}$), 121.3 (C$_{ar}$), 125.1 (HC$_{ar}$), 125.5 (=CH), 125.9 (=CH), 126.6

(HC$_{ant}$), 127.1 (C$_{ipso}$), 129.6 (C$_{ant}$), 132.8 (C$_{ipso}$), 132.9 (C$_{ipso}$), 133.1 (C$_{ipso}$), 133.3 (C$_{ipso}$), 150.7 (O-C), 151.3 (O-C). FAB+ Ms (m/z): 1418 [M]+ . Calc. for C$_{88}$H$_{108}$O$_{12}$P$_2$: C, 74.45; H, 7.67 (%). Found: C, 74.43; H, 7.69 (%).

1-Pyrene-methanol (13)

A solution of 1-pyrenecarboxaldehyde **13** (5 g, 21.7 mmol) in 50 mL of dry THF was added dropwise to a lithium aluminum hydride (0.82 g, 10.8 mmol) in 50 mL of dry THF. The reaction was carried out at 0 ^{o}C for 4 h. After this time, 10 mL of water were added and the reaction mixture was filtered in Celite®. The solvent was evaporated and the residue was dissolved in dichloromethane. The resulting solution was dried over sodium sulfate, filtered and the product was purified by silica gel chromatography using hexane as an eluent to afford 1-pyrene-methanol (**15**) as a yellow powder, yield 4.9 g, 21.11 mmol (97 %), m.p. 123-125 °C. FTIR. (pellet, KBr, cm^{-1}): 3279, 1590, 1181, 1064, 1008, 841, 706. UV-vis (CHCl$_3$, nm) λ$_{max}$: 344, 328, 315, 278, 267, 257, 244. ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm): 1.95 (s, 1H, OH), 5.31 (s, 2H, CH$_2$), 7.93-8.29 (m, 9H, H$_{pyr}$). ^{13}C NMR (CDCl$_3$), δ (ppm): 63.7 (CH$_2$), 122.9 (Ar), 124.6 (Ar), 124.8 (C$_{ar}$), 125.2 (Ar), 125.9 (Ar), 127.3 (Ar), 127.8 (Ar), 128.6 (C$_{ar}$), 130.7 (C$_{ar}$), 131.1 (C$_{ar}$), 133.6 (C$_{ipso}$). EM: m/z: 232 [M]$^+$. Calc. for C$_{17}$H$_{12}$O: C, 87.90; H, 5.21 (%); Found: C, 87.91; H, 5.20 (%).

1-Chlromethyl-pyrene (14)

A solution of pyridine (1 mL, 14.0 mmol) and SOCl$_2$ (1.45 mL, 14.0 mmol) in 100 mL of dry CH$_2$Cl$_2$ was added to **13** (4.1 g, 17.7 mmol), and then this mixture was cooled to -10° C. The reaction was carried out in nitrogen atmosphere for 7 h. After this, the solvent was evaporated and the resulting oil was dried and purified by silica gel chromatography using a mixture of hexane-dichloromethane 2:1 as an eluent to afford 1-chloromethil pyrene (**16**) as a brownish powder, yield 4.3 g, 17.19 mmol (99%), m.p. 148-149 °C. FTIR. (pellet, KBr, cm^{-1}): 3042, 1591, 1254, 842, 688. UV-vis (CHCl$_3$, nm) λ$_{max}$: 378, 349, 333, 280, 269, 245. ^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm): 5.31 (s, 2H, CH$_2$), 7.97-8.38 (m, 9H, H$_{pyr}$). ^{13}C NMR (CDCl$_3$), δ (ppm): 44.7 (CH$_2$), 122.7 (Ar), 124.5 (Ar), 124.7 (C$_{ar}$), 125.0 (C$_{ar}$), 125.6 (Ar), 126.1 (Ar), 127.2 (Ar), 127.6 (Ar), 127.9 (Ar), 128.3 (Ar), 129.11 (C$_{ar}$), 130.2 (C$_{ar}$), 130.6 (C$_{ar}$), 131.9 (C$_{ipso}$). EM: m/z: 250 [M]$^+$. Calc. for C$_{17}$H$_{11}$Cl: C, 81.44; H, 4.42; Cl, 14.14 (%); found: C, 81.44; H, 4.42(%).

1-Pyrenephosphonate (15)

Triethyl phosphite (4 ml, 24.07 mmol) and **16** (5.0 g, 19.94 mmol) were stirred at 140 °C for 5 h. The reaction mixture was cooled at room temperature and purified by silica gel chromatography using ethyl acetate as an eluent to afford 1-pyrenephosphonate (**17**) as yellow pale oil, yield 10.3 g, 19.9 mmol (98 %). FTIR. (pellet, KBr, cm^{-1}): 3042, 2982, 2906, 1243, 1058, 1024, 960, 790, 616. UV-vis (CHCl$_3$, nm) λ$_{max}$: 376, 345, 329, 314, 278, 267, 257, 244. ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm): 1.15 (t, 6H, CH$_3$, *J*= 6.7 Hz), 3.91 (m, 6H, H$_2$C-P, H$_2$C-O), 7.96-8.35 (m, 9H, H$_{pyr}$). ^{13}C NMR (CDCl$_3$), δ (ppm): 16.4 (CH$_3$), 30.1 and 32.8 (H$_2$C-P), 62.2 (H$_2$C-O), 123.7 (Ar), 124.7 (C$_{ar}$), 124.8 (Ar), 124.9 (Ar), 125.1 (Ar), 125.6 (C$_{ar}$), 125.9 (Ar), 127.1 (Ar), 127.3 (Ar), 127.5 (Ar), 128.7 (C$_{ar}$), 129.2 (C$_{ar}$), 129.4 (C$_{ar}$),

130.5 (C_{ar}), 131.2 (C_{ipso}). EM: m/z: 352 $[M]^+$. Calc. for $C_{21}H_{21}O_3P$: C, 71.58; H, 6.01; P, 8.79 (%); found: C, 71.56; H, 6.01; P, 8.77 (%).

(E)-10-(2-(Pyren-1-yl)vinyl)anthracene-9-carbaldehyde (16)

A solution of 9,10-anthracenedicarboxaldehyde **2** (3.0 g, 8.54 mmol), 1-pryrenephosphonate **15** (2 g, 8.54 mmol) in 100 ml of dry THF was stirred under nitrogen at room temperature, and *tert*-BuOK (1.04 g, 8.54 mmol) was added. The solution was stirred for 10 h, then water (2 ml) was added. The solvent was evaporated under vacuum and the residue was purified by silica gel chromatography using a mixture of 60:40 hexane-dichloromethane as an eluent to afford (*E*)-10-(2-(pyren-1-yl)vinyl)anthracene-9-carbaldehyde (**16**) as an orange powder, yield 2.31g, 5.34 mmol (63%), m.p. >300 ^{o}C. FTIR. (pellet, KBr, cm^{-1}): 3040, 1671, 1519, 1409, 1257, 1109, 843, 754, 618. UV-vis (CHCl₃, nm) λ_max: 435, 361, 270, 241. ^{1}H NMR (200 MHz, CDCl₃), δ (ppm): 7.57 (d, 1H, =CH, J_{trans}= 15 Hz), 7.58 (s, 1H, H_{pyr}), 7.72 (d, 1H, =CH, J_{trans}= 14.7 Hz), 7.72 (s, 1H, H_{pyr}), 8.05 (dd, 2H, H_{ant}, J= 7.5, 10.2 Hz), 8.13 (s, 2H, H_{pyr}), 8.20 (dd, 2H, H_{ant}, J= 7.8, 11.1 Hz), 8.31 (d, 2H, H_{pyr}, J= 8.1 Hz), 8.37 (d, 2H, H_{pyr}, J= 9.3 Hz), 8.61 (d, 2H, H_{ant}, J= 8.7 Hz), 8.63 (d, 1H, H_{pyr}, J= 7.8 Hz), 8.05 (d, 2H, H_{ant}, J= 9.0 Hz), 11.58 (s, 1H, HC=O). ^{13}C NMR (CDCl₃), δ (ppm): 122.8 (Ar), 1123.8 (Ar), 123.9 (Ar), 125.2 (Ar), 125.3 (=CH), 125.6 (Ar), 125.8 (Ar), 126.2 (Ar), 127.1 (Ar), 127.4 (Ar), 127.8 (Ar), 128.2 (Ar), 128.7 (Ar), 128.2 (Ar), 129.6 (C_{ar}), 131.2 (C_{ar}), 131.6 (C_{ipso}), 131.9 (C_{ipso}), 193.1 (HC=O). EM: m/z: 432 $[M]^+$. Calc. for $C_{33}H_{20}$: C, 91.64; H, 4.66 (%); Found; C, 91.64; H, 4.66 (%).

10-((E)-2,5-Dibutoxy-4-((E)-2-(10-((E)-2-(pyren-1-yl)vinyl) anthracen-9-yl)vinyl)styryl)anthracene-9-carbaldehyde (17)

A solution of **11** (0.63 g, 0.92 mmol) and 1-pryrenephosphonate **15** (2 g, 8.54 mmol) of in 20 ml of dry THF was stirred under nitrogen at room temperature, and *tert*-BuOK 0.113g (0.92 mmol) was added. The reaction was stirred and heated at 60 °C overnight, and then water (2 ml) was added, the solvent was evaporated under vacuum and the residue was purified by silica gel chromatography using a mixture of 60:40 hexane-dichloromethane as an eluent to afford 10-((*E*)-2,5-dibutoxy-4-((*E*)-2-(10-((*E*)-2-(pyren-1-yl)vinyl)anthracen-9-yl)vinyl)styryl)anthracene-9-carbaldehyde (**17**) as a orange powder, yield 0.45 g, 0.51 mmol (56 %), m.p. >300 ^{o}C. FTIR. (pellet, KBr, cm^{-1}): 3052, 2960, 2868, 1672, 1441, 1265, 1180, 1034, 752. UV-vis (CHCl₃, nm) λ_max: 437, 254. ^{1}H NMR (300 MHz, CDCl₃), δ (ppm): 0.95 (t, 6H, CH₃, J= 6.7 Hz), 1.53 (m, 4H, CH₂), 1.83 (m, 4H, CH₂), 4.17 (t, 4H, CH₂-O, J= 6.6 Hz), 7.35 (d,1H, =CH, J_{trans}= 16.2 Hz), 7.42 (s, 2H, Ar-H), 7.52 (d,1H, =CH, J_{trans}= 16.2 Hz), 7.53 (d,1H, =CH, J_{trans}= 16.2 Hz), 7.53 (s, 1H, H$_{p-yr}$), 7.55 (d,1H, =CH, J_{trans}= 16.2 Hz), 7.61-7.74 (m, 2H, H_{ant}), 7.75 (s, 2H, H_{pyr}), 7.96 (d,1H, =CH, J_{trans}= 16.2 Hz), 7.96 (m, 4H, H_{ant}), 8.05 (m, 4H, H_{ant}), 8.08 (d,1H, =CH, J_{trans}= 16.2 Hz), 8.06-811 (m, 2H, H_{ant}), 8.10 (s, 2H, H_{pyr}), 8.44 (d, 2H, H_{pyr}, J= 7.7 Hz), 8.43-8.58 (m, 2H, H_{ant},), 9.03 (d, 2H, H_{ant}, J= 9.0 Hz), 11.55 (s, 1H, HC=O). ^{13}C NMR (CDCl₃), δ (ppm): 13.8 (CH₃), 19.4 (CH₂), 31.5 (CH₂), 69.2 (CH₂-O), 111.2 (Ar), 123.8 (Ar), 125.1 (Ar), 125.3 (=CH), 125.5 (Ar), 126.2 (Ar), 126.3 (C_{ipso}), 126.6 (=CH), 127.1 (=CH), 128.7 (Ar), 129.6 (=CH), 131.5 (C_{ar}), 131.9 (C_{ar}),

132.8 (C_{ipso}), 133.3 (C_{ipso}), 151.3 (Ar-O). EM: m/z: 880 $[M]^+$. Calc. for $C_{65}H_{52}O_3$: C, 88.60; H, 5.95 (%); Found; C, 88.60; H, 5.95.

Diethyl 2,5-dibutoxy-4-((E)-2-(10-((E)-2,5-dibutoxy-4-((E)-2-(10-((E)-2,5-dibutoxy-4-((E)-2-(pyren-1-yl)vinyl)styryl) anthracen-9-yl)vinyl)styryl)anthracen-9-yl)vinyl)benzylphosphonate (18)

A solution of **17** (0.57 g, 0.40 mmol), and 1-pyrene carboxaldehyde **13** (0.11 g, 0.32 mmol) in 100 ml of dry THF was stirred under nitrogen and cooled at room temperature, and *tert*- BuOK (0.11 g, 0.98 mmol) was added. The solution was stirred for 10 h, and then water (2 ml) was added, the solvent was evaporated under vacuum and the residue was purified by silica gel chromatography using a mixture of 60:40 hexane-dichloromethane as an eluent to afford diethyl 2,5-dibutoxy-4-((*E*)-2-(10-((*E*)-2,5-dibutoxy-4-((*E*)-2-(10-((*E*)-2,5-dibutoxy-4-((*E*)-2-(pyren-1-yl)vinyl) styryl)anthracen-9-yl)vinyl)styryl)anthracen-9-yl)vinyl)benzylphosphonate (**18**) as an orange powder, yield 0.52 g, 0.34 mmol (86%), m.p. >300 ^{o}C . FTIR. (pellet, KBr, cm^{-1}): 3043, 2958, 2925, 2866, 1726, 1497, 1382, 1202, 1029, 756. UV-vis (CHCl₃, nm) λ_max: 677, 440, 264. ^{1}H NMR (300 MHz, CDCl₃), δ(ppm): 0.96 (m, 18H, CH₃), 1.32 (t, 6H, CH₃, J= 6.5 Hz), 1.56 (m, 12H, CH₂), 1.85 (m, 12H, CH₂), 3.33 (d, 2H, CH₂-P, J_{H-P}= 21.9 Hz), 4.13 (m, 16H, CH₂-O), 7.05 (s, 1H, H-Ar), 7.05 (s, 1H, H-Ar), 7.25 (d, 1H, =CH, J_{trans}= 17.1 Hz), 7.29 (s, 1H, H-Ar), 7.31 (s, 1H, H-Ar), 7.36 (d, 1H, =CH, J_{trans}= 16.5 Hz), 7.37 (br, 2H, H-Ar, H_{Py}), 7.43 (s, 1H, H-Ar), 7.47 (d, 1H, =CH, J_{trans}= 16.8 Hz), 7.52 (m, 10H, H_{Py}, H_{Ant}), 7.75 (d, 1H, =CH, J_{trans}= 15.9 Hz), 7.96 (d, 1H, =CH, J_{trans}= 17.1 Hz), 8.06 (m, 3H, H_{Py}), 8.06 (d, 1H, =CH, J_{trans}= 16.8 Hz), 8.17 (d, 1H, =CH, J_{trans}= 16.2 Hz), 8.17 (m, 3H, H_{Py}), 8.34 (d, 1H, =CH, J_{trans}= 16.2 Hz), 8.44 (d, 1H, =CH, J_{trans}= 15.9 Hz), 8.54 (m, 8H, H_{Ant}), 8.55 (d, 1H, =CH, J_{trans}= 16.8 Hz). ^{13}C NMR (CDCl₃), δ(ppm): 13.8 (CH₃), 16.4 (CH₃), 19.4 (CH₂), 31.6 (P-CH₂), 61.9 (O-CH₂), 69.2 (O-CH₂), 123.7 (HC$_{ar}$), 125.1 (HC$_{ar}$), 125.9 (=CH), 126.3 (=CH), 126.6 (HC$_{Py}$), 127.1 (HC$_{ant}$), 127.5 (HC$_{ant}$), 128.4 (C_{ipso}), 129.6 (C_{ant}), 130.7 (C_{ipso}), 133.0 (C_{ipso}), 131.6 (C_{ipso}), 132.8 (HC$_{py}$), 133.3 (C_{py}), 135.1 (C_{py}), 150.3 (O-C), 151.4 (O-C). EM: m/z: 1495 $[M]^+$. Calc. for $C_{101}H_{107}O_9P$: C, 81.09; H, 7.21 (%); Found; C, 81.10; H, 4.66 (%).

10-((E)-2,5-Dibutoxy-4-((E)-2-(10-((E)-2,5-dibutoxy-4-((E)-2-(10-((E)-2,5-dibutoxy-4-((E)-2-(pyren-1-yl)vinyl)styryl) anthracen-9-yl)vinyl)styryl)anthracen-9-yl)vinyl)styryl)anthracene-9-carbaldehyde (19)

A solution of 9,10-anthracenedicarboxaldehyde **2** (0.10 g, 0.42 mmol) and **18** (0.52 g, 0.34 mmol) in 100 ml of dry THF was stirred under nitrogen at room temperature, *tert*-BuOK (0.06 g, 0.53 mmol) was added. The solution was stirred for 10 h, and then water (2 ml) was added, the solvent was evaporated under vacuum and the residue was purified by silica gel chromatography using a mixture of 60:40 hexane-dichloromethane as an eluent to afford 10-((E)-2,5-dibutoxy-4-((E)-2-(10-((E)-2,5-dibutoxy-4-((E)-2-(10-((E)-2,5-dibutoxy-4-((E)-2-(pyren-1-yl)vinyl)styryl)anthracen-9-yl)vinyl)styryl)anthracen-9-yl)vinyl)styryl)   anthracene-9-carbaldehyde (**19**) as an orange powder, yield 0.53 g, 0.33 mmol (98 %), m.p. >300 oC. FTIR. (pellet, KBr, cm-1): 3046, 2955, 2930, 2868, 1627, 1413, 1383, 1198, 1029, 977,

755. UV-vis (CH$_2$Cl$_2$, nm) λ_{max}: 224, 260, 348, 449. 1H NMR (300 MHz, acetone-d$_6$), δ(ppm): 0.974 (m, 18H, CH$_3$), 1.53 (m, 12H, CH$_3$), 1.84 (m, 12H, CH$_2$), 4.28 (m, 12H, CH$_2$-O), 6.99 (d, 2H, H-Ar, J= 8.2, 8.0 Hz), 7.41 (d, 1H, =CH, J_{trans}= 16.5 Hz), 7.46-7.64 (br, 10H, H$_{Ar}$, =CH, H$_{Ant}$), 7.85-7.81 (br, 7H, =CH, H-Ar, H$_{Ant}$), 7.91 (d, 2H, H$_{Py}$, J= 7.7 Hz), 7.96 (d, 1H, =CH, J_{trans}= 15.9 Hz), 7.99 (d, 1H, =CH, J_{trans}= 16.2 Hz), 8.06 (br, 2H, H$_{Py}$), 8.12 (d, 1H, =CH, J_{trans}= 15.9 Hz,), 8.12 (br, 2H, H$_{Py}$), 8.17-8.18 (br, 5H, H$_{Ant}$, H$_{Py}$), 8.24 (d, 1H, =CH, J_{trans}= 16.8 Hz,), 8.25 (d, 1H, =CH, J_{trans}= 16.2 Hz), 8.43 (d, 4H, H$_{Ant}$, J= 9.3 Hz,), 8.51-8.66 (br, 7H, H$_{Ant}$, =CH, H$_{Py}$), 8.87 (br, 2H, H$_{Ant}$), 9.56 (br, 2H, H$_{Ant}$), 10.87 (s, 1H, HC=O). 13C NMR (acetone-d$_6$), δ(ppm): 14.1 (CH$_3$), 20.1 (CH$_2$), 32.3 (CH$_2$), 61.9 (O-CH$_2$), 111.5 (HC$_{ar}$), 111.9 (HC$_{ar}$), 124.9 (HC$_{ar}$), 125.4 (=CH), 125.5 (C$_{ar}$), 126.1 (=CH), 126.4 (HC$_{ar}$), 126.8 (HC$_{ar}$), 127.3 (HC$_{ar}$), 127.8 (HC$_{ar}$), 128.3 (HC$_{ar}$), 128.8 (HC$_{ar}$), 129.6 (C$_{ar}$), 130.5 (C$_{ar}$), 132.4 (C$_{ar}$), 133.5 (C$_{ar}$), 134.2 (C$_{ar}$), 135.1 (C$_{ar}$), 152.2 (O-C). EM: m/z: 1574 [M]+. Calc. for C$_{113}$H$_{106}$O$_7$: C, 86.11; H, 6.78 (%); Found; C, 86.12; H, 4.66 (%).

X-Ray Crystallography

Suitable crystals of compounds **3**, **4**, **14** and **15** (obtained by crystallization from CH$_2$Cl$_2$ at room temperature) were rolled in epoxy resin and mounted on a glass fiber. Bruker Apex AXS CCD area detector X-Ray diffractometer was the instrument used for the determination. The data were first reduced and corrected for absorption using psi-scans, and then solved using the program SHELL-XS. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were refined at calculated positions with thermal parameters constrained to the carbon atom on which they were attached.

SUPPLEMENTARY MATERIALS

Supplementary materials can be viewed at www.bentham.org/open/toocj

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