Analogs of Michler's ketone for two-photon absorption initiation of polymerization in the near infrared: synthesis and photophysical properties

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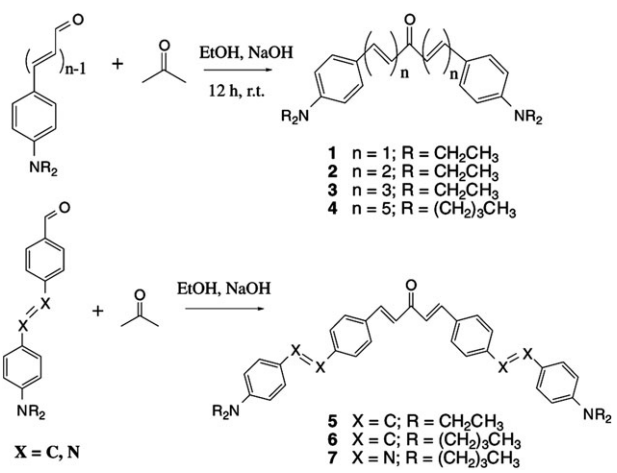
We present the synthesis of substituted ketones, conjugated analogs of Michler's ketone. These molecules exhibit broadband TPA properties between 700 and 1100 nm due to a charge transfer from the terminal amino groups to the central ketone function and with maximum cross sections from 200 to 325 $\times$ 10^{-50} cm^4 s $photon^{-1}$. Moreover, they present an interesting reducing character for radical creation. Both properties allow us to consider these molecules as promising photoinitiators of polymerization in the near infrared.

Introduction

Recently, two-photon absorption (TPA) in organic materials has been intensively studied in view of applications for optical power limiting,[1] photodynamic therapy,[2] three-dimensional optical data storage,[3] fluorescence imaging,[4] and microfabrication.[5] The three latter techniques take advantage of the high spatial resolution of two-photon excitation. TPA initiated polymerization (cationic radical photopolymerization[6]) is an interesting method for the 3D microfabrication and appears as a complementary technique to the well known layer-by-layer fabrication.[7] The quadratic dependence of TPA as a function of light intensity, limits the absorption process to the immediate vicinity of the focal point and has led to 3D micro-objects in a single step with a very high resolution.[8]

Two types of photo-initiator were used for TPA induced polymerization: (i) commercial UV-visible photoinitiators,[9] (ii) electron-rich molecules optimized for TPA and using Ti-sapphire with ultra-short pulses (around 100 femtoseconds) between 700 and 1000 nm.[5a,10] In order to enlarge the wavelength range for TPA microfabrication, Nd:YAG lasers were also used for this technique. Using the second harmonic at 532 nm of a Nd:YAG microlaser, weakly conjugated, compared to molecules used for the near IR, (biphenyl or fluorene derivatives[11]) TPA initiators were studied for 3D microfabrication. The engineering on TPA initiators in this range is emerging.[12]

This paper concerns molecular engineering for two-photon initiators in near infrared (700–1000 nm). Molecules **1**–**7** (Scheme 1), analogs of Michler's ketone (4,4′-bis(*N*,*N*-dimethylamino)benzophenone), which is a well-known initiator for conventional radical UV polymerization, have shown to be efficient TPA photoinitiators for polymerization at the fundamental wavelength of the Nd:YAG laser (1064 nm):[13] some figures of merit (minimum laser intensity and absorbed density energy to the polymerization threshold) were measured in order to quantify the phenomenon.[13b] These molecules fulfil required conditions to induce TPA radical polymerization: they present a D–π–A–π–D structure (where D is the donor amine function, A the acceptor ketone group and π the conjugated bridge), suitable for efficient TPA properties; furthermore, the amine function, at each end of the molecule, could be used as an electron donor to the monomer to initiate the polymerization mechanism (see for example this well-known mechanism in ref. 11*b*). The main goal of the present work is to show the interest of these molecules for TPA photopolymerization in the wide range of wavelengths between 700 and 1000 nm, since the tunable conjugation path in molecules of this family, polyenic of variable length (**1**–**4**), stilbenic (**5**, **6**) and azo systems in **7**, allow us to expect a TPA



Scheme 1

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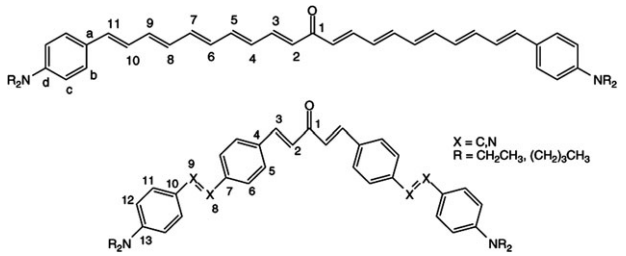


Fig. 1 General atom numbering for NMR description of new molecules.

efficiency in this wavelength range. In this paper, we present the synthesis and the photophysical properties of molecules **1–7**. Linear and two-photon absorption properties and electrochemical properties will be discussed as a function of the conjugation of the molecule.

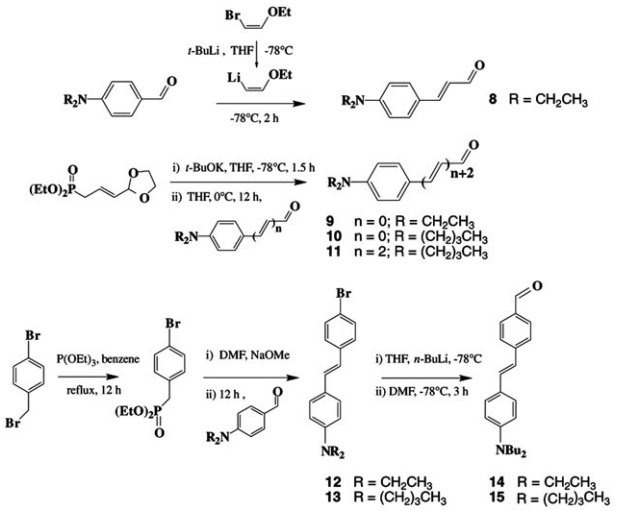
Results and discussion

Synthesis

Ketones **1–7** are obtained *via* a crossed aldol condensation starting from propanone and the corresponding aldehyde (Scheme 1). No chemoselectivity problem was observed, due to the purely nucleophilic character of the propanone in this reaction and the non-enolisable character of the implied aldehydes. The structure and stereochemistry of polyenal **2** were studied by ^{1}H NMR spectroscopy using phase sensitive COSY DQF and 2D-*J* resolved sequences: at 500 MHz, both sequences allowed the identification of the protons of most of the polyenic chains (according to atom numbering represented Fig. 1) and the determination of the coupling constants. The all *trans* configuration was confirmed by the $^{3}J_{CH=CH}$ values in the range 15.0 to 15.7 Hz and $^{3}J_{CH-CH}$ in the order of 11 Hz. As already reported in the literature,[14] odd protons are downfield shifted with respect to their even counterparts (*e.g.* δ H_5 6.86 *vs.* H_4 6.73 ppm in ketone **2**).

Starting aldehydes used in the synthesis of ketones **1–7** (Scheme 1) were synthesized following the procedure described in Scheme 2. The lower polyenal 3-(4-diethylamino-phenyl)-propenal **8** (Scheme 2) was obtained according to a slightly modified procedure described in the literature,[15] using commercial (*Z*)-1-bromo-2-ethoxy-ethene in presence of *t*-BuLi and 4-diethylamino-benzaldehyde.

Preparation of compounds (*E*,*E*)-5-[4-(diethylamino) phenyl]penta-2,4-dienal, **9**, (*E*,*E*)-5-[4-(dibutylamino)phenyl] penta-2,4-dienal, **10** and (*E*,*E*,*E*,*E*)-9-(4-dibutylamino-phenyl)-nona-2,4,6,8-tetraenal), **11** was achieved according to Horner–Wadsworth–Emmons reactions, starting from the (3-[1,3]dioxolan-2-yl-allyl)-phosphonic acid diethyl ester[16] and corresponding aldehydes (4-(diethylamino)benzaldehyde, 4-(dibutylamino)benzaldehyde and (*E*,*E*)-5-[4-(dibutylamino)-phenyl]penta-2,4-dienal, **10**, for **9**, **10** and **11**, respectively: Scheme 2). The synthesis of this type of aldehyde has been previously published by successive additions of one double bond *via* a Wittig reaction.[17] (*E*)-{4-[2-(4-Bromophenyl)vinyl]-phenyl}diethylamine **12** and the dibutyl analog (*E*)-{4-[2-(4-bromophenyl)vinyl]phenyl}dibutylamine **13** were similarly



Scheme 2

obtained starting from the corresponding aldehydes and (4-bromo-benzyl)-phosphonic acid diethyl ester, this last being synthesized according to an Arbuzov reaction starting from commercial 1-bromo-4-bromomethylbenzene and triethyl phosphite.[18]

On reaction with *n*-BuLi in DMF **12** and **13** gave the corresponding aldehydes (*E*)-4-[2-(4-diethylaminophenyl) vinyl]benzaldehyde **14** and (*E*)-4-[2-(4-dibutylaminophenyl) vinyl]benzaldehyde **15**, respectively. As far molecule **7** is concerned, the synthesis of starting [4-(4-bromo-phenylazo)-phenyl]-dibutyl-amine and 4-(4-dibutylamino-phenylazo)-benzaldehyde has already been described.[19]

Linear absorption

Linear absorption spectra of molecules **1–4**, and **5** and **7** are reported in Fig. 2 and Fig. 3, respectively.

Polyenic molecules **1–4** present a charge transfer (CT) S_0–S_1 transition at long wavelengths: AM1 quantum calculations have shown that the lowest transition in these systems is a HOMO–LUMO type consisting of a transition from amine functions towards the ketone group.

The bathochromic shift when the polyenic chain is increased (from 456 nm for **1** to 540 nm for **4** as reported on Table 1) due to an enhancement of the CT effect in the longest molecules.

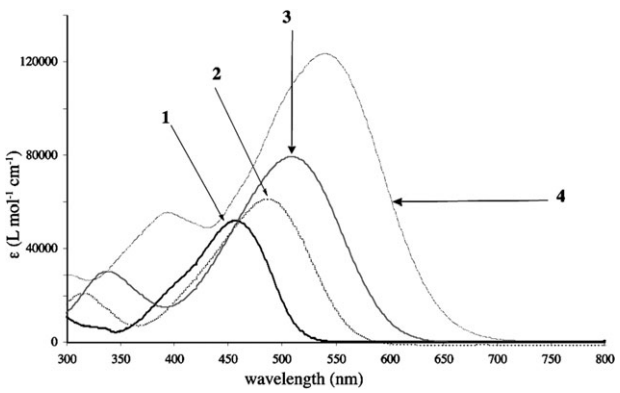


Fig. 2 UV-Vis absorption spectra of ketones **1–4** in chloroform.

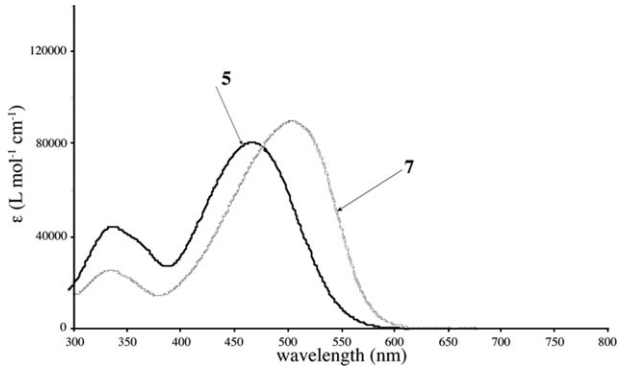


Fig. 3 UV-Vis absorption spectra of ketones **5**, **7** in chloroform.

Table 1 Physico-chemical properties of molecules **1–5** and **7**: linear absorption (maximum absorption wavelength λ_{abs}^{max}; molar extinction coeffcient ε_{max}), TPA (maximum TPA wavelength λ_{TPA}^{max}; maximum TPA cross-section σ_{TPA}^{max}) and electrochemical (anodic potential, E_{ap}) properties

Molecule	λ_{abs}^{max}/nm	ε_{max}/ M^{-1} cm^{-1}	λ_{TPA}^{max}/ nm	σ_{TPA}^{max} / cm^4 s photon^{-1}	E_{ap}/mV
1	456	52 300	800	250.10^{-50}	460
2	486	61 300	900	325.10^{-50}	260
3	509	79 500	950	200.10^{-50}	170
4	540	123 500	—	—	130
5	466	81 000	900	200.10^{-50}	170
7	503	90 100	—	—	520

Variations of the maximum absorption wavelength with respect to the number n of double bonds are displayed in Fig. 4 (n = 0 corresponds to Michler's ketone itself): a saturation effect is observed for the longest molecules.

Stilbenic and azobenzene molecules **5** and **7** present also a main band in the visible (Fig. 3) with a bathochromic shift in the case of **7** (466 and 503 nm, respectively) consistent with the increased donor character due of the azo function. The maximum wavelength of **5** is located between that of **1** and **2**, while a similar or longer charge transfer than that of **3** could be expected: a lower planarity in the case of **5**, confirmed by an AM1 quantum geometry optimization and which is assumed to be due to the aromatic character of the benzyl rings, could explain this trend.

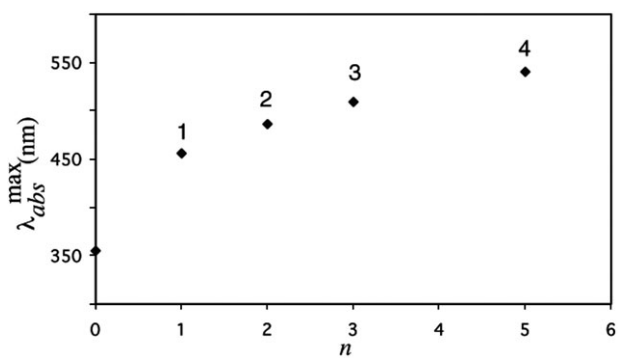


Fig. 4 Maximum absorption wavelength with respect to the number, n, of double bonds in ketones **1–4**.

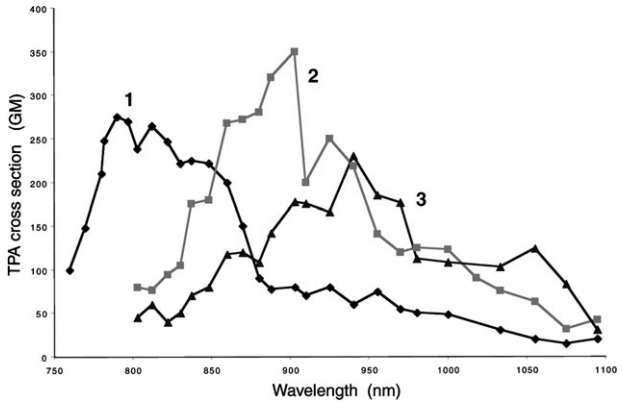


Fig. 5 Two-photon excitation spectra of molecules **1–3** in chloroform: diamonds, rectangles and triangles represent experimental points for molecules **1**, **2** and **3**, respectively.

Two-photon absorption

Two-photon excitation spectra of molecules **1–3** and **5** are shown in Fig. 5 and 6, respectively, and maxima of the bands are reported in Table 1. TPA efficiencies of molecules **4** and **7** could not be measured by our technique due to the weak fluorescence yields of these molecules.

Two-photon excitation spectra of molecules **1–3** present two bands (Fig. 5): (i) a long wavelength band at around 950, 1000 and 1050 nm, respectively, which could be ascribed to the S_0–S_1 transition, since it peaks nearly at a wavelength twice to that observed in linear absorption (456, 486 and 509 nm respectively, see Table 1); (ii) a higher band at shorter wavelengths (800, 900 and 950 nm, respectively) corresponding to a purely allowed two-photon transition. The observation of both bands arises from the non-centrosymmetry of the molecules, which allows both types of transitions. As for linear properties, the position of the short wavelength band presents a bathochromic shift with the increase of the polyenic chain. The TPA maximum efficiency was obtained for the molecule **2** (325.10^{-50} cm^4 s photon^{-1} or 325 GM).

The molecule **5** presents a similar structure in its TPA spectrum to that observed for molecules **1–3**, with a maximum of 200×10^{-50} cm^4 s photon^{-1} at nearly 900 nm (Fig. 6). In

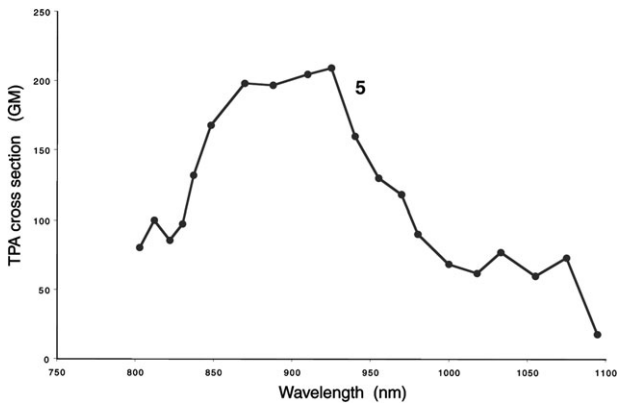


Fig. 6 Two-photon excitation spectra of molecule **5** in chloroform. Circles represent experimental points.

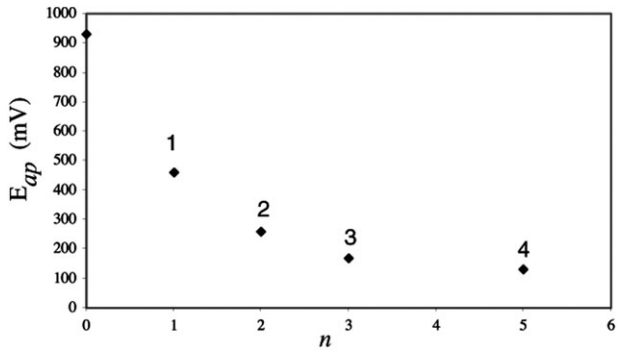


Fig. 7 Variations of E_{ap} with the number, n, of double bonds in molecules **1–4**.

good agreement with the linear properties (λ_{max} = 466 nm), TPA peaks are located between those of **1** and **2**.

In the light of Fig. 5 and 6, a tunable laser between 700 and 1000 nm could be used to excite the two-photon states of these molecules. The efficient excitation wavelength of the laser varies following the conjugation of the molecule: between 750 and 870 nm for **1**, 830 and 1000 nm for **2** and 850 and 1000 nm for **3** and **5**.

Electrochemical properties

The radicular photopolymerization is initiated by a mono-electronic transfer from the excited initiator to the monomer. Electrochemical properties, such as redox or anodic potentials, reflect the reducing properties of molecules. Redox potentials of molecules **1–5** and **7** could not be determined due to the irreversibility of the cycle of redox in cyclic voltammetry experiments. The electro-donating properties of these molecules were characterized by their anodic potential E_{ap} with respect to the Ag/Ag^+ potential: this parameter varies with the reducing properties of molecules. Values of E_{ap} are reported in Table 1. In agreement with mechanisms proposed in literature,[9b,20] the aromatic amine function is expected to be oxidized first in this type of molecule. In the case of molecules **1–4**, variations of E_{ap} with the number n of double bonds in molecules are displayed in Fig. 7 (the point at n = 0 corresponds the value obtained for Michler's ketone).

The value of E_{ap} decreases when the number of double bonds is increased with a convergence effect at 100 mV. This trend confirms the close relationship between the conjugation of molecules (or their number of electrons) and their reducing properties. The anodic potential of molecule **7** is significantly higher than that of its stilbenic analog **5**.

All these molecules present an anodic potential which is largely weaker than that measured for Michler's ketone itself and also have reducing properties higher than this reference molecule.

Conclusion

We present in this paper the synthesis of conjugated analogs of Michler's ketone. These ketones present wide TPA spectra in the near infrared between 750 and 1100 nm, with a bathochromic shift when the conjugation is increased: this family allows coverage of the whole range of wavelengths accessible with femtosecond tunable lasers, between 700 and 1000 nm. Moreover, the reducing properties of these molecules were studied through the determination of their anodic potential, showing that all systems present higher reducing properties than Michler's ketone. Anodic potential low values, which decrease with the conjugation of the molecule, were obtained for this family: this shows the ability of these molecules to give an electron from the donor group and create a radical. Combined TPA and reducing properties of these chromophores makes them a family of potential photoinitiators for polymerization in the near infrared.

Although the ability of **3** to induce TPA polymerization at a wavelength (910 nm) other than 1064 nm was already demonstrated by the design of micro-components for integrated optics,[13c] the measurement of the absorbed energy density (number of molecules in the excited state) required for the polymerization threshold is in progress for molecules **1–7**, in order to quantify more deeply the TPA photoinitiation properties of this family.

Experimental

TPA measurements

TPA spectra were obtained by up-conversion fluorescence measurements using a Nd:YAG laser pumped optical parametric oscillator supplying 2.6 ns pulses in the 780–1120 nm spectral range with a 10 Hz repetition rate. The fluorescence signal is detected by a fibre optic CCD Spectrometer. The pulse energy was kept low enough to ensure a quadratic dependence of the fluorescence signal on input energy. The TPA cross-section was determined from 2.10^{-3} mol L^{-1} solutions in chloroform of molecules, using the reference TPA cross-section of 210 GM at 840 nm for Rhodamine B in methanol as reported in Table 2 of ref. 21. For each of our compounds, fluorescence efficiencies, including the concentration dependent self-quenching, were taken into account by comparison with the one-photon fluorescence that was obtained at visible wavelengths in the same excitation and collection geometry.

Electrochemistry measurements

Electrochemical studies were performed using a Princeton Applied Research Model 173 potentiostat in a dry box (Jaram, <1 ppm O_2, H_2O) under an argon atmosphere. Cyclic voltammetry was carried out in CH_3CN using a 0.1 M tetrabutylammonium perchlorate supporting electrolyte. A conventional three electrode cell was used with a platinum disc (5 mm) as working electrode. Potentials are given relative to Ag/Ag^+ 10 mM in CH_3CN as the reference electrode.

Syntheses

Tetrahydrofuran and *N*,*N*-dimethylformamide solvents were distilled and dried over sodium and CaH_2, respectively before use. Thin-layer chromatography was carried out on Merck Kieselgel $60F_{254}$, precoated on alumina silica gel plates. Preparative flash chromatography was performed on Merck Gerduran 60. ^1H and ^{13}C NMR spectra were recorded on a

Bruker DPX 200 spectrometer (at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C) and also on a Varian Unity Plus at 499.84 MHz for ^{1}H. Chemical shifts δ are given in ppm. Elemental analysis were carried out by the Service Central d'Analyse, CNRS. UV-Vis spectra were recorded in the 200–800 nm range on a UV-Vis Jasco V-550; λ_{max} are given in nm and molar extinction coefficients, ε, in L mol^{-1} cm^{-1}. Melting temperatures, mp, were measured on a Perkin-Elmer DSC7 micro-calorimeter.

(*E*)-3-(4-[Diethylamino)phenyl]propenal (8). *tert*-Butyllithium (1.7 M in pentane, 11.5 mL, 17 mmol) was dropwise added under argon to commercial (*Z*)-1-bromo-2-ethoxyethylene (1.9 mL, 8.5 mmol) in solution in 11.5 mL of anhydrous THF at −78 °C and the reaction mixture was stirred for 40 min. This was followed by addition of 4-(diethylamino)benzaldehyde (1.4 g, 8 mmol). The resulting solution was stirred for 2 h at −78 °C before being hydrolysed in 30 min at 0 °C, by adding 5 mL of aqueous 1 M HCl. The reaction mixture was rendered basic (pH = 9) with 5 M aqueous sodium hydroxide and the organic material was extracted with diethyl ether. The ether layer was washed with brine, dried over Na_2SO_4, and evaporated to dryness after filtration. The crude product was then column chromatographed (diethyl ether–pentane 50 : 50) to give 1.1 g of the desired yellow compound **8** (68% yield): mp = 72 °C (lit:[22] 73 °C); ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 9.56 (d, $J_{1,2}$ = 7.9 Hz, 1H, CHO), 7.41 (d, $J_{b,c}$ = 9.1 Hz, 2H, H_b), 7.27 (d, $J_{2,3}$ = 15.6 Hz, 1H, H_3), 6.63 (d, $J_{b,c}$ = 9.1 Hz, 2H, H_c), 6.50 (dd, $J_{2,3}$ = 15.6 Hz, $J_{1,2}$ = 7.9 Hz, 1H, H_2), 3.40 (q, ^3J(H,H) = 7.1 Hz, 4H, CH_2), 1.19 (t, ^3J(H,H) = 7.0 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 193.71 (CHO), 153.91 (C_3), 150.11 (C_d), 130.84 (C_b), 123.32 (C_2), 121.04 (C_a), 111.25 (C_c), 44.55 (CH_2), 12.55 (CH_3). UV-Vis ($CHCl_3$): λ_{max} (ε) = 215 (7179); 251 (10884); 326 (5324); 394 (38881).

The Horner-Wadsworth-Emmons reaction. Typical general synthetic procedure for compounds 9–11. To 3-[1,3]dioxolan-2-yl-allyl)-phosphonic acid diethyl ester (20 mL, 5 mmol) in solution in anhydrous THF, were added under argon, 5 mmol of *t*-BuOK at −78 °C. After 90 min, 4-(diethylamino)benzaldehyde (5 mL, 3.4 mmol) in anhydrous THF was added, then solution was maintained at 0 °C for 12 h before to be hydrolysed in 30 min by an aqueous HCl solution (2 M, 5 mL) at −50 °C, followed by 1 h of stirring at room temperature. The reaction mixture was rendered basic (pH 9) with aqueous 5 M NaOH. The organic material was then extracted with diethyl ether, and the ether layer was washed with brine, dried over $MgSO_4$, filtered and evaporated to dryness.

(E,E)-5-[4-(Diethylamino)phenyl]penta-2,4-dienal (**9**). The crude product **9** was purified by crystallization (ethanol–water) to give an orange solid (0.55 g, 80% yield): mp = 103 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.53 (d, $J_{1,2}$ = 8.1 Hz, 1H; CHO), 7.35 (d, $J_{b,c}$ = 8.8 Hz, 2H, H_b), 7.24 (dd, $J_{2,3}$ = 16.1 Hz, 1H, H_3), 6.85 (m, 2H, H_4, H_5), 6.62 (d, $J_{b,c}$ = 8.8 Hz, 2H, H_c), 6.50 (dd, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 16.1 Hz, 1H, H_2), 3.38 (q, ^3J(H,H) = 7.1 Hz, 4H, CH_2), 1.17 (t, ^3J(H,H) = 7.0 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 194.23 (CHO), 154.65 (C_3), 149.61 (C_d), 144.33 (C_5), 130.22 (C_b), 129.30 (C_2), 123.38(C_a), 121.63 (C_4), 112.02 (C_c), 45.11 (CH_2), 13.24 (CH_3). UV-Vis ($CHCl_3$): λ_{max} (ε) = 275 (20827); 427 (32829). Anal. calcd for $C_{15}H_{19}ON$ (229.32 g mol^{-1}): C, 78.5; H, 8.35; N, 6.11; found: C, 78.43; H, 8.40; N, 6.10%.

(E,E)-5-[4-(Dibutylamino)phenyl]penta-2,4-dienal (**10**). Crude product **10** was obtained according to the general, previously described procedure, starting from 3-([1,3]dioxolan-2-yl-allyl)-phosphonic acid diethyl ester and 4-(dibutylamino)benzaldehyde. Purification by column chromatography (pentane–AcOEt 90 : 10) and a 3 h reaction in the presence of iodine in dichloromethane for isomerization, provided 1.06 g of a red solid (70% yield): ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 9.53 (d, $J_{1,2}$ = 8.0 Hz, 1H, CHO), 7.34 (d, $J_{b,c}$ = 9.2 Hz, 2H, H_b), 7.22 (dd, $J_{2,3}$ = 14.9 Hz, $J_{3,4}$ = 10.5 Hz, 1H, H_3), 6.84 (m, 2H, H_4, H_5), 6.58 (d, $J_{b,c}$ = 9.2 Hz, 2H, H_c), 6.14 (dd, $J_{2,3}$ = 14.9 Hz, $J_{1,2}$ = 8.0 Hz, 1H, H_c), 3.29 (t, J = 7.3 Hz, 4H, CH_2,), 1.57 (m, 4H, CH_2), 1.35 (m, 4H, CH_2), 0.94 (t, J = 6.8 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 193.59 (CHO), 153.99 (C_3), 149.38 (C_d), 143.67 (C_5), 129.49 (C_b), 128.65 (C_2), 122.61 (C_a), 120.95 (C_4), 111.44 (C_c), 50.75 (CH_2), 29.42 (CH_2), 20.29 (CH_2), 13.96 (CH_3).

(E,E,E,E)-9-[4-(Dibutylamino)phenyl]nona-2,4,6,8-tetraenal (**11**). Crude product **11** was obtained according to the general previously described procedure, starting from 3-([1,3]dioxolan-2-yl-allyl)-phosphonic acid diethyl ester and **10**. After purification by column chromatography (CH_2Cl_2), 0.74 g of **11** as a red solid was obtained (86% yield): mp = 122 °C; ^{1}H NMR (499.84 MHz, $CDCl_3$) δ: 9.53 (d, 1H, $J_{1,2}$ = 8.3 Hz, 1H, CHO), 7.27 (d, $J_{b,c}$ = 9.0 Hz, 2H, H_b), 7.14 (dd, $J_{3,4}$ = 14.9 Hz, $J_{2,3}$ = 11.0 Hz, 1H, H_3), 6.74 (dd, J = 14.4 Hz, J = 11.2 Hz, 1H, H_5), 6.64 (m, 3H, H_7, H_8, H_9), 6.56 (d, $J_{b,c}$ = 9.0 Hz, 2H, H_c), 6.40 (m, 2H, H_4, H_6), 6.11 (dd, $J_{1,2}$ = 14.9 Hz, $J_{2,3}$ = 8.3 Hz, 1H, H_2), 3.27 (t, J = 7.3 Hz, 4H, N–CH_2–CH_2), 1.56 (m, 4H, CH_2–CH_2–CH_2), 1.34 (m, 4H, CH_2–CH_2–CH_3), 0.94 (t, J = 7.3 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 193.48 (CHO), 152.44 (C_3), 148.41 (C_d), 143.66 (CH), 140.60 (CH), 137.13 (CH), 129.93 (CH), 128.96 (CH), 128.36 (C_{Ar}), 128.18 (CH), 123.86 (CH), 123.45 (CH), 111.54 (CH_{Ar}), 50.75 (CH_2), 29.46 (CH_2), 20.31 (CH_2), 13.98 (CH_3).

General procedure for compounds 12 and 13. To a solution of sodium methanolate (0.85 g, 15.7 mmol) in 50 mL DMF was first dropwise added (4-bromo-benzyl)-phosphonic acid diethyl ester (4.83 g, 15.7 mmol) in 30 mL DMF, then 4-(diethylamino)benzaldehyde (2.79 g, 15,7 mmol) and the reaction mixture was stirred for 40 min. The resulting solution was stirred for 12 h, then, 80 mL water was added and the reaction mixture was filtered to give the desired product.

(E)-{4-[2-(4-Bromophenyl)vinyl]phenyl}diethylamine (**12**). Purification by column chromatography, eluting with pentane–CH_2Cl_2 (65 : 35), lead to 4.24 g of the pure pale green compound **12** (82% yield): mp = 153 °C; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 7.37 (m, 6H, CH_{Ar}), 7.00 (d, $J_{3,2}$ = 16.3 Hz, 1H, H_3), 6.77 (d, $J_{2,3}$ = 16.3 Hz, 1H, H_2), 6.64 (d, J = 8.8 Hz, 2H, CH_{Ar}), 3.36 (q, J = 7.0 Hz, 4H, CH_2), 1.16 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) d: 147.60, 137.33, 131.58, 129.63, 127.92, 127.38, 124.24, 122.31, 119.91, 111.65,

44.39, 12.63. Anal. calcd for $C_{18}H_{20}NBr$ (330.27 g mol^{-1}) C, 65.46; H, 6.10; N, 4.24; found: C, 65.59; H, 5.89; N, 4.25%.

(E)-{4-[2-(4-Bromophenyl)vinyl]phenyl}dibutylamine (**13**). The crude product was purified by column chromatography, eluting with pentane–CH_2Cl_2 (90 : 10), and crystalised in ethanol, leading to 3.35 g of the pure green pale **13** (70% yield): mp = 122 °C; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 7.36 (m, 6H, H_2, H_3 et H_8), 6.99 (d, J = 16.2 Hz, 1H, H_6), 6.76 (d, J = 16.2 Hz, 1H, H_5), 6.60 (d, J = 8.9 Hz, 2H, H_9), 3.27 (t, J = 7.3 Hz, 4H, N–CH_2), 1.55 (m, 4H, CH_2), 1,35 (m, 4H, CH_2), 0,94 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 148.01, 137.35, 131.58, 129.65, 127.84, 127.37, 124.03, 122.22, 119.88, 111.61, 50.77, 29.47, 20.34, 14.00. Anal. calcd for $C_{22}H_{28}NBr$ (386,37 g mol^{-1}) C, 68.39; H, 7.30; N, 3.62; found: C, 68.16; H, 7.37; N, 3.62%.

Formylation. Typical synthetic procedure for compounds 14 and 15. Based on a lithium–bromine exchange, followed by electrophilic attack with the dimethylformamide (DMF). *n*-Butyllithium (2.5 M in hexane, 1.4 mL, 3.4 mmol) was dropwise added under argon, to (*E*)-{4-[2-(4-bromophenyl) vinyl]phenyl}diethylamine (1.0 g, 3.0 mmol) in solution in 15 mL of anhydrous THF at −78 °C. After 20 min reaction, DMF (300 mL, 4 mmol) was introduced, the temperature was maintained at −78 °C during 3 h before the reaction mixture was hydrolyzed with 1 mL water. Organic material was extracted with diethyl ether and the ether layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated to dryness after filtration.

(E)-4-[2-(4-Diethylaminophenyl)vinyl]benzaldehyde (**14**). The product was purified by column chromatography (CH_2Cl_2–pentane 50 : 50) to give 650 mg of the desired yellow compound **14** (78% yield): mp = 156 °C; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 9.93 (s, 1H, H_1), 7.80 (d, $J_{3,4}$ = 8.3 Hz, 2H, H_3), 7.56 (d, J = 8.3 Hz, 2H, H_4), 7.39 (d, J = 8.9 Hz, 2H, H_9), 7.17 (d, J = 16.2 Hz, 1H, H_7), 6.87 (d, J = 16.2 Hz, 1H, H_6), 6.64 (d, J = 8.9 Hz, 2H, H_{10}), 3.38 (q, J = 7.0 Hz, 4H, CH_2), 1.18 (t, 6H, CH_3, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 191.60, 148.09, 144.76, 134.39, 132.64, 130.28, 128.49, 126.17, 123.77, 122.06, 111.58, 44.44, 12.66. Anal. calcd for $C_{19}H_{21}NO$ (279.38 g mol^{-1}) C, 81.68; H, 7.57; N, 5.01; found: C, 81.85; H, 7.50; N, 4.99%.

(E)-4-[2-(4-Dibutylaminophenyl)vinyl]benzaldehyde (**15**). After purification of the crude product by column chromatography (CH_2Cl_2–pentane, 20 : 80) and crystallization in ethanol, 737 mg of **15** as yellow crystals were obtained (71% yield): mp = 105 °C. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 9.93 (s, 1H, H_1), 7.80 (d, J = 8.3 Hz, 2H, H_3), 7.56 (d, J = 8.3 Hz 2H, H_4), 7.38 (d, J = 8.9 Hz, 2H, H_9), 7.17 (d, J = 16.2 Hz, 1H, H_7), 6.87 (d, J = 16.2 Hz, 1H, H_6), 6.61 (d, J = 8.9 Hz, 2H, H_{10}), 3.29 (t, J = 7.3 Hz, 4H, N–CH_2–CH_2), 1.58 (m, 4H, CH_2–CH_2–CH_2), 1.36 (sextet, J = 7.1 Hz, 4H, CH_2–CH_2–CH_3), 0.95 (t, J = 7.1 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 191.58, 148.48, 144.76, 134.34, 132.63, 130.25, 128.39, 126.13, 123.56, 121.94, 111.55, 50.7, 29.46, 20.33, 13.99. Anal. calcd for $C_{23}H_{29}NO$ (335.49 g mol^{-1}): C, 82.34; H, 8.71; N, 4.17; found: C, 82.48; H, 8.77; N, 4.24%.

Crossed aldol condensation. Typical general synthetic procedure for compounds 1–4. To a solution of (*E*)-3-[4-(diethylamino)phenyl]propenal (250 mg, 1.23 mmol) and propanone (45 mL, 0.62 mmol) in 15 mL ethanol, were dropwise added an aqueous sodium hydroxide solution (7.5 mol L^{-1}, 616 mL, 4.6 mmol). After 12 h stirring at room temperature and in darkness, the reaction mixture was filtered and the aqueous mother liquor extracted with dichloromethane. Purification by column chromatography, eluting with pentane–propanone (85 : 15) and crystallization in a mixture of CH_2Cl_2–pentane led to 194 mg of violet crystals.

(E,E)-1,5-Bis-[4-(diethylamino)phenyl]penta-1,4-dien-3-one (**1**). Obtained according to the previously described general procedure starting from 4-(diethylamino)benzaldehyde (3.5 g, 0.02 mol), propanone (0.73 mL, 0.01 mol) in 25 mL ethanol and an aqueous NaOH solution (7.5 mol L^{-1}, 10 mL, 75 mmol): crystallization in ethanol of the crude product, previously washed with cold water, provided 2.8 g of orange needles with 75% yield: mp = 167 °C (litt:[23] 168 °C); ^{1}H NMR (499.84 MHz, $CDCl_3$) δ: 7.65 (d, $J_{3,2}$ = 15.7 Hz, 2H, H_3), 7.47 (d, $J_{b,c}$ = 8.8 Hz, 4H, H_b), 6.84 (d, $J_{2,3}$ = 15.7 Hz, 2H, H_2), 6.63 (d, $J_{c,b}$ = 8.8 Hz, 4H, H_c), 3.39 (q, J = 7.1 Hz, 8H, CH_2), 1.18 (t, J = 7.0 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 188.90 (C_1), 149.33 (C_d), 142.84 (C_3), 130.38 (C_b), 122.16 (C_a), 120.88 (C_2), 111.30 (C_c), 44.48 (CH_2), 12.61 (CH_3). UV-Vis ($CHCl_3$): λ_{max} (ε) = 259 (17255); 456 (52308).

(E,E,E,E)-1,9-Bis-[4-(diethylamino)phenyl]nona-1,3,6,8-tetraen-5-one (**2**). Yield = 73%; mp = 166 °C; ^{1}H NMR (499,84 MHz, $CDCl_3$) δ: 7.45 (dd, $J_{3,2}$ = $J_{3,4}$ = 15.5 Hz, 2H, H_3), 7.33 (d, $J_{b,c}$ = 8.5 Hz, 4H, H_b), 6.86 (d, $J_{5,4}$ = 15.5 Hz, 2H, H_5), 6.73 (dd, $J_{4,3}$ = $J_{4,5}$ = 15.5 Hz, 2H, H_4), 6.61 (d, $J_{c,b}$ = 8.5 Hz, 4H, H_c), 6.43 (d, $J_{2,3}$ = 15.5 Hz, 2H, H_2), 3.38 (q, J = 7.1 Hz, 8H, CH_2), 1.17 (t, J = 7.0 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 188,97 (C_1), 148,47 (C_d), 143,85 (C_3), 142,03 (C_5), 129.05 (C_b), 126,67 (C_2), 123.59 (C_a), 122,19 (C_4), 111.44 (C_c), 44,45 (CH_2), 12,63 (CH_3). UV-Vis ($CHCl_3$): λ_{max} (ε) = 316 (21131); 486 (61256). Anal. calcd for $C_{29}H_{36}ON_2$, 0.33 H_2O (434.56 g mol^{-1}): C, 80.15; H, 8.50; N, 6.44; found: C, 80.18; H, 8.37; N, 6.50%.

(E,E,E,E,E,E)-1,13-Bis-[4-(diethylamino)phenyl]trideca-1,3,5,6,8,10,12-hexaen-7-one (**3**). Obtained according to the general procedure starting from (*E,E*)-5-[4-(diethylamino)phenyl]penta-2,4-dienal (219 mg, 0.96 mmol), propanone (35 µL, 0,48 mmol) and an aqueous NaOH solution (7.5 mol L^{-1}, 480 µL, 3.6 mol). Purification by column chromatography, eluting with pentane–propanone (86 : 14) and crystallization in a mixture of CH_2Cl_2–hexane led to 150 mg of **3** as a violet solid (65% yield): mp = 189 °C (decomposition); ^{1}H NMR (499.84 MHz, $CDCl_3$) δ: 7.36 (m, 2H, H_3), 7.29 (d, $J_{b,c}$ = 8.9 Hz, 4H, H_b), 6.76 (m, 2H, H_5), 6.68 (m, 4H, H_4, H_7), 6.60 (d, $J_{c,b}$ = 8.9 Hz, 4H, H_c), 6.40 (m, 4H, H_2, H_6), 3.36 (q, J = 7.1 Hz, 8H, CH_2), 1.16 (t, J = 7.0 Hz, 12H, CH_3) ^{13}C NMR ($CDCl_3$) δ: 188.79 (C_1), 148.05 (C_d), 143.17 (C_3, C_5), 137.81 (C_7), 128.57 (C_b), 128.43 (C_2), 127.44 (C_6), 123.98 (C_a), 123.49 (C_4), 111.52 (C_c), 44.42 (CH_2), 12.64 (CH_3). UV-Vis ($CHCl_3$): λ_{max} (ε) = 256 (18140); 339 (30610); 509 (79510). Anal. calcd for

$C_{33}H_{40}ON_2$, 0.5 H_2O (489.70 g mol^{-1}): C, 80.94; H, 8.44; N, 5.72; found: C, 80.48; H, 8.16; N, 5.54%.

(E,E,E,E,E,E,E,E,E,E)-1,21-Bis-[4-(dibutylamino)phenyl] heneicosa-1,3,5,7,9,12,14,16,18,20-decaen-11-one (**4**). Obtained according to a slightly modified general procedure and starting from (*E*,*E*,*E*,*E*)-9-[4-(dibutylamino)phenyl]nona-2,4,6,8-tetraenal (630 mg, 1.86 mmol), propanone (69 μL, 0.93 mmol) in 40 mL ethanol and an aqueous NaOH solution (7.5 mol L^{-1}, 1.3 mL, 9.3 mmol): after 12 h reaction at 50 °C, aldehyde (56 mg, 0.18 mmol) are again added and the mixture was allowed to react for an other 12 h in the same conditions. Purification by column chromatography on silica, eluting with dichloromethane led to 246 mg of the pure black product while 207 mg of a mixture of the desired product (193 mg) with 14 mg of 12-(4-dibutylaminophenyl)dodeca-3,5,7,9,11-pentaen-2-one (purity determined by NMR) was also obtained (38% yield): mp = 200 °C (decomposition); ^{1}H NMR (499.84 MHz, $CDCl_3$) δ: 7.33 (dd, J = 15.0 Hz, J = 11.5 Hz, 2H, H_3,), 7.26 (d, $J_{b,c}$ = 9.0 Hz, 4H, H_b), 6.64 (m, 4H), 6.55 (d, $J_{c,b}$ = 9.0 Hz, 4H, H_c), 6.49 (m, 6H), 6.33 (m, 8H), 3.29 (t, J = 7.5 Hz, 8H, N–CH_2), 1.54 (m, 8H, CH_2–CH_2–CH_2), 1.34 (m, 8H, CH_2–CH_2–CH_3), 0.94 (t, J = 7.5 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 189.22 (C_1), 148.70 (C_d), 143.44 (C_3), 142.86 (CH), 138.99 (CH), 138.07 (CH), 135.78 (CH), 131.37 (CH), 130.76 (2 CH), 128.84 (CH), 128.70 (C_b), 124.93 (C_a), 124.73 (CH), 112.21 (C_c), 51.40 (CH_2), 30.12 (CH_2), 20.96 (CH_2), 14.62 (CH_3). UV-Vis ($CHCl_3$): λ_{max} (ε) = 301 (29032); 394 (55915); 540 (123650). Anal. calcd for $C_{49}H_{64}ON_2$, 0.5 H_2O (706.06 g mol^{-1}): C, 83.35; H, 9.28; N, 3.97; found C, 83.37; H, 9.10; N, 4.08%.

Typical general synthetic procedure for compounds 5–7. To a solution of (*E*)-4-[2-(4-diethylaminophenyl)vinyl]benzaldehyde (500 mg,1.8 mmol) and propanone (66 μL, 0.9 mmol) in 40 mL ethanol, was dropwise added an aqueous sodium hydroxide solution (7.5 mol L^{-1}, 900 μL, 6.75 mmol). After 5 h stirring at 60 °C and in darkness, the reaction mixture was filtered. The solid obtained was first washed with hexane then ether, before being purified by column chromatography, and eluting with dichloromethane; it afforded 330 mg of a red solid.

(E,E,E,E)-1,5-Bis-{4-[2-(4-diethylaminophenyl)vinyl]phenyl} penta-1,4-dien-3-one (**5**). 65% yield: mp = 280 °C ^{1}H NMR (499.83 MHz. $CDCl_3$) δ: 7.71 (d, $J_{2,3}$ = 15.8 Hz, 2H, H_3), 7.57 (d, $J_{5,6}$ = 8.4 Hz, 4H, H_5), 7.48 (d, $J_{5,6}$ = 8.4 Hz, 4H, H_6), 7.39 (d, $J_{11,12}$ = 8.8 Hz, 4H, H_{11}), 7.1 (d, $J_{8,9}$ = 16,1 Hz, 2H, H_9), 7.05 (d, $J_{2,3}$ = 15.8 Hz, 2H, H_2), 6.87 (d, $J_{8,9}$ = 16.1 Hz, 2H, H_8), 6.65 (d, $J_{11,12}$ = 8.8 Hz, 4H, H_{12}), 3.38 (q, J = 7.0 Hz, 8H, CH_2), 1.18 (t, J = 7.0 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 188.81 (C_1), 147.74 (C_{13}), 142.85 (C_3), 140.81 (C_7), 132.95 (C_4), 130.58 (C_9), 128.86 (C_5), 128.16 (C_{11}), 126.32 (C_6), 124.54 (C_2), 124.23 (C_{10}), 122.70 (C_8), 111.62 (C_{12}), 44.41 (CH_2), 12.64 (CH_3). UV-Vis ($CHCl_3$): λ_{max} (ε) = 257 (22090); 339 (44370); 509 (80960). Anal. calcd for $C_{41}H_{44}N_2O$, 0.5 H_2O (580.81 g mol^{-1}) C, 83.49; H, 7.69; N, 4.75; found C, 83.68; H, 7.64; N, 4.90%.

(E,E,E,E)-1,5-Bis-{4-[2-(4-dibutylaminophenyl)vinyl]phenyl} penta-1,4-dien-3-one (**6**). Obtained according to the general, previously described, procedure starting from (*E*)-4-[2-(4-dibutylaminophenyl)vinyl]benzaldehyde (450 mg, 1.4 mmol), propanone (50 μL, 0.7 mmol) in 30 mL ethanol and an aqueous NaOH solution (7.5 mol L^{-1}, 670 μL, 5 mmol). Purification by column chromatography, eluting with pentane–propanone (82 : 18) and crystallizing in ethanol led to 335 mg of the desired solid with 72% yield: mp = 159 °C; ^{1}H NMR (499.83 MHz, $CDCl_3$) δ: 7.72 (d, $J_{2,3}$ = 16 Hz, 2H, H_3), 7.56 (d, $J_{5,6}$ = 8.5 Hz, 4H, H_5), 7.48 (d, $J_{5,6}$ = 8.5 Hz, 4H, H_6), 7.38 (d, $J_{11,12}$ = 9.0 Hz, 4H, H_{11}), 7.10 (d, $J_{8,9}$ = 16.0 Hz, 2H, H_9), 7.05 (d, $J_{2,3}$ = 16.0 Hz, 2H, H_2), 6.88 (d, $J_{8,9}$ = 16.0 Hz, 2H, H_8), 6.61 (d, 4H, H_{12}, $J_{11,12}$ = 9.0 Hz), 3.28 (t, J = 7.1 Hz, 8H, N–CH_2–CH_2), 1.61 (m, 8H; CH_2–CH_2–CH_2), 1.35 (sextet, J = 7,2 Hz, 8H, CH_2–CH_2–CH_3), 0.95 (t, J = 7.2 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm): 188.81 (C_1), 148.17 (C_{13}), 142.86 (C_3), 140.84 (C_7), 132.93 (C_4), 130.60 (C_9), 128.86 (C_5), 128.09 (C_{11}), 126.31 (C_6), 124.54 (C_2), 124.04 (C_{10}), 122.61 (C_8), 111.61 (C_{12}), 50.78 (CH_2), 29.48 (CH_2–CH_2–CH_2), 20.34 (CH_2–CH_2–CH_3), 14.00 (CH_3). UV-Vis ($CHCl_3$): λ_{max} (ε) = 243 (18480); 340 (36960); 466 (54350). Anal. calcd for $C_{49}H_{60}N_2O$, 0.5 H_2O (693.03 g mol^{-1}): C, 83.83; H, 8.76; N, 3.99; found C, 83.64; H, 8.84; N, 4.02%.

(E,E)-1,5-Bis-[4-(4-dibutylaminophenylazo)phenyl]penta-1,4-dien-3-one (**7**). Obtained according to the general procedure starting from 4-(4-dibutylaminophenylazo)benzaldehyde (400 mg, 1.2 mmol), propanone (44 μL, 0.6 mmol) in 30 mL ethanol and an aqueous NaOH solution (7.5 mol L^{-1}, 600 μL, 4.5 mmol). Purification by crystallization in ethanol led to 287 mg of a dark red solid (70% yield): mp = 144 °C. ^{1}H NMR (499.83 MHz, $CDCl_3$) δ: 7.86 (m, 8H, H_6 et H_{11}); 7.78 (d, $J_{3,2}$ = 16.0 Hz, 2H. H_3), 7.71 (d, $J_{5,6}$ = 8.5 Hz, 4H, H_5), 7.13 (d, $J_{2,3}$ = 16.0 Hz, 2H, H_2), 6.68 (d, $J_{11,12}$ = 9.5 Hz, 4H, H_{12}), 3.36 (t, J = 7.5 Hz, 8H, N–CH_2–CH_2), 1.62 (m, 8H; CH_2–CH_2–CH_2), 1.38 (sext, J = 7.5 Hz, 8H, CH_2–CH_2–CH_3), 0.97 (t, J = 7.5 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 188.61, 154.56, 150.93, 143.29, 142.73, 135.30, 129.26, 125.62, 122.72, 111.13, 50.99, 29.50, 20.30, 13.96. UV-Vis ($CHCl_3$): λ_{max} (ε) = 265 (20620); 334 (25775); 503 (89690). Anal. calcd for $C_{45}H_{56}N_6O$, 0.5 H_2O (705.98 g mol^{-1}): C, 76.56; H, 8.14; N, 11.90; found C, 76.30; H, 8.01; N, 12.07%.

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