1,4-Benzoquinones with Styryl Substituents

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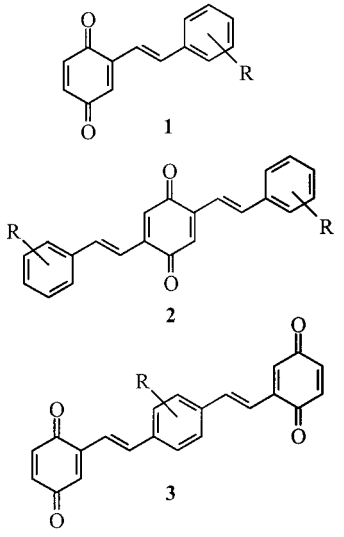
2-Styryl-1,4-benzoquinone (**1**) and compounds **2** and **3** containing **1** as a substructure all proved to be highly reactive towards thermal or photochemical [4π + 2π] cyclodimerization reactions. Chemo-, regio- and stereoselective processes lead to dimers (compounds **1**–**10**), which can undergo secondary reactions consisting of the addition of nucleophiles combined with a twofold keto-enol tautomerism (**10** → **12**). An alternative process is dehydrogenation/oxidation followed by an intramolecular [4π + 2π] cycloaddition (**10** → **11**). The same selective [4π + 2π] cyclodimerization can be observed in solution upon irradiation (e.g., **1a** → **10a**), in contrast to irradiation in the crystalline state which yields a [2π + 2π] dimer (e.g., **1a** → **13**). If more than one styrylbenzoquinone moiety is present in the same molecule the oligomers **2a** (*n* = 1–3) and **3a** (*n* = 1–4) are obtained.

Introduction

Oligo- and poly(1,4-phenylenevinylene)s (OPV and PPV, respectively) and related compounds are attracting a great deal of attention in materials science for their electroluminescent, semiconductive, photoconductive, NLO material, photoelectric, photoresistive, and other, properties.[1−11] Alkoxy substituents on the benzene rings — especially in the 2- and 5-positions — not only enhance solubility and facilitate processability, but also improve the electronic and optoelectronic properties of the substance. However, these systems are particularly prone to oxidation reactions because of their high-lying HOMOs.[12] Recently we published[13] a paper on the oxidation of 2-styrylhydroquinones as model compounds which showed that the generated 2-styryl-1,4-benzoquinones **1** are extremely susceptible to dimerization reactions. The corresponding C-C bond formations in OPVs and PPVs may thus contribute towards the observed crosslinking that occurs as these materials age. Therefore we extended our studies to the series of quinones **1** and generated the related quinones **2** and **3** (Scheme 1) which are derivatives of 1,4-distyrylbenzene. Overall, the present knowledge on quinones with conjugated side chains is very limited.[12−16]



Scheme 1. 1,4-Benzoquinones with styryl substituents

Results and Discussion

The preparation of the target compounds **1a**−**d** was based on benzaldehydes with protected hydroxy functions in the 2- and 5-positions. Allyl, methyl and *tert*-butyldimethylsilyl groups were used as protecting groups. The Horner reaction between 2,5-diallyloxybenzaldehyde and diethyl 2,5-dimethylbenzylphosphonate provided the stilbene derivative **4a** in 74% yield. Analogous procedures led to the compounds **4b** and **4c** in 86% and 91% yield, respectively.[13] The stilbene **4d** was obtained in a yield of 86% by a Wittig reaction between 2,5-bis(*tert*-butyldimethylsilyloxy)benzaldehyde and 4-bromo-2,5-dipropoxybenzyltriphenylphosphonium bromide. The *E* configuration predominated strongly in compounds **4a**−**c**, whereas **4d** contained an appreciable amount of the *Z* isomer. After subsequent deprotection, only the *E* isomer was present for all stilbenes **5a**−**d** by NMR spectroscopic analysis. Three different deprotection treatments were applied according to the group to be

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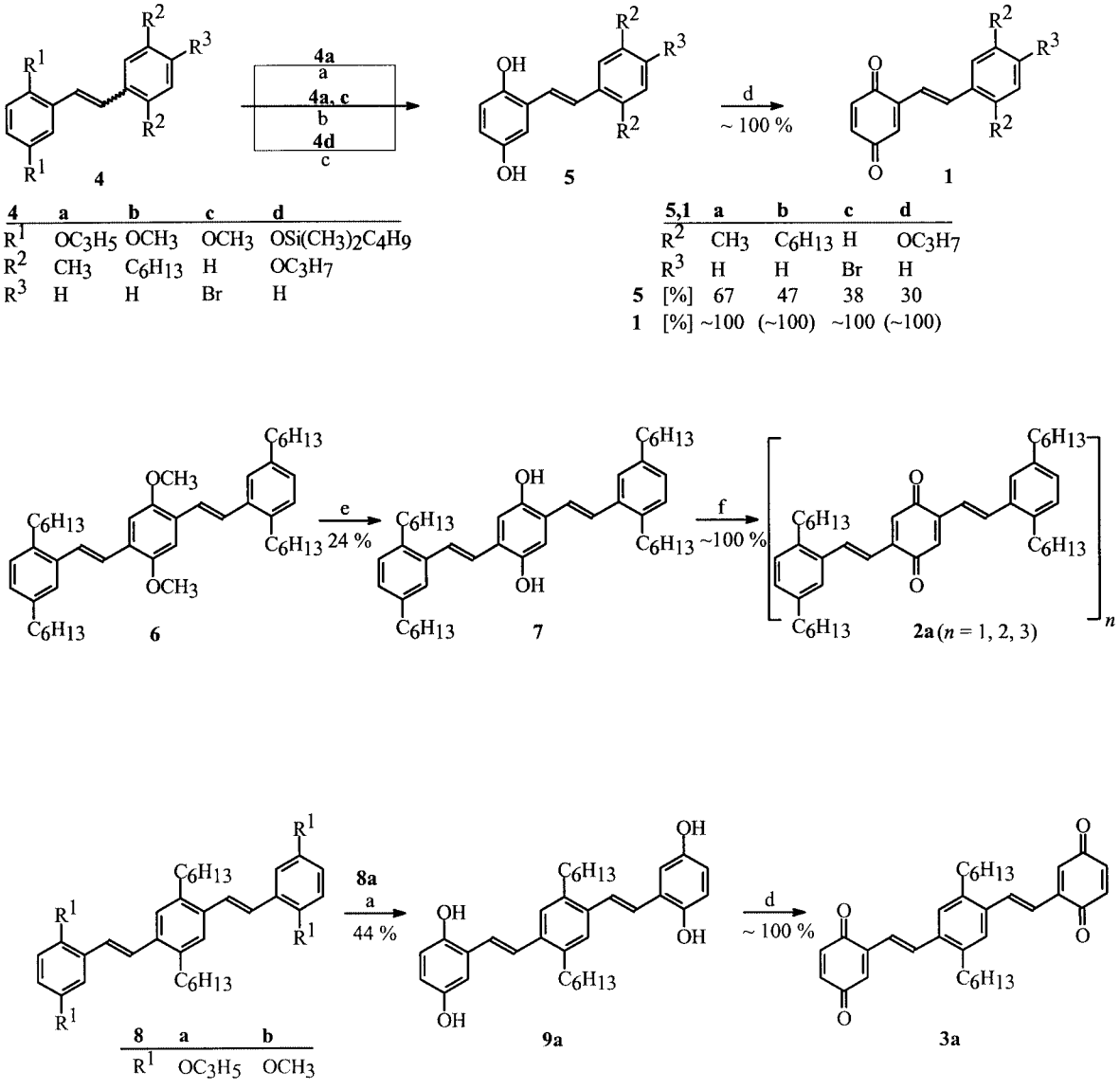
removed: $NaBH_4$ in the presence of Pd^0 for the cleavage of allyl, BBr_3 for the cleavage of methyl and tetrabutylammonium fluoride for the cleavage of silyl. The first method was the most successful and gave the highest yields. The oxidation of **5a**−**d** was performed with Ag_2O and led, in quantitative yields, to the quinones **1a**−**d**. However, quinones **1b** and **1d** dimerized in situ and only **1a** and **1c**[13] could be isolated as monomers (Scheme 2).

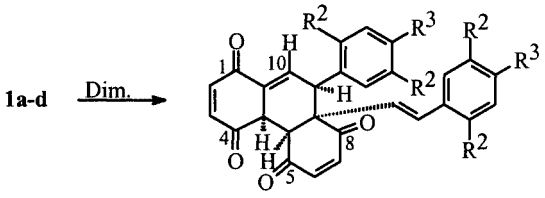
The attempt to synthesize 2,5-distyrylbenzoquinones **2** started with 1,4-dihexylbenzene, which was obtained in a yield of 60% by the reaction of 1,4-dibromobenzene and *n*-hexylmagnesium bromide in the presence of Ni^{II}.[14] A subsequent Rieche−Gross formylation furnished 2,5-dihexylbenzaldehyde in 74% yield, which was then used for a Horner reaction. The other component of the Horner reaction was tetraethyl [2,5-dimethoxy-1,4-phenylenebis(methylene)]diphosphonate, which was obtained in a yield of 58% by the Arbusow reaction between 1,4-bis(bromomethyl)-2,5-dimethoxybenzene and triethyl phosphite. The bis(bromomethyl) compound (87% yield), together with the mono(bromomethyl) product (yield 12%), account for an almost quantitative bromomethylation of 1,4-dimethoxybenzene. The Horner reaction led to the *E*,*E* distyrylbenzene **6** (57% yield), whose methoxy groups were cleaved with lithium diphenylphosphide. The resulting hydroquinone **7** (24%) was treated with NaOCl which led by quantitative oxidation to the quinone **2a**, which is, according to MS, a mixture of monomeric, dimeric and trimeric species (Scheme 2).

The synthetic approach to the twofold quinones **3** started with the *E*,*E* configured distyrylbenzene derivatives **8a** and **8b**, which were obtained from Horner reactions. The bromomethylation of 1,4-dihexylbenzene yielded 62% of 1,4-bis(-bromomethyl)-2,5-dihexylbenzene and 35% of 1-bromomethyl-2,5-dihexylbenzene. The Arbusow reaction of the dibromo product with triethyl phosphite gave 85% of tetraethyl [2,5-dihexyl-1,4-phenylenebis(methylene)]diphospho-

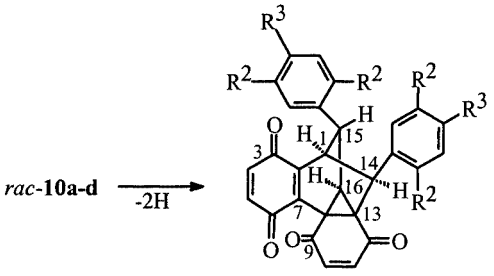


Scheme 2. Preparation of 1,4-benzoquinones with styryl groups; reagents: (a) $NaBH_4$, $Pd[P(C_6H_5)_3]_4$, THF; (b) BBr_3, CH_2Cl_2; (c) $(n\text{-}C_4H_9)_4N^+F^-$, THF; (d) Ag_2O, $MgSO_4$, $(C_2H_5)_2O$; (e) $LiP(C_6H_5)_2$, THF; (f) NaOCl, aliquat 336, HCl, $H_2O/CHCl_3$

nate which furnished 75% of **8a** by Horner reaction with 2,5-diallyloxybenzaldehyde, and 63% of **8b** by Horner reaction with 2,5-dimethoxybenzaldehyde. The cleavage of four methyl ether functions turned out to be very difficult, therefore we undertook the cleavage of fourfold allyl ether **8a** by reduction with $NaBH_4$ in the presence of Pd^0, which resulted in a yield of 44%. The deprotected bishydroquinone **9a** was oxidized in the final reaction step with Ag_2O. The quantitative process yielded the bisbenzoquinone **3a**, which precipitated from diethyl ether and thus did not oligomerize. However, if **3a** was dissolved in chloroform, oligomerization occurred at room temperature as evidenced by FD-MS analysis which indicated peaks for dimeric, trimeric and tetrameric species.

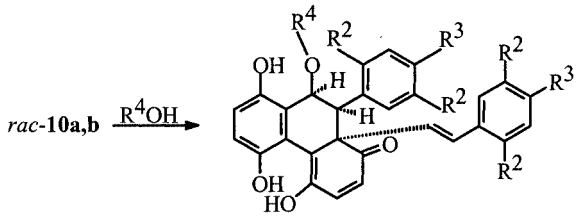


rac-**10a-d**



rac-**11a-d**

rac-**10,11**	**a**	**b**	**c**	**d**
R^2	CH_3	*n*-C_6H_{13}	H	OC_3H_7
R^3	H	H	Br	H
10 [%]	84	~100	93	> 16
11 [%]	24	19	17	16



rac-**12a,b,c**

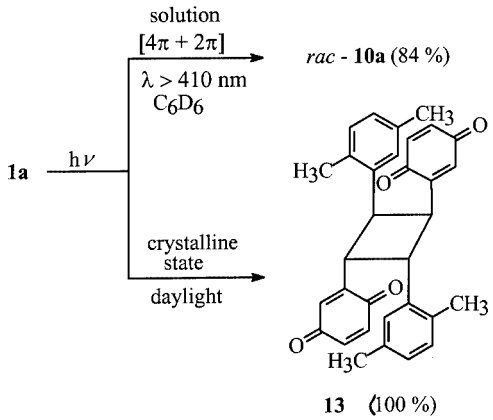
rac-**12**	**a**	**b**	**c**
R^2	CH_3	CH_3	*n*-C_6H_{13}
R^3	H	H	H
R^4	H	C_2H_5	H
[%]	58	82	16

Scheme 3. Dimerization of **1a**−**d** and subsequent reactions

The aforementioned dimerization of **1a**−**d** is a highly chemo-, regio- and stereoselective Diels−Alder reaction which yielded the 4a*R**,4b*S**,8a*R**,9*S** configuration of the phenanthrene derivatives **10a**−**d**. Similar dimers have been obtained by electrochemical oxidation.[15] An explanation for the selectivities based on frontier orbital theory was given in the previous paper.[13] Apart from **10d**, the dimeric systems **10a**−**c** are fairly stable in the pure state and in solution, although they undergo a complicated series of reactions in the presence of silica gel. The predominant route furnished the polycyclic compounds **11a**−**d** (Scheme 3); MS analysis of **11a**−**d** indicated that a dehydrogenation/oxidation process had occurred. An intramolecular cycloaddition of the olefinic 2π component of the styryl group and the newly generated 4π component then ensued. The regioselective [4π + 2π] process is a consequence of the steric arrangement. Thus, the 4a*R*,4b*S*,8a*R*,9*S* configuration of **10a**−**d** led to the 1*R*,8*S*,13*S*,14*S*,15*S*,16*S* configuration of **11a**−**d** [and accordingly (4a*S*,4b*R*,8a*S*,9*R*)-**10a**−**d** led to (1*S*,8*R*,13*R*,14*R*,15*R*,16*R*)-**11a**−**d**].

In the presence of nucleophiles such as water or ethanol, the dimers **10** undergo an acid-catalyzed addition reaction in the 1- and 10-positions, accompanied by aromatization of one of the six-membered rings. Since a second tautomeric keto-enol transformation is involved, three of the four carbonyl groups disappear in the transformations **10a**,**b** → **12a**−**c**.

Inspired by a related reaction,[16] we also studied the photochemistry of **1a** (Scheme 4). Irradiation in C_6D_6 at wavelengths gretaer than 410 nm yielded the dimer **10a**. Interestingly, the photochemical [4π + 2π] cycloaddition, which is forbidden as a concerted reaction, showed the same high chemo-, regio- and stereoselectivity as the thermal Diels−Alder reaction. However, in contrast to the quantitative thermal process, analysis by ^1H NMR spectroscopy of the photoreaction revealed small amounts of a further product. Thus, the photochemical reaction is much faster



Scheme 4. Photochemistry of **1a** in solution and in the crystalline state

than the thermal process (e.g., at 60 °C), but on the whole is somewhat less selective.

Upon exposure to sunlight, crystals of **1a** are transformed into the dimer **13**.[17] The topochemical process represents a head-to-tail [2π + 2π] cycloaddition whereby the *trans* configurations of the original double bonds are preserved in the generated four-membered ring. *E*/*Z* photo-induced isomerization was not observed either in solution or in the solid state.

Conclusion

1,4-Benzoquinones with styryl groups are extremely reactive species and readily undergo [4π + 2π] cycloaddition reactions. They are highly chemo-, regio- and stereoselective both in thermal and in photochemical dimerizations (**1** → **10**). If more than one styryl-substituted 1,4-benzoquinone unit is present in the starting material the oligomeric cycloadducts **2a** (*n* = 2, 3) and **3a** (*n* = 2−4), are formed. Moreover, the dimers can add nucleophiles like water or ethanol (**10** → **12**), a reaction which is catalyzed by acid and can readily occur on the surface of silica gel.[18] Another secondary reaction of the dimers is dehydrogenation/oxidation, which is followed by an intramolecular [4π + 2π] cycloaddition (**10** → **11**).

Experimental Section

General Remarks: Melting points were measured using a Büchi apparatus and are uncorrected. NMR spectra were measured on Bruker AM 400 and WT 200 instruments using $CDCl_3$ as the solvent, unless otherwise stated, with TMS as an internal standard. MS spectra were measured on Finnigan MAT 95 and Varian MAT CH7A instruments.

Preparation of (*E*)-2-(2,5-Diallyloxyphenyl)-1-(2,5-dimethylphenyl)-ethene (4a)

2,5-Diallyloxybenzaldehyde: Allyl bromide (4.78 g, 39.5 mmol), K_2CO_3 (6.33 g, 45.8 mmol) and a trace of KI were added to a solution of 2,5-dihydroxybenzaldehyde (2.0 g, 14.5 mmol) in acetone (30 mL). After stirring at room temperature overnight the solid particles were removed and the solvent evaporated under reduced pressure (1 kPa). The product was purified by filtration through silica gel (70−230 mesh, 7 × 10 cm) using dichloromethane as eluent to afford a colorless oil (yield 2.17 g, 69%) **4a**. ^{1}H NMR ($CDCl_3$): δ = 4.50 (d, 2 H, OCH_2), 4.59 (d, 2 H, OCH_2), 5.23−5.37 (m, 4 H, allyl CH_2), 5.95−6.11 (m, 2 H, allyl CH), 6.91 (d, 1 H, arom. H), 7.12 (dd, 1 H, arom. H), 7.32 (d, 1 H, arom. H), 10.47 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 69.4, 69.9 (OCH_2), 111.5, 114.8, 124.1 (arom. CH), 117.9, 118.0 (allyl CH_2), 125.4, 152.7, 155.8 (arom. C_q), 132.7, 133.0 (allyl CH), 189.4 (CHO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 218 (27) [$M^{+\cdot}$], 177 (16), 40 (100). $C_{13}H_{14}O_3$ (218.3): calcd. C 71.54, H 6.47; found C 71.54, H 6.60.

Diethyl 2,5-Dimethylbenzylphosphonate: A mixture of 2-chloromethyl-1,4-dimethylbenzene (10.0 g, 0.07 mol) and triethyl phosphite (25 mL, 24.2 g, 1.5 mol) was kept for 5 h at 170 °C after which the excess triethylphosphite was removed under vacuum (10^2 Pa). The product was purified by vacuum distillation (b.p. 164 °C/930 Pa) to afford a colorless liquid (yield 14.2 g, 85%). ^{1}H NMR ($CDCl_3$): δ = 1.22 (t, 6 H, CH_3), 2.27 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 3.11 (d, $|^2J_{P,H}|$ = 22.0 Hz, 2 H, CH_2P), 3.97 (m, 4 H, OCH_2), 6.92 (d, 1 H, arom. H), 7.03 (m, 2 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.2, 16.4 (CH_3), 19.4, 20.9 (Ar-CH_3), 31.0 (d, $|^1J_{C,P}|$ = 138.1 Hz, CH_2P), 62.0, 62.1 (OCH_2), 127.8 (d, $|^5J_{C,P}|$ = 4.0 Hz, arom. CH), 129.7 (d, $|^2J_{C,P}|$ = 9.6 Hz, arom. C_q), 130.3 (d, $|^4J_{C,P}|$ = 3.2 Hz, arom. CH), 131.3 (d, $|^3J_{C,P}|$ = 5.6 Hz, arom. CH), 133.8 (d, $|^3J_{C,P}|$ = 6.4 Hz, arom. C_q), 135.3 (d, $|^4J_{C,P}|$ = 4.0 Hz, arom. C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 256 (83) [$M^{+\cdot}$], 199 (60), 119 (100). $C_{13}H_{21}O_3P$ (256.3): calcd. C 60.93, H 8.26; found C 60.90, H 8.56.

(*E*)-2-(2,5-Diallyloxyphenyl)-1-(2,5-dimethylphenyl)ethene (4a): A solution of 2,5-diallyloxybenzaldehyde (5.89 g, 0.03 mol) and diethyl 2,5-dimethylbenzylphosphonate (7.0 g, 0.03 mol) in dry DME (150 mL) was added dropwise to a suspension of NaH (60% dispersion in mineral oil; 10.8 g, 0.27 mol), in dry DME (90 mL). After stirring at room temperature overnight, water (20 mL) was cautiously added dropwise and the solution extracted with chloroform (200 mL) which was then washed with brine and dried with Na_2SO_4. The solvent was evaporated under vacuum (10^2 Pa) and the product purified by column chromatography over silica gel (70−230 mesh, 4 × 30 cm) using petroleum ether (b.p. 40−70 °C)/diethyl ether (30:1) as eluent. The product **4a** was obtained as a viscous oil (yield 6.39 g, 74%).[19] ^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 4.53 (m, 4 H, OCH_2), 5.28 (m, 2 H, allyl CH_2), 5.42 (m, 2 H, allyl CH_2), 6.07 (m, 2 H, allyl CH), 6.76 (dd, 1 H, arom. H), 6.82 (d, 1 H, arom. H), 6.97 (dd, 1 H, arom. H), 7.05 (d, 1 H, arom. H), 7.16 (d, 1 H, arom. H), 7.30 ("s", 2 H, olefin H), 7.42 (br. s, 1 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.5, 21.1 (CH_3), 69.5, 70.3 (OCH_2), 113.3, 114.1, 114.2, 124.4, 126.1, 127.6, 128.2, 130.3 (arom. and olefin CH), 117.3, 117.6 (allyl CH_2), 128.4, 132.8, 135.5, 136.6, 150.7, 153.0 (arom. C_q), 133.6, 133.7 (allyl CH) ppm. FD-MS: *m*/*z* (%) = 320 (100) [$M^{+\cdot}$]. $C_{22}H_{24}O_2$ (320.4): calcd. C 82.46, H 7.55; found C 81.92, H 7.25.

The stilbene derivatives **4b** and **4c** and their precursors were prepared according to literature methods.[13,20−22]

(*E*)-1-{2,5-Bis[*tert*-butyldimethylsilyloxy]phenyl}-2-(2,5-dipropoxyphenyl)ethene (4d)

4-Bromo-2,5-dipropoxybenzyltriphenylphosphonium Bromide: A solution of 1-bromo-4-bromomethyl-2,5-dipropoxybenzene[23] (10.0 g, 0.03 mol) in dry acetonitrile (20 mL) was added dropwise under argon to a solution of triphenylphosphane (7.07 g, 0.03 mol) in dry acetonitrile (100 mL). The mixture was heated to reflux for two days and the precipitated product collected by filtration. The filtrate was concentrated under vacuum (10^2 Pa) and acetone added (50 mL), leading to the precipitation of additional product. The total yield was 12.97 g (77%) of a colorless solid, m.p. 218 °C. ^{1}H NMR ($CDCl_3$): δ = 0.70 (t, 3 H, CH_3), 0.88 (t, 3 H, CH_3), 1.26 (m, 2 H, CH_2), 1.58 (m, 2 H, CH_2), 3.22 (t, 2 H, OCH_2), 3.60 (t, 2 H, OCH_2), 5.24 (d, $|^2J_{P,H}|$ = 14.0 Hz, 2 H, CH_2P), 6.74 (s, 1 H, arom. H), 7.30 (d, $|^4J_{P,H}|$ = 2.8 Hz, 1 H, arom. H), 7.64 (m, 15 H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.2, 10.5 (CH_3), 22.2, 22.4 (CH_2), 25.0 (d, $|^1J_{C,P}|$ = 48 Hz, CH_2P), 69.9, 71.4 (OCH_2), 112.6, 115.3, 149.6, 151.0 (arom. C_q), 116.2, 118.0 (arom. CH), 130.0, 130.1, 134.2, 134.6 (C_6H_5) ppm. FD-MS: *m*/*z* (%) = 550/548 (100) [$C_{31}H_{33}Br^+O_2P$], Br isotope pattern. $C_{31}H_{33}Br_2O_2P$ (628.4): calcd. C 59.25, H 5.29; found C 59.52, H 5.19.

(*E*)-1-{2,5-Bis[*tert*-butyldimethylsilyloxy]phenyl}-2-(2,5-dipropoxyphenyl)ethene (4d): A 2.7 M solution of *n*-butyllithium in heptane

(6.3 mL, 17 mmol) was added by syringe to a suspension of 4-bromo-2,5-dipropoxybenzyltriphenylphosphonium bromide (9.43 g, 15 mmol) in dry THF (150 mL) at −10 °C under argon. After stirring for 30 min at room temperature, a solution of 2,5-bis(*tert*-butyldimethylsilyloxy)benzaldehyde[21] (5.0 g, 15 mmol) in dry THF (25 mL) was added to the reaction mixture. The mixture was stirred at room temperature for 30 min and then poured onto ice/water (200 mL). After extraction with diethyl ether (200 mL), the organic phase was washed with water and dried with Na_2SO_4. The solvent was evaporated under vacuum (10^2 Pa) and the product extracted from the solid residue with refluxing hexane. The solvent was removed under vacuum (10^2 Pa) and the product purified by column chromatography over silica gel (70−230 mesh, 4 × 30 cm) using petroleum ether (b.p. 40−70 °C)/diethyl ether (20:1) as eluent. An *E*/*Z* mixture of **4d** was obtained as a yellow liquid (yield 6.51 g, 86%). Transformation to the *E* isomer, a colorless oil, was performed by refluxing the mixture in toluene (100 mL) with iodine (40 mg) for 2 h. ^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 6 H, $SiCH_3$), 0.19 (s, 6 H, $SiCH_3$), 0.97 [s, 9 H, $C(CH_3)_3$], 1.04 [s, 9 H, $C(CH_3)_3$], 1.06 (t, 3 H, CH_3), 1.07 (t, 3 H, CH_3), 1.80 (m, 4 H, CH_2), 3.88 (t, 2 H, OCH_2), 3.91 (t, 2 H, OCH_2), 6.62 (dd, 1 H, arom. H), 6.67 (dd, 1 H, arom. H), 6.68 (d, 1 H, arom. H), 6.82 (d, 1 H, arom. H), 7.13 (d, 1 H, arom. H), 7.17 (d, 1 H, arom. H), 7.36/7.41 (AB, $^3J_{trans}$ = 16.7 Hz, 2 H, olefin H) ppm. ^{13}C NMR ($CDCl_3$): δ = −4.5, −4.3 ($SiCH_3$), 10.6, 10.7 (CH_3), 14.0 (*tert*-butyl C_q), 22.6, 22.8 (CH_2), 25.9 (*tert*-butyl CH_3), 70.2, 71.3 (OCH_2), 110.8, 114.5, 115.5, 116.4, 119.6, 119.7 (arom. CH), 122.0, 126.4, 147.7, 149.9, 150.8, 153.5 (arom. C_q), 122.7, 123.5 (olefin CH) ppm. MS (EI, 70 eV): *m*/*z* (%) = 556 (100) [$M^{+\cdot}$], 457 (27). $C_{32}H_{52}O_4Si_2$ (556.9): calcd. C 69.01, H 9.41; found C 69.07, H 9.42.

(*E*)-2-[2-(2,5-Dimethylphenyl)ethenyl]hydroquinone (5a): A mixture of **4a** (1.9 g, 5.9 mmol), $NaBH_4$ (446 mg, 11.8 mmol) and tetrakis-(triphenylphosphane)palladium (58 mg, 0.05 mmol) in dry THF (230 mL) was stirred at room temperature for 2 days. The mixture was then poured into water (100 mL) and acidified with 2 M HCl (5 mL). After extraction with ethyl acetate, the organic phase was washed with brine and dried with Na_2SO_4. The solvent was evaporated under vacuum (10^2 Pa) and the residue purified by column chromatography over silica gel (70−230 mesh, 3 × 40 cm) using petroleum ether (b.p. 40−70 °C)/ethyl acetate (5:3) as eluent to give **5a** as a colorless solid (yield 0.95 g, 67%), m.p. 167 °C. ^{1}H NMR ([D_6]DMSO): δ = 2.29 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 6.53 (dd, 1 H, hydroquinone ring), 6.67 (d, 1 H, hydroquinone ring), 6.96 (m, 2 H, hydroquinone ring/arom. H), 7.06 (d, 1 H, arom. H), 7.21 ("s", 2 H, olefin H), 7.40 (br. s, 1 H, arom. H), 8.75 (s, 1 H, OH), 9.05 (s, 1 H, OH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 19.0, 20.6 (CH_3), 111.9, 115.7, 116.5 (CH, hydroquinone ring), 124.3, 124.7, 124.9, 125.2, 130.2 (arom. and olefin CH), 127.8, 132.0, 134.9, 136.1, 147.7, 149.9 (arom. C_q) ppm. FD-MS: *m*/*z* (%) = 241 (100) [$M^{+\cdot}$]. $C_{16}H_{16}O_2$ (240.3): calcd. C 79.97, H 6.71; found C 80.04, H 7.04.

Hydroquinone derivatives **5b** and **5c** were prepared according to the literature.[13]

(*E*)-2-[2-(2,5-Dipropoxyphenyl)ethenyl]hydroquinone (5d): A solution of tetra-*n*-butylammonium fluoride (3.02 g, 9.58 mmol) in dry THF (80 mL) was added to a solution of **6d** (1.0 g, 1.57 mmol) in dry THF (80 mL). After stirring for 1 h at room temperature the mixture was diluted with hexane (70 mL), washed with a saturated solution of $NaHCO_3$ and brine and dried with Na_2SO_4. The solvent was evaporated under reduced pressure (1 kPa) and the product purified by column chromatography over silica gel (70−230 mesh, 3 × 40 cm) with petroleum ether (b.p. 40−70 °C)/ethyl acetate (5:3) as eluent. Recrystallization twice from chloroform yielded **5d** as a colorless solid (yield 154 mg, 30%), m.p. 155 °C. ^{1}H NMR ([D_6]DMSO): δ = 0.97 (t, 3 H, CH_3), 1.02 (t, 3 H, CH_3), 1.72 (m, 4 H, CH_2), 3.89 (m, 4 H, OCH_2), 6.51 (dd, 1 H, hydroquinone ring), 6.66 (d, 1 H, hydroquinone ring), 6.77 (dd, 1 H, arom. H), 6.87 (d, 1 H, hydroquinone ring), 6.91 (d, 1 H, arom. H), 7.10 (d, 1 H, arom. H), 7.27/7.34 (AB, $^3J_{trans}$ = 16.4 Hz, 2 H, olefin H), 8.76 (s, 1 H, OH), 9.01 (s, 1 H, OH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 10.4, 10.6 (CH_3), 22.1, 22.2 (CH_2), 69.3, 70.1 (OCH_2), 111.5, 114.0, 114.0, 114.1, 115.7, 116.6 (arom. CH), 121.8, 127.2, 147.8, 149.9, 150.1, 152.7 (arom. C_q), 124.3, 124.4 (olefin CH) ppm. MS (EI, 70 eV): *m*/*z* (%) = 328 (100) [$M^{+\cdot}$], 286 (17), 244 (16). $C_{20}H_{24}O_4$ (328.4): calcd. C 73.15, H 7.30; found C 72.90, H 7.60.

(*E*)-2-[2-(2,5-Dimethylphenyl)ethenyl]benzoquinone (1a): $MgSO_4$ (1.53 g, 12.7 mmol) and freshly-prepared Ag_2O (1.16 g, 5.0 mmol) were added to a solution of **7a** (0.60 g, 2.5 mmol) in dry diethyl ether (140 mL). After stirring for 30 min at room temperature the solid particles were removed and washed several times with diethyl ether (40 mL). The solvent of the combined organic phases was removed under vacuum (10^2 Pa) to provide **1a** as a red solid (yield 0.60 g, 100%), m.p. > 200 °C. ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 6.77 (m, 2 H, benzoquinone ring), 6.87 (br. s, 1 H, benzoquinone ring), 7.00/7.69 (AB, $^3J_{trans}$ = 16.1 Hz, 2 H, olefin H), 7.06 (br. s, 2 H, arom. H), 7.44 (br. s, 1 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.3, 21.0 (CH_3), 119.9, 126.5, 127.6, 130.4, 130.7 (arom. and olefin CH), 134.1, 134.7, 135.9 (arom. C_q), 135.7, 136.5, 136.7 (CH, benzoquinone ring), 142.2 (C_q, benzoquinone ring), 187.1, 187.7 (CO) ppm. FD-MS: *m*/*z* (%) = 239 (100) [M + H]$^+$. $C_{16}H_{14}O_2$ (238.3): calcd. C 80.65, H 5.92; found C 81.00, H 6.27.

The preparation of **1c** was performed as described previously.[13]

Preparation of (*E*,*E*)-2,5-Bis(2,5-dihexylstyryl)-1,4-dimethoxybenzene (6)

2,5-Dihexylbenzaldehyde: Titanium tetrachloride (11.27 mL, 19.49 g, 103 mmol) was added dropwise to a solution of 1,4-dihexylbenzene (15.0 g, 61 mmol) in dry dichloromethane (150 mL) at 0 °C. After stirring for 30 min at 0 °C, dichloromethyl methyl ether (8.13 mL, 10.48 g, 92 mmol) was added dropwise. The mixture was stirred for 2 h at room temperature and then poured onto ice/water (200 mL). The separated water layer was extracted with dichloromethane (200 mL). The combined organic phases were washed with water followed by a saturated solution of $NaHCO_3$ and then dried with Na_2SO_4. After removal of the solvent under reduced pressure (1 kPa), the product was purified by column chromatography over silica gel (70−230 mesh, 10 × 15 cm) using petroleum ether (b.p. 40−70 °C)/diethyl ether (20:1) as eluent. The product was obtained as a colorless liquid (yield 12.4 g,74%). ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.29 (m, 12 H, CH_2), 1.57 (m, 4 H, CH_2), 2.61 (t, 2 H, CH_2), 2.96 (t, 2 H, CH_2), 7.15 (d, 1 H, 3-H), 7.29 (dd, 1 H, 4-H), 7.62 (d, 1 H, 6-H), 10.26 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.1 (CH_3), 22.6, 22.6, 28.9, 29.2, 31.2, 31.7, 32.0, 32.5, 35.3 (CH_2, partly superimposed), 130.8, 130.9 (C-3, C-6), 134.0 (C-4), 133.5 (C-1), 141.1, 143.2 (C-2, C-5), 192.4 (CHO) ppm. FD-MS: *m*/*z* (%) = 274 (100) [$M^{+\cdot}$]. $C_{19}H_{30}O$ (274.2): calcd. C 83.15, H 11.02; found C 83.17, H 11.37.

Bromomethylation of 1,4-Dimethoxybenzene: A 33% solution of HBr in glacial acetic acid (14 mL, 0.08 mol) was added dropwise to a suspension of 1,4-dimethoxybenzene (5.0 g, 0.04 mol) and paraformaldehyde (2.37 g, 0.08 mol) in glacial acetic acid (25 mL). The mixture was stirred for 1 h at 50 °C. The doubly bromomethylated product precipitated and was isolated by filtration, dissolved in

chloroform (80 mL) and the solution dried with Na_2SO_4. After filtration, partial evaporation of the solvent under vacuum (10^2 Pa) enabled precipitation of colorless crystals (yield 10.14 g, 87%), m.p. 198 °C. The remaining reaction mixture was added to water (100 mL) and the precipitate isolated by filtration and purified by column chromatography over silica gel (70−230 mesh, 3 × 10 cm) using toluene as eluent. The monobromomethyl compound thus obtained formed almost colorless crystals (yield 1.11 g, 12%), m.p. 73 °C.

1,4-Bis(bromomethyl)-2,5-dimethoxybenzene: ^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 6 H, OCH_3), 4.51 (s, 4 H, CH_2Br), 6.85 (s, 2 H, 3-H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.6 (CH_2), 56.3 (OCH_3), 113.9 (C-3, C-6), 127.4 (C-1, C-4), 151.3 (C-2, C-5) ppm. MS (EI, 70 eV): *m*/*z* (%) = 326.4/324.5/322.5 (23) [$M^{+\cdot}$], Br_2 isotope pattern, 245.2/243.1 (100). $C_{10}H_{12}Br_2O_2$ (323.9): calcd. C 37.07, H 3.73; found C 37.09, H 3.75.

1-Bromomethyl-2,5-dimethoxybenzene: ^{1}H NMR ($CDCl_3$): δ = 3.75 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 4.52 (s, 2 H, CH_2Br), 6.80 (m, 2 H, arom. H), 6.88 (m, 1 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.9 (CH_2), 55.8, 56.2 (OCH_3), 112.2, 115.0, 116.4 (arom. CH), 127.0 (C-1), 151.7, 153.4 (C-2, C-5) ppm. MS (EI, 70 eV): *m*/*z* (%) = 232/230 (16) [$M^{+\cdot}$], Br isotope pattern, 151 (100). $C_9H_{11}BrO_2$ (231.9): calcd. C 46.78, H 4.80; found C 47.01, H 4.89.

Tetraethyl [2,5-Dimethoxy-1,4-phenylenebis(methylene)]diphosphonate: 1,4-Bis(bromomethyl)-2,5-dimethoxybenzene (10.9 g, 34 mmol) and triethylphosphite (13.3 g, 80 mmol) were kept for 5 h at 170 °C after which the excess triethylphosphite was removed under vacuum (10^2 Pa). The product crystallized from the residue as colorless crystals (yield 11.54 g, 78%), m.p. 103 °C. ^{1}H NMR ($CDCl_3$): δ = 1.19 (t, 12 H, CH_3), 3.17 (d, $|^2J_{P,H}|$ = 20.0 Hz, 4 H, CH_2P), 3.72 (s, 6 H, OCH_3), 3.98 (m, 8 H, OCH_2), 6.86 (d, $|^4J_{P,H}|$ = 1.5 Hz, 2 H, 3-H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.4 (CH_3), 26.9 (d, $|^1J_{C,P}|$ = 141 Hz, CH_2P), 56.2 (OCH_3), 61.9 (OCH_2), 114.1 (C-3, C-6), 119.4 (C-1, C-4), 151.0 (C-2, C-5) ppm. MS (EI, 70 eV): *m*/*z* (%) = 438 (100) [$M^{+\cdot}$], 301 (27). $C_{18}H_{32}O_8P_2$ (437.9): calcd. C 49.32, H 7.36; found C 48.93, H 7.06.

(*E*,*E*)-2,5-Bis(2,5-dihexylstyryl)-1,4-dimethoxybenzene (6): A solution of 2,5-dihexylbenzaldehyde (2.0 g, 7.2 mmol) and tetraethyl [2,5-dimethoxy-1,4-phenylenebis(methylene)]diphosphonate (1.58 g, 3.6 mmol) in dry DMF (60 mL) was added dropwise to a solution of $KOC(CH_3)_3$ (4.2 g, 37.6 mmol) in dry DMF (40 mL) under argon at 0 °C. The mixture was stirred at room temperature for 3 h and then poured onto a mixture of ice/water (100 mL) and 2 M HCl (10 mL). After extraction with dichloromethane (250 mL), the organic phase was washed with water (50 mL) followed by a saturated solution of $NaHCO_3$ (50 mL) and then dried with Na_2SO_4. The solvent was evaporated under vacuum (10^2 Pa) and the product purified by column chromatography over silica gel (70−230 mesh, 4 × 50 cm) using petroleum ether (b.p. 40−70 °C)/diethyl ether (15:1) as eluent to give **19** as yellow crystals (yield 1.39 g, 57%), m.p. 68 °C. ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 12 H, CH_3), 1.32 (m, 24 H, CH_2), 1.59 (m, 8 H, CH_2), 2.60 (t, 4 H, CH_2), 2.71 (t, 4 H, CH_2), 3.91 (s, 6 H, OCH_3), 7.01 (dd, 2 H, arom. H), 7.07 (d, 2 H, arom. H), 7.11 (s, 2 H, arom. H), 7.31/7.40 (AB, $^3J_{trans}$ = 16.1 Hz, 4 H, olefin H), 7.45 (d, 2 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.9, 14.0 (CH_3), 22.6, 22.6, 29.1, 29.3, 31.3, 31.5, 31.7, 31.8, 33.2, 35.7 (CH_2), 56.4 (OCH_3), 110.1, 125.7, 127.6, 129.5 (arom. CH), 124.3, 127.4 (olefin CH), 127.3, 136.0, 138.0, 140.6, 151.7 (arom. C_q) ppm. FD-MS: *m*/*z* (%) = 679 (100) [$M^{+\cdot}$]. $C_{48}H_{70}O_2$ (678.5): calcd. C 84.90, H 10.39; found C 84.61, H 10.20.

(*E*,*E*)-2,5-Bis(2,5-dihexylstyryl)hydroquinone (7): A 2.7 M solution of *n*-butyllithium in hexane (8.2 mL, 22.1 mmol) was added by syringe to a solution of diphenylphosphane (3.5 mL, 3.74 g, 20.1 mmol) in freshly distilled THF (30 mL) under argon at 0 °C. After stirring for 30 min at room temperature, a solution of **6** (1.36 g, 2.0 mmol) in dry THF (20 mL) was added by syringe. The mixture was refluxed for 5 h and then held at room temperature overnight; it was then poured into water (200 mL). After extraction with ethyl acetate, the organic phase was washed with brine and dried with Na_2SO_4 followed by removal of the solvent under reduced pressure (1 kPa). Purification required repeated column chromatography over silica gel (70−230 mesh, 4 × 50 cm) with petroleum ether (b.p. 40−70 °C)/ethyl acetate mixtures (4:1 at first, later 15:1). Compound **7** was obtained as a yellow oil (yield 314 mg, 24%), which partly solidified upon storage at ca. −5 °C. ^{1}H NMR ([D_6]DMSO): δ = 0.83 (t, 12 H, CH_3), 1.27 (m, 24 H, CH_2), 1.53 (m, 8 H, CH_2), 2.56 (t, 4 H, CH_2), 2.67 (t, 4 H, CH_2), 6.99 (d, 2 H, arom. H), 7.04 (s, 2 H, arom. H), 7.07 (d, 2 H, arom. H), 7.20/7.29 (AB, $^3J_{trans}$ = 16.0 Hz, 4 H, olefin H), 7.41 (br. s, 2 H, arom. H), 9.15 (s, 2 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.6, 29.1, 29.3, 31.3, 31.6, 31.8, 33.1, 35.7 (CH_2, partly superimposed), 113.9, 123.2, 125.5, 125.6, 128.3, 129.6 (arom. and olefin CH), 127.9, 135.6, 138.1, 140.7, 147.4 (arom. C_q) ppm. FD-MS: *m*/*z* (%) = 651 (100) [$M^{+\cdot}$], 1302 (20) [$M^{2+\cdot}$]. $C_{46}H_{66}O_2$ (650.5): calcd. C 84.87, H 10.22; found C 84.45, H 10.37.

(*E*,*E*)-2,5-Bis(2,5-dihexylstyryl)-1,4-benzoquinone and its Higher Oligomers (2a): A 13% aqueous solution of NaOCl (0.08 mL, 0.16 mmol), containing a drop of aliquat 336 (methyltrioctylammonium chloride) and 5 drops of 2 M HCl, was added slowly to a solution of **7** (24 mg, 0.04 mmol) in $CHCl_3$ (2.5 mL). After stirring for 15 min at room temperature, the mixture was diluted with $CHCl_3$ (10 mL) and water (5 mL). The organic phase was separated, washed with water and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure (1 kPa) furnished **2a** as a red oil (yield 24 mg, 100%) consisting of a mixture of monomeric, dimeric and trimeric species. Attempted separation of the mixture was unsuccessful and therefore only characterization by IR and MS is reported. IR (neat): $\tilde{\nu}$ = 2940 cm^{-1}, 2900, 2840, 1670, 1610, 1560, 1480, 1450, 1365, 1270, 1230, 1180, 960, 880, 820, 720. FD-MS: *m*/*z* (%) = 649.2 (100) [M + H]$^+$, 1298.2 (29) [M_2 + H]$^+$, 1946.7 (7) [M_3 + H]$^+$.

Preparation of the (*E*,*E*)-2,5-Bis(2,5-dialkoxystyryl)-1,4-dihexylbenzenes 8a and 8b

Bromomethylation of 1,4-Dihexylbenzene: A 33% solution of HBr in glacial acetic acid (11.3 mL, 63.8 mmol) was added dropwise to a suspension of 1,4-dihexylbenzene (5.23 g, 21.3 mmol) and paraformaldehyde (1.91 g, 63.8 mmol) in glacial acetic acid (45 mL). The mixture was stirred for 6 days at 95 °C, cooled to room temperature, diluted with water (200 mL) and extracted with diethyl ether (200 mL). The organic phase was neutralized with a saturated solution of $NaHCO_3$, dried with Na_2SO_4 and concentrated under vacuum (10^2 Pa). Column chromatography of the residue over silica gel (70−230 mesh, 4 × 15 cm) with petroleum ether (b.p. 40−70 °C) as eluent provided the monobromomethyl compound, a viscous oil, as the first fraction (yield 2.53 g, 35%) and the bis(bromomethyl) compound, a colorless solid with m.p. 69 °C, as the second fraction (yield 5.68 g, 62%).

2,5-Bis(bromomethyl)-1,4-dihexylbenzene: ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 6 H, CH_3), 1.33 (m, 12 H, CH_2), 1.60 (m, 4 H, CH_2), 2.65 (t, 4 H, CH_2), 4.48 (s, 4 H, CH_2Br), 7.13 (s, 2 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.6, 29.4, 30.8, 31.3, 31.7, 31.8 (CH_2), 131.8 (arom. CH), 135.9, 139.7 (arom. C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 434/432/430 (7) [$M^{+\cdot}$], Br_2 isotope pattern,

353/351 (24) [$M^{+\cdot}$ − Br], 283/281 (100), Br isotope pattern. $C_{20}H_{32}Br_2$ (432.3): calcd. C 55.57, H 7.46; found C 55.69, H 7.46.

2-Bromomethyl-1,4-dihexylbenzene: ^{1}H NMR ($CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.30 (m, 12 H, CH_2), 1.58 (m, 4 H, CH_2), 2.54 (t, 2 H, CH_2), 2.67 (t, 2 H, CH_2), 4.52 (s, 2 H, CH_2Br), 7.07 (m, 3 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.1 (CH_3), 22.6, 22.6, 29.0, 29.4, 31.0, 31.3, 31.7, 31.8, 32.0, 32.1, 35.4 (CH_2), 129.0, 129.6, 130.5 (arom. CH), 135.0, 139.0, 140.9 (arom. C_q) ppm. MS (EI, 70 eV): *m/z* (%) = 340/338 (5) [$M^{+\cdot}$] Br isotope pattern, 259 (19), 189 (100). $C_{19}H_{31}Br$ (339.4): calcd. C 67.25, H 9.21; found C 67.12, H 9.36.

Tetraethyl [2,5-Dihexyl-1,4-phenylenebis(methylene)]diphosphonate: 2,5-Bis(bromo-methyl)-1,4-dihexylbenzene (9.0 g, 0.02 mol) and triethylphosphite (10.4 mL, 0.06 mol) were heated for 4 h at 170 °C after which the excess triethylphosphite was removed under vacuum (10^2 Pa). The product was purified by column chromatography over silica gel (70−230 mesh, 4 × 20 cm) using ethyl acetate as eluent to provide the diphosphonate as a colorless liquid (yield 9.74 g, 85%). ^{1}H NMR ($CDCl_3$): δ = 0.85 (t, 6 H, CH_3), 1.22 (m, 24 H, CH_2 and CH_3 of OC_2H_5), 1.49 (m, 4 H, CH_2), 2.59 (t, 4 H, CH_2), 3.10 (d, $|^2J_{P,H}|$ = 20.5 Hz, 4 H, CH_2P), 3.94 (m, 8 H, OCH_2), 7.07 (d, $|^4J_{P,H}|$ = 1.5 Hz, 2 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 16.4 (CH_3 of OC_2H_5), 22.6, 29.4, 30.8, 31.8, 32.5 (CH_2), 30.1 (d, $|^1J_{C,P}|$ = 131.1 Hz, CH_2P), 62.0 (OCH_2), 128.0 (arom. CH), 131.7, 138.9 (arom. C_q) ppm. MS (EI, 70 eV): *m/z* (%) = 546 (100) [$M^{+\cdot}$], 489 (13). $C_{28}H_{52}O_6P_2$ (546.3): calcd. C 61.52, H 9.59; found C 61.71, H 9.34.

(*E*,*E*)-2,5-Bis[2,5-(diallyloxy)styryl]-1,4-dihexylbenzene (8a): A solution of tetraethyl [2,5-dihexyl-1,4-phenylenebis(methylene)]diphosphonate (0.44 g, 0.8 mmol) and 2,5-diallyloxybenzaldehyde (0.35 g, 1.6 mmol) in dry DME (9.0 mL) was added dropwise to a solution of sodium hydride [60% dispersion in mineral oil (0.58 g, 14.6 mmol)] in dry DME (5 mL) under argon. After stirring at room temperature for 5 h, water (10 mL) was added in portions. The precipitated product was isolated by filtration and the filtrate was then extracted with chloroform (50 mL). The organic phase was washed with water, brine and then dried with Na_2SO_4. Evaporation of the solvent under vacuum (10^2 Pa) yielded additional product. After drying under vacuum, **8a** was obtained as a yellow solid (yield 404 mg, 75%), m.p. 122 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (m, 6 H, CH_3), 1.33 (m, 12 H, CH_2), 1.61 (m, 4 H, CH_2), 2.73 (t, 4 H, CH_2), 4.54 (m, 8 H, OCH_2), 5.28 (m, 4 H, allyl CH_2), 5.42 (m, 4 H, allyl CH_2), 6.08 (m, 4 H, allyl CH), 6.75 (dd, 2 H, arom. H), 6.83 (d, 2 H, arom. H), 7.15 (d, 2 H, arom. H), 7.34 ("s", 4 H, olefin H), 7.42 (s, 2 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 29.4, 31.3, 31.8, 33.3 (CH_2), 69.5, 70.3 (OCH_2), 113.2, 117.2, 117.6, 128.5 (arom. CH), 114.2, 114.3 (allyl CH_2), 124.1, 135.4, 138.5, 150.7, 153.0 (arom. C_q), 126.8, 127.1 (olefin CH), 133.6, 133.7 (allyl CH) ppm. FD-MS: *m/z* (%) = 675 (100) [M + H]$^+$. $C_{46}H_{58}O_4$ (675.0): calcd. C 81.86, H 8.66; found C 81.85, H 8.75.

(*E*,*E*)-2,5-Bis(2,5-dimethoxystyryl)-1,4-dihexylbenzene (8b): A solution of the diphosphonate (3.2 g, 5.86 mmol) and 2,5-dimethoxybenzaldehyde (1.95 g, 11.7 mmol) in dry DMF (130 mL) was added dropwise to a solution of $KOC(CH_3)_3$ (6.57 g, 58.6 mmol) in dry DMF (100 mL) under argon at 0 °C. The mixture was stirred at room temperature for 3 h and then poured onto ice/water (200 mL) and 2 M HCl (15 mL). After extraction with dichloromethane (250 mL), the organic phase was washed with water (50 mL) followed by a saturated solution of $NaHCO_3$ and then dried with Na_2SO_4. The solvent was evaporated under vacuum (10^2Pa) and the product purified by column chromatography over silica gel (70−230 mesh, 4 × 50 cm) using a mixture of petroleum ether (b.p. 40−70 °C) and ethyl acetate (5:2) as eluent. Recrystallization from ethanol gave the product as yellow crystals (yield 2.10 g, 63%), m.p. 98 °C. ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, 6 H, CH_3), 1.32 (m, 8 H, CH_2), 1.40 (m, 4 H, CH_2), 1.62 (m, 4 H, CH_2), 2.74 (t, 4 H, CH_2), 3.82 (s, 6 H, OCH_3), 3.85 (s, 6 H, OCH_3), 6.78 (dd, 2 H, arom. H), 6.84 (d, 2 H, arom. H), 7.14 (d, 2 H, arom. H), 7.31/7.36 (AB, $^3J_{trans}$ = 16.1 Hz, 4 H, olefin H), 7.44 (s, 2 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 29.4, 31.4, 31.7, 33.3 (CH_2), 55.8, 56.4 (OCH_3), 112.3, 112.5, 113.3, 126.9, 127.2, 128.1 (arom. and olefin CH), 123.9, 135.4, 138.5, 151.7, 153.9 (arom. C_q) ppm. FD-MS: *m/z* (%) = 571 (100) [M + H]$^+$. $C_{38}H_{50}O_4$ (570.4): calcd. C 79.96, H 8.83; found C 79.89, H 8.73.

(*E*,*E*)-2,5-Bis(2,5-dihydroxystyryl)-1,4-dihexylbenzene (9a): A mixture of **8a** (600 mg, 0.89 mmol), sodium borohydride (133 mg, 3.5 mmol) and tetrakis(triphenylphosphane)palladium (41 mg, 0.04 mmol) in dry THF (100 mL) was stirred at room temperature for 2 days. The mixture was then poured into water (100 mL) and acidified with 2 M HCl (5 mL). After extraction with dichloromethane, the organic phase was washed with brine and dried with Na_2SO_4. The solvent was evaporated under vacuum (10^2 Pa) and the resulting residue purified by column chromatography over silica gel (70−230 mesh, 3 × 40 cm) using petroleum ether (b.p. 40−70 °C)/ethyl acetate (3:2) as eluent to give **9a** as a greenish solid (yield: 200 mg, 44%) m.p. >200 °C. ^{1}H NMR ([D_6]DMSO): δ = 0.84 (m, 6 H, CH_3), 1.29 (m, 12 H, CH_2), 1.52 (m, 4 H, CH_2), 2.71 (m, 4 H, CH_2), 6.52 (dd, 2 H, hydroquinone rings), 6.67 (d, 2 H, hydroquinone rings), 6.91 (br. s, 2 H, hydroquinone rings), 7.24 (br. "s", 4 H, olefin H), 7.40 (s, 2 H, arom. H), 8.76 (s, 2 H, OH), 9.07 (s, 2 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3), 22.0, 28.5, 30.9, 31.0, 32.4 (CH_2), 111.9, 115.6, 116.5, 124.5, 124.5, 126.1 (arom. and olefin CH), 124.3, 134.6, 137.8, 147.8, 149.9 (arom. C_q) ppm. FD-MS: *m/z* (%) = 515.0 (100) [M + H]$^+$. $C_{34}H_{42}O_4$ (514.3): calcd. C 79.34, H 8.22; found C 79.27, H 8.50.

2-[(*E*)-2-{4-[(*E*)-2-(2,5-Dioxocyclohexa-1,3-dien-1-yl)ethenyl]-2,5-dihexylphenyl}]ethenyl)-1,4-benzoquinone (3a): $MgSO_4$ (230 mg, 1.9 mmol) and freshly-prepared Ag_2O (183 mg, 0.8 mmol) were added to a solution of **9a** (100 mg, 0.19 mmol) in dry diethyl ether (15 mL). After stirring at room temperature overnight the solid particles were removed and washed several times with diethyl ether (80 mL). To preclude oligomerization, the solvent of the combined organic phases was removed immediately under vacuum (10^2 Pa) providing **3a** as a red solid (yield 100 mg, 100%), m.p. >200 °C. ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, 6 H, CH_3), 1.30 (m, 8 H, CH_2), 1.37 (m, 4 H, CH_2), 1.56 (m, 4 H, CH_2), 2.72 (t, 4 H, CH_2), 6.77 (dd, 2 H, benzoquinone ring), 6.80 (d, 2 H, benzoquinone ring), 6.86 (m, 2 H, benzoquinone ring), 7.04/7.72 (AB, $^3J_{trans}$ = 16.2 Hz, 4 H, olefin H), 7.45 (s, 2 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.6, 29.2, 31.6, 31.7, 33.2 (CH_2), 120.6, 136.6, 136.8, 140.1 (benzoquinone and arom. CH), 127.6, 127.8 (olefin CH), 134.9, 135.4, 142.1, 187.0, 187.7 (benzoquinone and arom. C_q) ppm. FD-MS: *m/z* (%) = 511 (100) [M + H]$^+$. $C_{34}H_{38}O_4$ (510.7): calcd. C 79.97, H 7.50; found C 79.77, H 7.61.

Oligomerization of 3a: A solution of monomeric **3a** (25 mg 0.05 mmol) in chloroform (25 mL) was allowed to stand overnight. Analysis by FD-MS revealed indicative peaks (as the protonated species) for a series of oligomers of **3a** (n = 1−4).

***rel*-(4a*S*,4b*R*,8a*S*,9*R*)-9-(2,5-Dimethylphenyl)-8a-[(*E*)-2-(2,5-dimethylphenyl)ethenyl]-4a,4b,8a,9-tetrahydrophenanthrene-1,4,5,8-tetrone (*rac*-10a):** Compound **1a** (500 mg, 2.1 mmol) in chloroform

(50 mL) was kept at room temperature for 4 days. The solution was concentrated under vacuum (10^2 Pa) followed by the addition of a mixture of petroleum ether (b.p. 40−70 °C)/ethyl acetate (5:2) which caused the precipitation of pure **10a** as a yellow solid (yield 840 mg, 84%), m.p. 152 °C. ^{1}H NMR ($CDCl_3$):[24] δ = 2.11 (s, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 3.47 (m, 1 H, 4a-H), 4.07 (d, ^3J = 4.3 Hz, 1 H, 4b-H), 4.48 (t, ^3J = ^5J = 3.5 Hz, 1 H, 9-H), 6.00/6.27 (AB, ^3J = 10.6 Hz, 2 H) and 6.96/7.02 (AB, ^3J = 10.6 Hz, 2 H) [2-H/3-H and 6-H/7-H], 6.37/6.75 (AB, $^3J_{trans}$ = 16.4 Hz, 2 H, olefin H), 6.40 (br. s, 1 H), 6.89 (dd, 1 H), 6.96 (d, 1 H), 7.02 (m, 2 H), 7.29 (br. s, 1 H, arom. H), 7.02 (m, 1 H, 10-H) ppm. ^{13}C NMR ($CDCl_3$):[24] δ = 19.4, 19.7, 20.8, 20.9 (CH_3), 42.9, 43.0 (C-4a, C-9), 53.4 (C-4b), 59.1 (C-8a), 126.6, 129.0, 129.1, 130.4, 131.8, 132.0 (arom. CH), 129.9, 132.1 (olefin CH), 131.7 (C-10a), 132.5, 133.0, 134.7, 135.8, 135.9, 136.0 (arom. C_q), 137.8 (C-10), 138.8, 140.3, 140.6, 142.3 (C-2, C-3, C-6, C-7), 184.1 (C-1), 194.3, 195.2, 198.1 (C-4, C-5, C-8) ppm. FD-MS: *m*/*z* (%) = 477 (100) $[M + H]^+$. $C_{32}H_{28}O_4$ (476.6): calcd. C 80.65, H 5.92; found C 80.68, H 5.56.

The dimers ***rac*-10b** and ***rac*-10c** were prepared as described previously.[13] The compound ***rac*-10d** was not isolated and was directly transformed into ***rac*-11d**.

***rel*-(1*S*,8*S*,13*R*,14*R*,15*R*,16*R*)-14,15-Bis(2,5-dimethylphenyl)pentacyclo[6.6.2.0^{2,7}.0^{8,13}.0^{13,16}]hexadeca-2(7),4,10-triene-3,6,9,12-tetrone (*rac*-11a):** Column chromatography of the crude dimer **10a** (160 mg) over silica gel (70−230 mesh, 3 × 70 cm) with petroleum ether (b.p. 40−70 °C)/ethyl acetate (5:2) provided **11a**, a viscous oil, as the first fraction (yield 39 mg, 24%). ^{1}H NMR ($CDCl_3$): δ = 1.98 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3) 2.40 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 2.92 (br. s, 1 H, 16-H), 3.93 (dd, ^3J = 4.7, ^3J = 2.3 Hz, 1 H, 15-H), 4.34 (t, ^3J = 4.7 Hz, 1 H, 1-H), 4.42 (d, ^3J = 4.7 Hz, 1 H, 14-H), 6.14/6.52 (AB, ^3J = 10.2 Hz, 2 H) and 6.76/6.92 (AB, ^3J = 10.6 Hz, 2 H) [4-H/5-H and 10-H/11-H], 6.17 (br. s, 1 H), 6.68 (br. s, 1 H), 6.75 (m, 1 H), 6.88 (m, 2 H), 6.95 (d, 1 H) [arom. H] ppm. ^{13}C NMR ($CDCl_3$): δ = 18.9, 19.0, 20.7, 21.2 (CH_3), 36.4, 40.6, 43.3, 44.3 (C-1, C-14, C-15, C-16), 38.9, 46.0 (C-8, C-13), 126.7, 127.9, 128.1, 128.2, 130.5, 130.7 (arom. CH), 132.1, 132.8, 132.9, 133.7, 135.0, 135.6, 138.1, 138.3 (C-2, C-7 and arom. C_q), 134.7, 137.0, 138.8, 139.0 (C-4, C-5, C-10, C-11), 181.8, 182.8, 189.1, 190.6 (C-3, C-6, C-9, C-12) ppm. FD-MS: *m*/*z* (%) = 474 (100) $[M^{+\cdot}]$. $C_{32}H_{26}O_4$ (474.6): calcd. C 80.99, H 5.52; found C 80.73, H 5.49.

The preparation of the polycyclic compounds ***rac*-11b** and ***rac*-11c** has been described previously.[13]

***rel*-(1*S*,8*S*,13*R*,14*R*,15*R*,16*R*)-14,15-Bis(2,5-dipropoxyphenyl)-pentacyclo[6.6.2.0^{2,7}.0^{8,13}.0^{13,16}]-hexadeca-2(7),4,10-triene-3,6,9,12-tetrone (*rac*-11d):** Na_2SO_4 (50 mg, 3.5 mmol) and freshly-prepared Ag_2O (92.7 mg, 0.4 mmol) were added to a solution of **5d** (100 mg, 0.3 mmol) in dry THF (20 mL). After stirring for 1 h at room temperature, the solid particles were removed and washed with THF (80 mL) several times. The solvent of the combined organic phases was then removed under vacuum (10^2 Pa). Column chromatography of the residue over silica gel (70−230 mesh, 3 × 70 cm) using petroleum ether (b.p. 40−70 °C)/ethyl acetate (5:2) as eluent furnished **11d** as a viscous oil (yield 31 mg, 16%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3 H, CH_3), 0.96 (t, 3 H, CH_3), 1.12 (m, 6 H, CH_3), 1.59 (m, 4 H, CH_2), 1.68 (q, 2 H, CH_2), 1.90 (m, 2 H, CH_2), 2.86 (br. s, 1 H, 16-H), 3.52 (m, 2 H, OCH_2), 3.77−3.98 (m, 6 H, OCH_2), 4.10 (dd, ^3J = 4.7, ^3J = 2.3 Hz, 1 H, 15-H), 4.55 (d, ^3J = 4.5 Hz, 1 H, 14-H), 4.59 (t, ^3J = 4.5 Hz, 1 H, 1-H), 5.95 (d, 1 H, arom. H), 6.17/6.51 (AB, ^3J = 10.3 Hz, 2 H) and 6.74/6.89 (AB, ^3J = 10.6 Hz, 2 H) [4-H/5-H and 10-H/11-H], 6.45 (d, 1 H, arom. H), 6.54 (dd, 1 H, arom. H), 6.61 (d, 1 H, arom. H), 6.65 (m, 2 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.4, 10.8 (CH_3), 22.5, 22.6, 22.9 (CH_2), 37.5, 38.0, 41.9, 43.0 (C-1, C-14, C-15, C-16), 38.9, 45.6 (C-8, C-13), 70.3, 70.4 (OCH_2), 112.3, 112.5, 113.7, 114.4, 114.7, 115.0 (arom. CH), 124.2, 125.6, 137.9, 139.5, 151.0, 151.1, 152.5, 152.7 (C-2, C-7 and arom. C_q), 135.0, 136.9, 138.7, 139.1 (C-4, C-5, C-10, C-11), 182.0, 182.9, 189.4, 190.6 (C-3, C-6, C-9, C-12) ppm. MS (EI, 70 eV): *m*/*z* (%) = 652 (100) $[M^{+\cdot} + 2H]$, 650 (83) $[M^{+\cdot}]$. $C_{40}H_{42}O_8$ (650.8): calcd. C 73.83, H 6.51; found C 73.64, H 6.48.

Simultaneous Transformation of *rac*-10a into *rac*-12a,b: Compounds **12a,b** were primarily obtained by column chromatography of **10a** (70 mg) over silica gel (70−230 mesh, 3 × 70 cm) using chloroform (contaminated with small amounts of ethanol and water)/ethyl acetate (5:1) as eluent. The ethanol adduct **12b** was obtained as the first fraction (yield 32 mg, 40%) and the water adduct **12a** as the second fraction (yield 26 mg, 35%).

***rel*-(8a*S*,9*R*,10*R*)-9-(2,5-Dimethylphenyl)-8a-[(*E*)-2-(2,5-dimethylphenyl)ethenyl]-8a*H*-9,10-dihydro-1,4,5,10-tetrahydroxyphenanthren-8-one (*rac*-12a):** An increased yield of the water adduct **12a** was accomplished by eliminating possible formation of the ethanol adduct **12b**. Column chromatography of **10a** (90 mg) over silica gel (70−230 mesh, 3 × 50 cm) with dichloromethane/ethyl acetate (5:1) as eluent delivered exclusively **12a** as a yellow solid (yield 52 mg, 58%), m.p. 142 °C. ^{1}H NMR ($C_2D_2Cl_4$): δ = 1.80 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.64 (d, ^3J = 9.2 Hz, 1 H, OH attached to C-10), 4.36 (br. s, 1 H, 9-H), 4.81 (d, ^3J = 9.2 Hz, 1 H, 10-H), 5.62/6.70 (AB, ^3J = 10.2 Hz, 2 H, 6-H/7-H), 6.27/6.39 (AB, $^3J_{trans}$ = 16.0 Hz, 2 H, olefin H), 6.57 (br. s, 1 H, arom. H), 6.76/6.86 (AB, ^3J = 8.6 Hz, 2 H, 2-H/3-H), 6.81 (d, 1 H, arom. H), 6.84 (m, 2 H, arom. H), 6.91 (d, 1 H, arom. H), 6.99 (s, 1 H, OH attached to C-1), 7.14 (br. s, 1 H, arom. H), 8.42 (br. s, 1 H) and 8.51 (br. s, 1 H) [OH attached to C-4, C-5] ppm. ^{13}C NMR ($C_2D_2Cl_4$): δ = 19.0, 20.5, 21.3, 21.5 (CH_3), 53.6 (C-9), 57.4 (C-8a), 71.9 (C-10), 116.5, 122.0, 124.5 (C-4a, C-4b, C-10a), 117.5, 118.0 (C-2, C-3), 125.7 (C-7), 126.1, 128.3, 128.3, 129.3, 130.5, 130.6 (arom. CH), 132.2, 133.4 (olefin CH), 132.9, 132.9, 135.1, 135.4, 136.1, 137.2 (arom. C_q), 144.6 (1 C, C-6), 144.8, 146.5, 150.9 (C-1, C-4, C-5), 201.4 (C-8).[24] FD-MS: *m*/*z* (%) = 477 (100) $[M - OH]^+$. $C_{32}H_{30}O_5$ (492.6): calcd. C 77.71, H 6.11; found C 77.57, H 6.03.

***rel*-(8a*S*,9*R*,10*R*)-9-(2,5-Dimethylphenyl)-8a-[(*E*)-2-(2,5-dimethylphenyl)-ethenyl]-10-ethoxy-8a*H*-9,10-dihydro-1,4,5-trihydroxyphenanthren-8-one (*rac*-12b):** A solution of **10a** (50 mg, 0.1 mmol) in chloroform (5 mL) together with ethanol (5 mL, 3.93 g, 85 mmol) and a small amount of silica gel (70−230 mesh) was stirred at room temperature for 2 h. After filtration, the solvents were evaporated under vacuum (10^2 Pa) and the product purified from traces of the water adduct **12a** by column chromatography over silica gel (70−230 mesh, 3 × 20 cm) with chloroform/ethyl acetate (5:1). Compound **12b** was obtained as a yellow solid (yield 41 mg, 82%), m.p. 147 °C. ^{1}H NMR ($CDCl_3$): δ = 1.32 (t, 3 H, CH_3 of OC_2H_5), 1.87 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 3.56 (m, 1 H, OCH_2), 4.05 (m, 1 H, OCH_2), 4.42 (br. s, 1 H, 9-H), 4.64 (br. s, 1 H, 10-H), 5.57/6.67 (AB, ^3J = 9.8 Hz, 2 H, 6-H/7-H), 6.16/6.30 (AB, $^3J_{trans}$ = 16.0 Hz, 2 H, olefin H), 6.59 (br. s, 1 H, arom. H), 6.76/6.83 (AB, ^3J = 8.6 Hz, 2 H, 2-H/3-H), 6.85 (m, 3 H, arom. H), 6.95 (d, 1 H, arom. H), 7.10 (br. s, 1 H, arom. H), 7.47 (s, 1 H, OH attached to C-1), 8.12 (br. s, 2 H, OH attached to C-4, C-5) ppm. ^{13}C NMR ($CDCl_3$):

δ = 15.5 (CH_3 of OC_2H_5), 18.9, 19.9, 20.9, 21.0 (CH_3), 48.3 (C-9), 57.2 (C-8a), 64.4 (OCH_2), 80.4 (C-10), 116.8, 122.1, 122.7 (C-4a, C-4b, C-10a), 117.0, 117.8 (C-2, C-3), 125.0 (C-7), 126.5, 127.9, 128.0, 128.8, 129.7, 130.3 (arom. CH), 130.5, 134.3 (olefin CH), 132.0, 132.2, 135.0, 135.3, 136.2, 137.3 (arom. C_q), 144.2, 146.0, 151.3 (C-1, C-4, C-5), 144.4 (1 C, C-6), 201.7 (C-8).[24] FD-MS: *m/z* (%) = 477 (100) $[M - C_2H_5O]^+$, 523 (29) $[M^{+\cdot}]$, 953 (32) $[(M - C_2H_5OH)^{2+}]$. $C_{34}H_{34}O_5$ (522.5): calcd. C 78.14, H 6.56; found C 77.90, H 6.35.

***rel*-(8a*S*,9*R*,10*R*)-9-(2,5-Dihexylphenyl)-8a-[(*E*)-2-(2,5-dihexylphenyl)ethenyl]-8a,9,10-trihydro-1,4,5,10-tetrahydroxyphenanthrene-8-one (*rac*-12c):** Column chromatography of **10b** (200 mg) over silica gel (70−230 mesh, 3 × 70 cm) with petroleum ether (b.p. 40−70 °C)/diethyl ether (5:2) provided ***rac*-11b** as a viscous oil (38 mg, 19%). Increasing the solvent ratio to 5:3 then furnished **12c** as a viscous oil which was obtained as a yellow solid (yield 32 mg, 16%; m.p. 104 °C) after petroleum ether-induced precipitation from solution. ^{1}H NMR ($CDCl_3$): δ = 0.85 (m, 12 H, CH_3), 1.13−1.56 (m, 32 H, CH_2), 2.17 (m, 2 H, CH_2), 2.31 (t, 2 H, CH_2), 2.42 (d, ^3J = 11.2 Hz, 1 H, OH attached to C-10), 2.50 (t, 3 H, CH_2), 3.15 (m, 1 H, CH_2), 4.47 (s, 1 H, 9-H), 4.79 (d, ^3J = 11.2 Hz, 1 H, 10-H), 5.69/6.70 (AB, ^3J = 10.0 Hz, 2 H, 6-H/7-H), 6.42/6.48 (AB, $^3J_{trans}$ = 16.1 Hz, 2 H, olefin H), 6.61 (br. s, 1 H, arom. H), 6.86/6.91 (AB, ^3J = 8.8 Hz, 2 H, 2-H/3-H), 6.89 (m, 1 H, arom. H), 6.94 (m, 2 H, arom. H), 6.99 (d, 1 H, arom. H), 7.15 (br. s, 1 H, arom. H), 7.39 (br. s, 1 H), 8.28 (br. s, 1 H) [OH attached to C-4, C-5] ppm. ^{13}C NMR ($CDCl_3$): δ = 13.9, 14.0 (CH_3), 22.4, 22.5, 22.6, 28.7, 28.9, 29.0, 29.2, 30.8, 31.0, 31.4, 31.5, 31.6, 31.6, 31.7, 32.5, 32.9, 35.4, 35.5 (CH_2, partly superimposed), 52.7 (C-9), 57.0 (C-8a), 71.6 (C-10), 115.1, 121.5, 124.6 (C-4a, C-4b, C-10a), 117.3, 117.8 (C-2, C-3), 125.7 (C-7), 125.8, 127.2, 127.4, 128.0, 129.2, 129.5 (arom. CH), 132.5, 133.4 (olefin CH), 134.4, 136.2, 137.4, 137.9, 140.0, 140.7 (arom. C_q), 143.4, 146.4, 151.6 (C-1, C-4, C-5), 144.0 (C-6), 200.1 (C-8) ppm.[24] FD-MS: *m/z* (%) = 757 (100) $[M^{+\cdot} - H_2O]$. $C_{52}H_{70}O_5$ (775.1): calcd. C 82.49, H 9.05; found C 82.05, H 9.40.

Comparison of Thermal and Photochemical Dimerizations: A solution of quinone **1a** (7.0 mg, 0.03 mmol) in 0.6 mL of C_6D_6 was irradiated for 30 min at 60 °C using a 300 W halogen lamp equipped with a UV filter (λ ≥ 410 nm). For reference, a similar solution was kept for 30 min at 60 °C in the dark. Analysis by ^{1}H NMR spectroscopy showed the formation of ***rac*-10a** (84%) and some side products in the photochemical experiment and 10% of ***rac*-10a** in the thermal experiment (together with 90% of the starting material).

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