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Synthesis and Fluorescence Characterization of MEHPPV Oligomers

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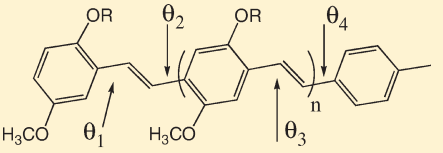
Supporting Information

ABSTRACT: Trimer, tetramer, and pentamer oligomers based on the polymer backbone structure of poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV) have been synthesized by Horner−Wadsworth−Emmons reactions. The fluorescence spectra, emission quantum yields, and lifetimes of the oligomers have been characterized in dilute chloroform solutions. The oligomers exhibit a sequential increase in absorption and emission wavelength maxima and a decrease in fluorescence lifetime as the π conjugation length is increased. The shortening in excited state lifetime is shown to be due to an increase in the rates of both radiative and nonradiative processes. The absence of a mirror-image relationship for the absorption and fluorescence spectra of the oligomers is attributed to the photoexcitation of a range of torsional configurations followed by relaxation to a more planar arrangement that then emits.



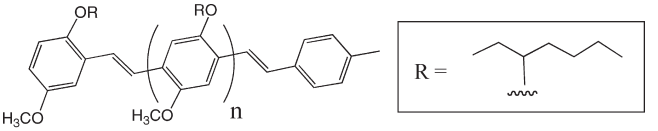
n = 1-3; R = -CH_3; R = -C_6H_{13}; R = -$CH_2CH(Et)C_4H_9$

θ_{1-4} = +/− 10°− 15°

INTRODUCTION

Conjugated polymers based on poly(phenylenevinylene) (PPV) have been extensively studied as the key components in a range of photoactive and electroactive materials.[1−5] The interest in these materials arises from their luminescent and semiconducting properties that have seen them used in organic light emitting diodes and in photovoltaic devices.[6,7] PPV derivatives that are substituted with methoxy and 2-ethylhexyloxy substituents on the phenyl rings (e.g., poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene], MEHPPV) have found particular application since they are more soluble and more readily fabricated into useful materials than unsubstituted derivatives.[8,9] It has been proposed that in MEHPPV conformational defects along the polymer backbone break the extended π conjugation, leading to light absorption by shorter conjugated sequences with a distribution of lengths that constitute the polymer chromophores. Following photoexcitation, energy transfer among the chromophores that make up the chain ultimately leads to the population of the lowest energy chromophores made up of longer conjugated sequences, and it is these that are thought responsible for the observed polymer fluorescence.[10] More recent studies have shown that this picture is too simplistic and that the excited states of conjugated polymers evolve over a broad range of time scales from femtoseconds onward and involve exciton relaxation, localization, and energy transfer processes that are influenced by dynamic polymer chain conformations.[11] In addition there is evidence quantum coherence can contribute to energy transfer dynamics in conjugated polymers such as MEHPPV at room temperature.[11,12]

Rather than extended main chain conjugated polymers, we are interested in the properties of polymers that contain shorter chains of oligo-MEHPPV (from 3 to 5 units) as pendant chromophores on polymer chains, and how these chromophores interact with each other, and with energy and electron acceptor chromophores that may also be included. To understand the photophysical properties of these polymers, however, we first needed to prepare model MEHPPV oligomers that closely resemble the chromophores present on the polymer chain so that the photophysics of the individual chromophores are well characterized. To this end we report here the preparation and full characterization of the MEHPPV oligomers **1**−**3** (Figure 1) and describe their fluorescence and other photophysical properties.



1; n = 1
2; n = 2
3; n = 3

Figure 1. MEHPPV oligomers studied in this work.

RESULTS AND DISCUSSION

Synthesis of Oligomers. The oligomers **1**−**3** were prepared by sequential Horner−Wadsworth−Emmons reactions according to Scheme 1. This sequence began with the substituted aldehyde **6** and the phosphonate **5**, both of which were obtained in a few steps from 4-methoxyphenol. Coupling of **5** and **6** was followed by lithiation and formylation producing the aldehyde **8**,

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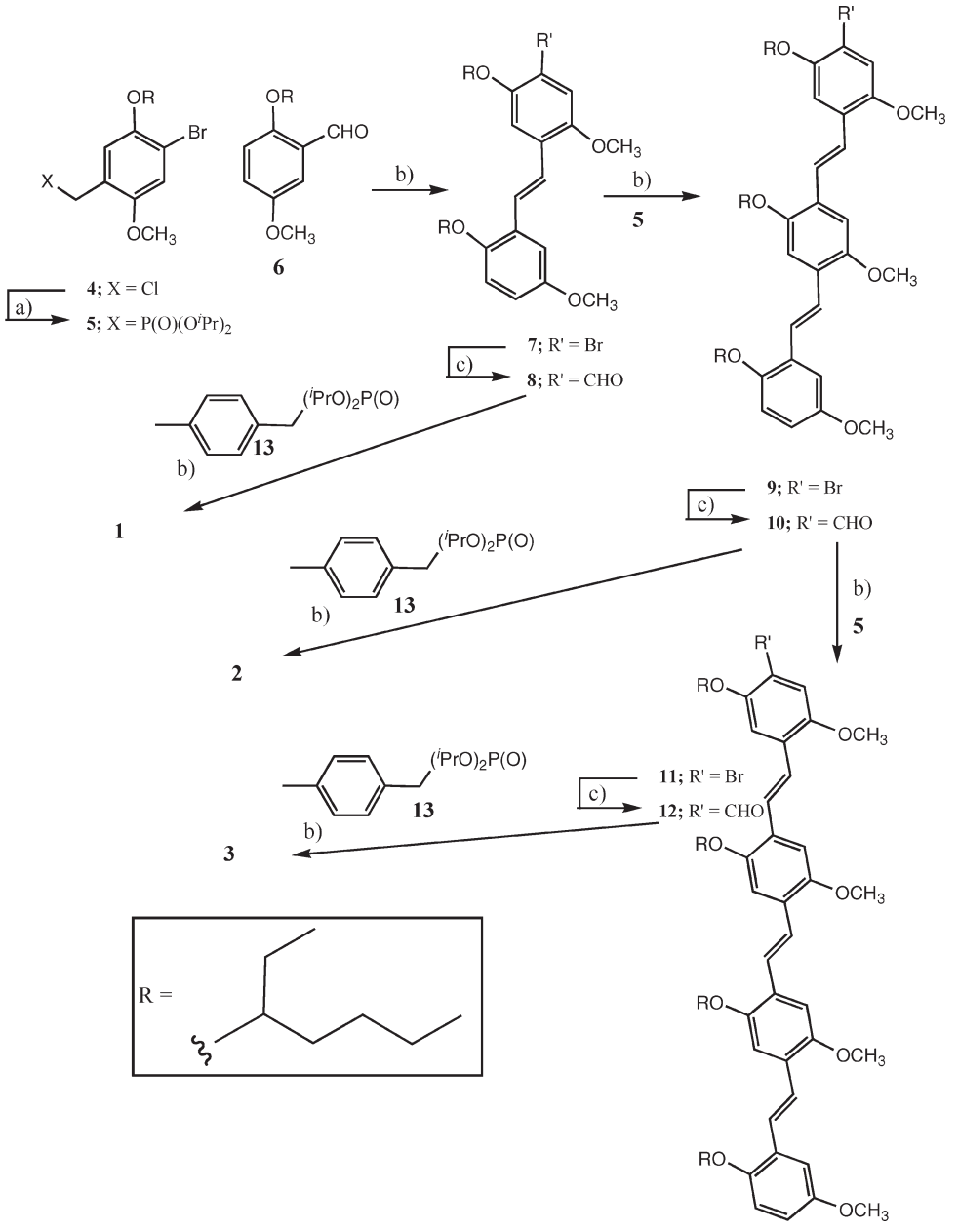
Scheme 1. Synthesis of Ethylhexyloligomers 1−3[a]



[a] Reagents and conditions: (a) $(i\mathrm{PrO})_3\mathrm{P}$; (b) KOBu^t, THF; (c) BuLi, THF, $\mathrm{Me_2NCHO}$.

which was either coupled with the phosphonate **13** to give the trimer **1** or alternatively coupled with phosphonate **5** to give the trimer **9**. After lithiation and formylation of **9** the resulting aldehyde **10** was coupled with either the phosphonate **13** to give the tetramer **2** or alternatively with phosphonate **5** to give the tetramer **11**, which ultimately gave the pentamer **3** following a similar sequence of reactions.

Photophysical Characterization. The absorption and fluorescence spectra of compounds **1**−**3** in chloroform are shown in Figures 2 and 3. The absorption and emission spectra show a sequential red-shift with increasing conjugation length. The pentamer exhibits a broad absorption with maximum at 451 nm and a structured fluorescence with peak maximum at 518 nm. These may be compared to the corresponding absorption and emission maxima for the trimer of 397 and 452 nm, and the tetramer of 431 and 493 nm in the same solvent. The maximum molar absorption coefficients (ε), fluorescence lifetimes (τ_f), and fluorescence quantum yields (ϕ_f) in chloroform are provided in Table 1. The radiative (k_r) and nonradiative (k_{nr}) rate constants can be calculated from the quantum yield and lifetime data by using eqs 1 and 2 and are also provided in Table 1.

$$k_r = \phi_f/\tau_f \quad (1)$$

$$k_{nr} = (1-\phi_f)/\tau_f \quad (2)$$

The observation of structured emission spectra compared to a structureless broad absorption band has been noted previously

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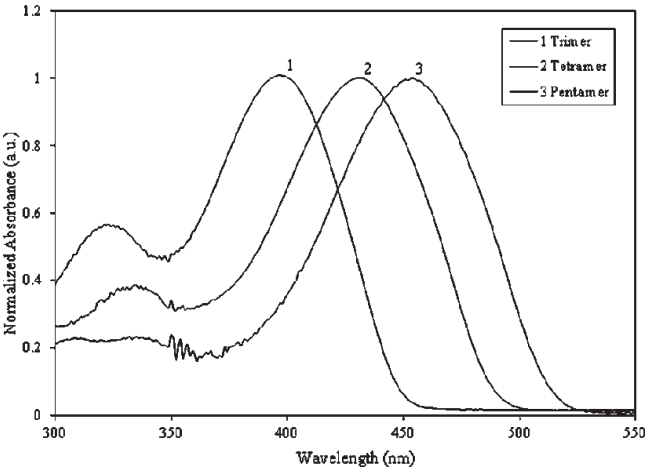


Figure 2. Room temperature absorption spectra of the oligomers in chloroform.

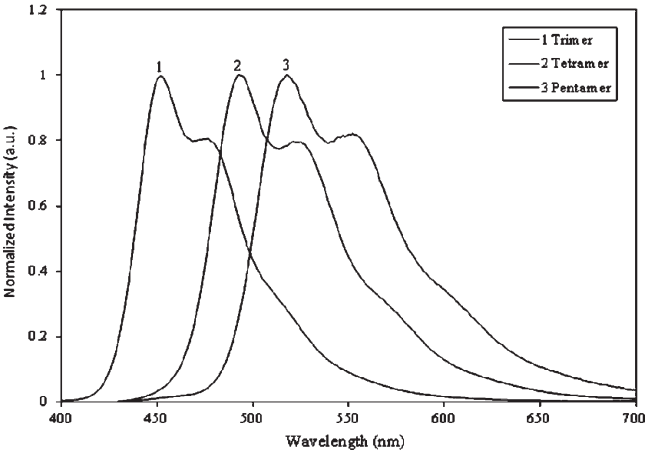


Figure 3. Fluorescence spectra of the oligomers in chloroform with excitation at the corresponding absorption maxima.

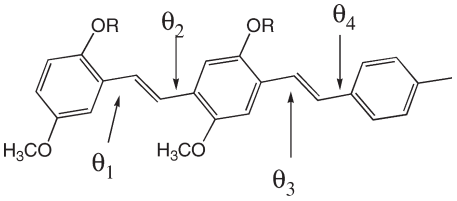
for MEHPPV polymers.[13] The broad absorption has been attributed to an inhomogeneous superposition of absorption spectra arising from a distribution of chain segments with different conjugation lengths, while the emission has been thought to occur from low-energy conjugated sequences populated by energy transfer.[10] However, the non-"mirror-image" relationship between absorption and emission spectra observed for dilute solutions of the oligomers of well-defined conjugation length studied in this work suggests, instead, that this is an inherent property of these molecules. Previous theoretical and experimental studies of related phenylene vinylene polymers and oligomers have suggested that the broad absorption spectra can be attributed to the presence of a range of ground state torsional configurations.[14,15]

To investigate this possibility analysis of the possible conformations of the simple model trimer **14** was carried out and reveals that the molecule can plausibly exist as a mixture of six different rotamers which differ by ca. 180° rotations about the single bonds which separate the five π-systems (denoted as $\theta_1-\theta_3$ in Figure 4). Of these possible rotamers the structure shown in Figure 4 is the lowest energy, with the next lowest being ca. 0.88 kcal/mol higher in energy. Structure **14** is not planar but

Table 1. Selected Photophysical Data for the Oligomers in Chloroform at 298 K[a]

	trimer **1**	tetramer **2**	pentamer **3**
Φ_f	0.36	0.34	0.32
τ_f (ns)	1.5	1.3	0.8[b]
k_r (10^8 s^{-1})	2.5	2.6	3.6
k_{nr} (10^8 s^{-1})	4.4	5.1	8.7
ε_{max} (dm^3 mol^{-1} cm^{-1})	39000	59000	87000

[a] Fluorescence lifetimes (τ_f) measured at 450 nm for **1** and 500 nm for **2** and **3**. [b] Note: The fluorescence decay of the pentamer contained a minor (10%) component with a lifetime of 1.2 ns (see text).



14; R = -CH_3
15; R = -C_6H_{13}

Figure 4. Conformations of the trimers **14** and **15**.

exists as a family of eight so-called "twistomers" where the four dihedral angles $\theta_1-\theta_4$ deviate from 0° by angles varying from 10° to 15°. These twistomers have similar energies and lie within 0.2 kcal/mol of one another, and therefore are all likely to be populated at room temperature.

The qualitative predictions from molecular mechanics are borne out in the crystal structure of the trimer derivative **15** (synthesized according to Scheme 2, with hexyloxy side chains instead of ethylhexyloxy groups to remove stereoisomer heterogeneity). Thus trimer **15** adopts a conformation analogous to that shown in Figure 4, and also shows a slight twist of the aromatic rings with dihedral angles $\theta_1-\theta_4$ all deviating from planarity by ca. 10−15° (Figure 5).

The range of rotamers and torsional configurations can be expected to have slightly different electronic arrangements and transition energies that can lead to the spectral broadening observed in the solution absorption spectra. Further evidence is found by recording the absorption spectra of the representative tetramer **2** as a function of temperature (see Figure 6). In this case 2-methyltetrahydrofuran was used as the solvent to provide an optically clear matrix as the solution was cooled. As the temperature is lowered there is a marked red-shift and progressive development of structure in the spectra consistent with absorption by a restricted set of configurations.

Our interpretations are consistent with previous theoretical studies of other phenylene vinylene oligomers that concluded the asymmetry of absorption and fluorescence spectra at room temperature can be associated with larger torsional flexibility in the ground state compared to the excited state.[14,15] The emission arises from a restricted subset of low torsional angle configurations leading to the structured emission observed. A previous ultrafast spectroscopy study of related PPV trimers detected a picosecond time-scale process (<40 ps) following excitation that was also attributed by the authors to a rapid conformational relaxation to more planar configurations.[16]

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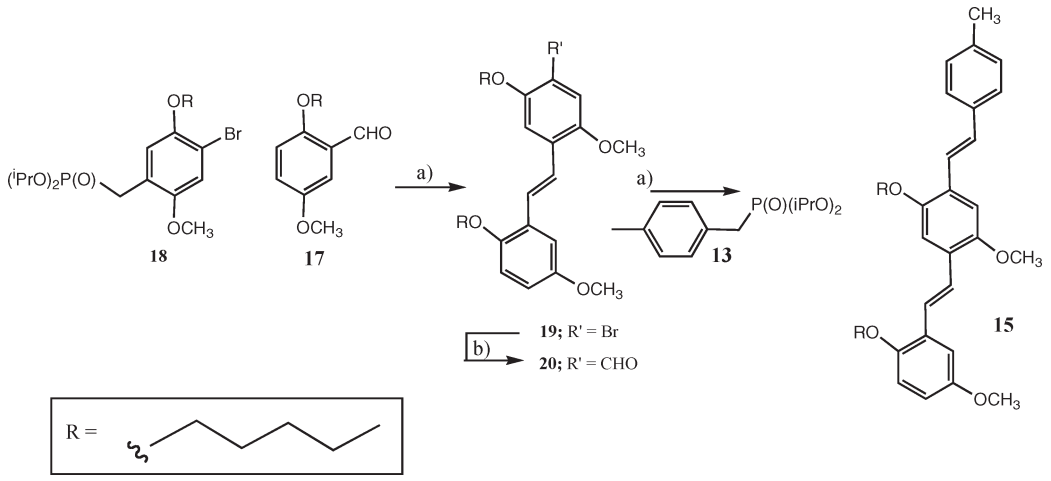
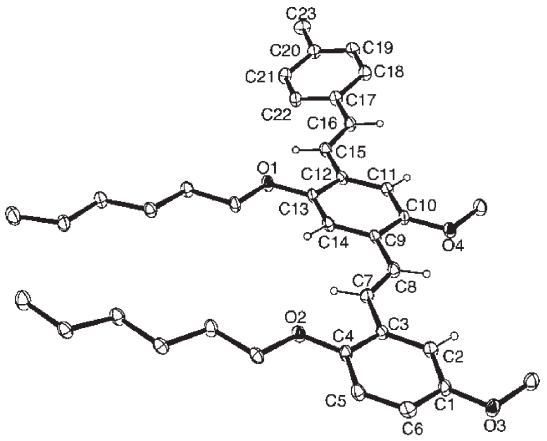
Scheme 2. Synthesis of Hexyloxy Trimer 15[a]



[a] Reagents and conditions: (a) KOBu^t, THF; (b) BuLi, THF, Me_2NCHO.



θ_1 =-8.7(7)°, θ_2 =7.4(7)°,

θ_3 = -15.0(7)°, θ_4 = -6.9(7)°

Figure 5. X-ray structure of the trimer **15** containing hexyloxy side chains.

Extending the conjugation length of the oligomers leads to the expected red-shift in absorption and emission spectra and an increase in the absorption coefficient. There is a decrease in fluorescence lifetime in order from trimer > tetramer > pentamer. This trend is shown to arise from an increase in both the radiative and nonradiative rate constants for the oligomers. It can be noted from Table 1 that the relatively larger increase in nonradiative rate compared to the radiative rate leads to the observed decrease in fluorescence quantum yield with increasing conjugation length. The results can be compared to published data on the conjugated polymer MEHPPV where a fluorescence quantum yield and lifetime in chloroform of 0.35 and 330 ps respectively have been reported.[17] While the fluorescence decay profiles for the trimer and tetramer can be fitted adequately by single decay components in each case, for the pentamer an additional minor contribution (10% at 510 nm) of a component with a longer lifetime of 1.2 ns was required. While the origin of this component remains uncertain it may arise from a contribution by an emitting rotamer configuration in this compound. Within the time resolution of our time-correlated photon counting instrumentation we were unable to resolve the ultrafast component (<40 ps) in the fluorescence decay profiles that has been reported previously for related PPV trimers and assigned to excited state torsional relaxation processes.[16]

In conclusion, MEHPPV type oligomers **1**−**3** have been successfully synthesized by Horner−Wadsworth−Emmons reactions. Their electronic absorption and fluorescence spectra can be explained by the photoexcitation of a range of torsional conformations followed by emission from more planar arrangements. The incorporation of these chromophores as pendant groups in polymers and the photochemistry of these materials will be reported in a future communication.

EXPERIMENTAL SECTION

General Methods. All reactions were performed in oven-dried glassware. Starting materials were used without further purification, except for DMF, which was purified by stirring with $CaSO_4$ for 24 h followed by vacuum distillation over 4 Å molecular sieves. THF was purified by refluxing over sodium and benzophenone until the solution became dark, followed by distillation. Acetone was purified by distillation, followed by storage over 4 Å molecular sieves. CH_2Cl_2 was dried with use of a solvent purification apparatus as described by Pangborn et al.[18] Thin layer chromatography was performed on aluminum sheets precoated with silica gel, using mixtures of EtOAc/*n*-hexane, Et_2O/*n*-hexane, and CH_2Cl_2/*n*-hexane. Detection was achieved via irradiation by UV light. Flash chromatography was performed by using the method of Still et al., using silica gel grade 230−400 mesh.[19] Automated column chromatography was performed with a flash purification system. NMR data was recorded on 400 and 500 MHz instruments. Chemical shifts are expressed in parts per million (δ), using residual solvent (^{1}H NMR δ 7.26 ppm for $CDCl_3$; ^{13}C NMR δ 77.16 ppm for $CDCl_3$). Melting points were obtained by using an automated melting point apparatus and are uncorrected. Fourier transform infrared spectra and high-resolution electrospray ionization mass spectra were recorded at The University of Melbourne.

Photophysics. UV−vis absorption spectra were recorded on a UV−vis−NIR spectrophotometer. All solution absorption spectra were recorded against solvent blanks in matched 1.0 cm path length quartz cells. Fluorescence spectra were recorded on a spectrofluorometer. The

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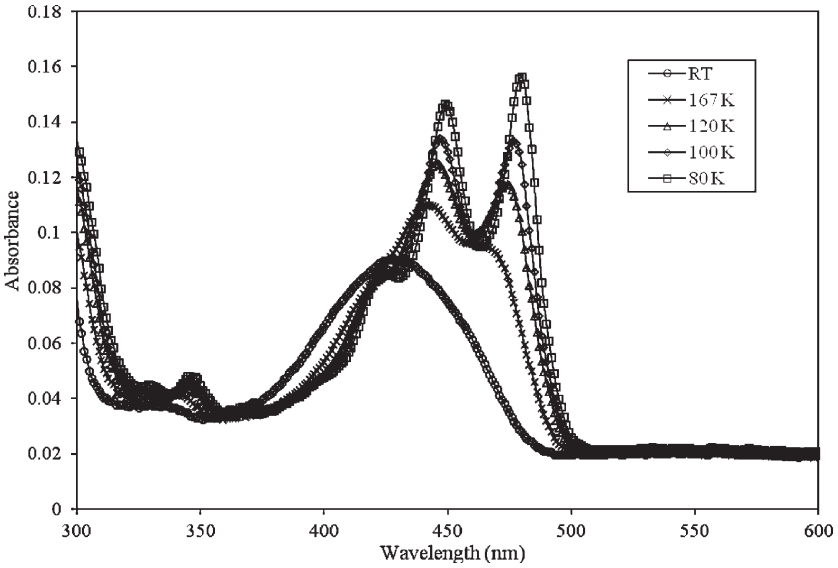

Figure 6. Absorption spectra of the tetramer **2** in 2-methyltetrahydrofuran as a function of temperature.

optical densities of the solutions were kept below 0.20 at the excitation wavelength to minimize reabsorption effects. Fluorescence quantum yield measurements were carried out by using the comparative method against a known fluorescence standard (coumarin 343 in ethanol, ϕ_f = 0.63).[20] The uncertainty in fluorescence quantum yield determinations is estimated at ±5%. Fluorescence decay profiles were recorded by the time-correlated single photon counting technique, using the frequency doubled (390 nm) output of a mode-locked and cavity-dumped Ti: sapphire laser as the excitation source. Fluorescence lifetimes were determined by analysis of the fluorescence decay profiles by iterative reconvolution procedures. The uncertainty in fluorescence lifetimes is ±0.1 ns. Full details of the instrumentation can be found elsewhere.[21] Low-temperature studies were carried out in a liquid nitrogen cryostat fitted with a temperature controller.

Synthesis

Preparation of 2-(2-ethylhexyloxy)-5-methoxy benzaldehyde, 6: (i) Bromine (6.8 mL, 21.1 g, 132 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of 4-methoxyphenol (14.92 g, 120 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The mixture was brought to room temperature and stirred for 2 h, then washed with sat. aq $NaHCO_3$ (2 × 50 mL) and water (2 × 50 mL). The aqueous layers were then re-extracted with additional CH_2Cl_2 (50 mL) and the combined organic layers dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the product as a dark brown oil. The dark oil was further purified by Kugel−Rohr distillation (0.6 mbar, 120 °C) to afford 2-bromo-4-methoxyphenol as a clear yellow oil, which solidified upon cooling (23.56 g, 97%), mp 42−43 °C (lit.[22] mp 43−44 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (3H, s), 5.12 (1H, s), 6.80 (1H, dd, J = 2.9, 8.9 Hz), 6.95 (1H, d, J = 8.9 Hz), 7.01 (1H, d, J = 2.9 Hz). FT-IR (neat, cm^{-1}) 3404, 2943, 1609, 1584, 1489, 1439, 1417, 1333, 1276, 1256, 1205, 1176, 1029.

(ii) 2-Ethylhexyl bromide (19.0 mL, 20.6 g, 107 mmol) was added to a stirred solution of 2-bromo-4-methoxyphenol (12.95 g, 64 mmol) and KOH (7.798 g, 139 mmol) in acetone (80 mL) and the resulting mixture was stirred at reflux for 47 h. The mixture was then concentrated under reduced pressure, taken up in ether, washed with H_2O (3 × 80 mL), 10% KOH (3 × 50 mL), sat. aq $NaHCO_3$ (2 × 80 mL), and sat. aq NaCl (3 × 80 mL), dried (MgSO4), filtered, and concentrated under reduced pressure to give a dark brown oil. Excess 2-ethylhexyl bromide was removed by Kugel−Rohr distillation (0.6 mbar, 120 °C) to give a light brown residue. Subsequent Kugel−Rohr distillation of the light brown residue (0.6 mbar, 150 °C) gave 2-bromo-1-(2-ethylhexyloxy)-4-methoxybenzene as a pale yellow oil (18.87 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89−0.96 (6H, m), 1.30−1.35 (4H, m), 1.40−1.61 (4H, m), 1.70−1.79 (1H, m), 3.76 (3H, s), 3.84 (2H, d, J = 5.6 Hz), 6.79 (1H, dd, J = 2.8, 9.0 Hz), 6.83 (1H, d, J = 8.9 Hz), 7.11 (1H, d, J = 2.8 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.3, 14.2, 23.2, 24.0, 29.2, 30.6, 39.6, 56.0, 72.5, 112.9, 113.8, 114.4, 119.0, 150.2, 154.0. FT-IR (neat, cm^{-1}) 2928, 1492, 1462, 1439, 1380, 1270, 1210, 1181, 1040. HRMS (ESI)$^+$ m/z 315.0954 ($C_{15}H_{24}BrO_2$ [M + H]$^+$ requires 315.0960).

(iii) *n*-BuLi (1.6 M, 31 mL, 50 mmol) was added dropwise to a stirred solution of 2-bromo-1-(2-ethylhexyloxy)-4-methoxybenzene (10.5 g, 9.38 mmol) in THF (200 mL) at −78 °C, and the resulting solution was stirred at −78 °C for 10 min. DMF (4.6 mL, 60 mmol) was then added dropwise and the resulting mixture was stirred at −78 °C for 45 min, then room temperature for 15 min. The reaction was then quenched with sat. aq $NaHCO_3$ (50 mL) and the THF removed under reduced pressure. The residue was taken up in ether and washed with sat. aq NaCl (3 × 50 mL) and H_2O (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the aldehyde **6** as a yellow oil (8.724 g, 100%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88−0.96 (6H, m), 1.25−1.36 (4H, m), 1.38−1.59 (4H, m), 1.72−1.78 (1H, m), 3.80 (3H, s), 3.93 (2H, dd), 6.94 (1H, d, J = 9.1 Hz), 7.12 (1H, dd, J = 9.0, 3.3 Hz), 7.33 (1H, d, J = 3.3 Hz), 10.48 (1H, s). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 11.05, 13.94, 22.92, 23.90, 29.01, 30.53, 39.45, 55.53, 71.28, 109.92, 114.15, 123.39, 153.36, 156.48, 189.24. FT-IR (neat, cm^{-1}) 2958, 2928, 2560, 1638, 1613, 1585, 14949, 1463, 1422, 1388, 1276, 1216, 1158, 1040. HRMS (ESI)$^+$ m/z 287.1617 ($C_{16}H_{24}NaO_3$ [M + Na]$^+$ requires 287.1618).

Diisopropyl 4-bromo-5-(2-ethylhexyloxy)-2-methoxybenzylphosphonate, 5: A solution of 2-bromo-1-(2-ethylhexyloxy)-4-methoxy benzene (20.27 g, 64.3 mmol), *p*-formaldehyde (7.723 g, 257.2 mmol), concentrated HCl (36%, 22.1 mL, 257 mmol) and glacial acetic acid (22.1 mL, 386 mmol) was heated at 80 °C for 24 h. After 24 h the solution was cooled to room temperature and the mixture taken up in *n*-hexane (100 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (3 × 80 mL), sat. aq. NaCl (3 × 80 mL) and the combined aqueous layers re-extracted with additional *n*-hexane (1 × 50 mL). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated under reduced pressure to give an inseparable 3:1 mixture of the desired product **4** and its 6-chloromethyl isomer as a light brown oil (23.70 g, 100%) ^{1}H NMR (signals for **4**) (500 MHz, $CDCl_3$) δ 0.87−0.96 (m, 6H),

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1.31−1.35 (m, 4H), 1.42−1.58 (m, 4H), 1.73−1.78 (m, 1H), 3.83 (s, 3H), 3.86 (d, 2H, J = 2.7 Hz), 4.59 (s, 2H), 7.08 (s, 1H), 7.26 (s, 1H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ 151.4, 149.9, 125.6, 116.4, 115.5, 110.4, 72.4, 56.4, 41.1, 39.5, 30.5, 29.1, 23.9, 23.0, 14.06, 11.2. HRMS (ESI)$^+$ m/z 385.0541 ($C_{16}H_{24}BrClNaO_2$ [M + Na]$^+$ requires 385.0546).

The isomeric mixture of **4** in triisopropyl phosphite (27.14 g, 29.9 mL, 130.3 mmol) was then stirred at reflux for 16 h. Removal of the excess triisopropyl phosphite by Kugel−Rohr distillation gave a mixture of 4- and 6-diisopropyl phosphonates as a brown oil. The brown oil was separated by flash chromatography (EtOAc/petroleum spirit as eluent) to give the desired product **5** as a light brown oil (25.08 g, 78% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89−0.94 (6H, m), 1.20 (6H, d, J = 6.2 Hz), 1.28 (6H, d, J = 6.2 Hz), 1.30−1.35 (4H, m), 1.38−1.58 (4H, m), 1.70−1.79 (1H, m), 3.14 (2H, d, J = 21.8 Hz), 3.77 (3H, s), 3.85 (2H, d, J = 5.6 Hz), 4.58−4.68 (2H, m), 6.99 (1H, d, J = 2.7 Hz), 7.03 (1H, d, J = 1.0 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.1, 14.0, 23.0, 23.8 (d, J = 5.0 Hz), 23.9, 24.1 (d, J = 3.7 Hz), 27.4 (d, J = 141 Hz), 29.0, 30.5, 39.5, 56.2, 70.5 (d, J = 6.9 Hz), 72.3, 110.4 (d, J = 4.5 Hz), 115.9, 116.6, 120.7 (d, J = 8.2 Hz), 149.6, 151.5 (d, J = 7.5 Hz). FT-IR (neat, cm^{-1}) 1211. HRMS (ESI)$^+$ m/z 515.1532 ($C_{22}H_{38}BrNaO_5P$ - [M + Na]$^+$ requires 515.1538).

Diisopropyl 4-methylbenzylphosphonate, 13: A solution of *p*-methylbenzyl bromide (5.061 g, 27.35 mmol) in triisopropyl phosphite (14.5 mL, 58.8 mmol) was refluxed for 24 h. The unreacted triisopropyl phosphite was then removed by Kugel−Rohr distillation to give the product as a clear oil (6.479 g, 89%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.17 (6H, d, J = 6.2 Hz), 1.27 (6H, d, J = 6.2 Hz), 2.31 (3H, s), 3.06 (2H, d, J = 21.5 Hz), 4.55−4.62 (2H, m), 7.09 (2H, d, J = 8.1 Hz), 7.18 (2H, dd, J = 2.4, 8.1 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 20.8, 23.59, 23.63, 23.86, 23.89, 33.6, 34.7, 70.1, 70.2, 128.6, 128.81, 128.83, 129.5, 129.6, 135.9. FT-IR (neat, cm^{-1}) 1236. HRMS (ESI)$^+$ m/z 293.1278 ($C_{14}H_{23}NaO_3P$ [M + Na]$^+$ requires 293.1283).

(*E*)-1-Bromo-2-(2-ethylhexyloxy)-4-(2′-(2-ethylhexyloxy)-5′-methoxystyryl)-5-methoxybenzene, 7: A solution of aldehyde **6** (1.593 g, 6.03 mmol) and phosphonate **5** (1.985 g, 4.03 mmol) in THF (20 mL) was added to a stirred solution of potassium *tert*-butoxide (1.844 g, 16.4 mmol) in THF (30 mL) at 0 °C. The mixture was brought to room temperature and stirred for 2.5 h. The reaction was then quenched with sat. aq NH_4Cl (15 mL) and the THF removed under reduced pressure. Ether was added and the organic phase was washed with sat. aq NH_4Cl (3 × 50 mL) and sat. aq NaCl (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a light brown oil. The light brown oil was purified by flash chromatography (CH_2Cl_2/petroleum spirit as eluent) to give the product as a lime green oil (2.065 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81−0.97 (12H, m), 1.27−1.40 (8H, m), 1.41−1.62 (8H, m), 1.74−1.81 (2H, m), 3.82 (3H, s), 3.83 (3H, s), 3.91 (4H, m), 6.78 (1H, dd, J = 2.9, 8.9 Hz), 6.83 (1H, d, J = 8.9 Hz), 7.08 (1H, s), 7.15 (1H, s), 7.18 (1H, d, J = 2.9 Hz), 7.38 (1H, d, J = 16.6 Hz), 7.46 (1H, d, J = 16.7 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.3, 11.5, 14.2, 23.20, 23.22, 24.1, 24.4, 29.2, 29.3, 30.7, 31.0, 39.8, 39.9, 56.0, 56.5, 71.6, 72.5, 111.2, 111.6, 111.7, 113.6, 114.0, 116.7, 123.1, 124.3, 127.1, 127.8, 150.2, 151.4, 151.5, 153.8. FT-IR (neat, cm^{-1}) 971. HRMS (ESI)$^+$ m/z 385.0541 ($C_{32}H_{47}BrNaO_4$ [M + Na]$^+$ requires 385.0540).

(*E*)-2-(2-Ethylhexyloxy)-4-(2′-(2-ethylhexyloxy)-5′-methoxystyryl)-5-methoxybenzaldehyde, 8: *n*-BuLi (1.6 M, 8.80 mL, 14.1 mmol) was added dropwise to a stirred solution of bromide **7** (5.399 g, 9.38 mmol) in THF (130 mL) at −78 °C, and the resulting dark solution was stirred at −78 °C for 10 min. DMF (1.35 mL, 17.5 mmol) was then added dropwise and the resulting solution was stirred at −78 °C for 45 min, then room temperature for 15 min. The reaction was quenched with sat. aq $NaHCO_3$ (50 mL) and the THF removed under reduced pressure. The residue was taken up in ether and washed with sat. aq NaCl (3 × 50 mL) and H_2O (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the aldehyde as an orange oil (4.922 g, 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88−0.94 (12H, m), 1.28−1.40 (8H, m), 1.42−1.62 (8H, m), 1.76−1.83 (2H, m), 3.84 (3H, s), 3.88−3.93 (2H, m), 3.89 (3H, s), 4.00 (2H, d, J = 5.3 Hz), 6.82 (1H, dd, J = 2.9, 8.9 Hz), 6.86 (1H, d, J = 8.9 Hz), 7.20 (1H, d, J = 2.9 Hz), 7.23 (1H, s), 7.34 (1H, s), 7.49 (1H, d, J = 16.7 Hz), 7.62 (1H, d, J = 16.7 Hz), 10.47 (1H, s). ^{13}C NMR ($CDCl_3$, 500 MHz) δ 11.3, 11.5, 14.20, 14.22, 23.17, 23.23, 24.2, 24.4, 29.27, 29.32, 30.8, 31.0, 39.8, 39.9, 56.0, 56.2, 71.4, 71.6, 109.0, 110.3, 112.0, 113.6, 114.8, 122.9, 124.1, 127.2, 127.4, 135.1, 151.3, 151.7, 153.8, 156.7, 189.2. FT-IR (neat, cm^{-1}) 1676, 972. HRMS (ESI)$^+$ m/z 547.3393 ($C_{33}H_{48}NaO_5$ [M + Na]$^+$ requires 547.3394).

(*E,E*)-1-Bromo-2-(2-ethylhexyloxy)-4-(2′-(2-ethylhexyloxy)-4′-(2″-(2-ethylhexyloxy)-5″-methoxystyryl)-5′-methoxystyryl)-5-methoxybenzene, 9: A solution of aldehyde **8** (0.762 g, 1.45 mmol) and phosphonate **5** (1.073 g, 2.17 mmol) in THF (15 mL) was added to a stirred solution of potassium *tert*-butoxide (0.651 g, 5.80 mmol) in THF (15 mL) at 0 °C. The mixture was brought to room temperature and stirred for 4 h. The reaction was then quenched with sat. aq NH_4Cl (10 mL) and the THF removed under reduced pressure. Ether was added and the organic phase was washed with sat. aq NH_4Cl (3 × 50 mL) and sat. aq. NaCl (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a light brown oil. The light brown oil was purified by column chromatography (ether/petroleum spirit as eluent) to give the product as an orange oil (1.021 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88−1.00 (18H, m), 1.27−1.42 (12H, m), 1.44−1.66 (12H, m), 1.76−1.82 (3H, m), 3.83 (3H, s), 3.86 (3H, s), 3.87−3.97 (9H, m), 6.78 (1H, dd, J = 3.0, 8.9 Hz), 6.84 (1H, d, J = 8.9 Hz), 7.09 (1H, s), 7.15 (1H, s), 7.17 (2H, s), 7.22 (1H, d, J = 3.0 Hz), 7.41 (1H, d, J = 16.6 Hz), 7.46−7.53 (3H, m). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.4, 11.5, 14.23, 14.24, 23.22, 23.25, 24.1, 24.4, 29.3, 29.4, 30.7, 30.98, 31.01, 39.8, 39.95, 40.01, 56.0, 56.55, 56.63, 71.4, 71.7, 72.5, 109.4, 110.1, 111.2, 111.5, 111.6, 113.6, 113.9, 116.7, 122.5, 123.5, 123.7, 124.4, 126.8, 127.2, 127.5, 128.1, 150.3, 151.4, 151.45, 151.49, 151.6, 153.9. FT-IR (neat, cm^{-1}) 971. HRMS (ESI)$^+$ m/z 835.4497 ($C_{49}H_{72}BrO_6$ [M + H]$^+$ requires 835.4512).

(*E,E*)-2-(2-Ethylhexyloxy)-4-(2′-(2-ethylhexyloxy)-4′-(2″-(2-ethylhexyloxy)-5″-methoxystyryl)-5′-methoxystyryl)-5-methoxybenzaldehyde, 10: *n*-BuLi (1.6 M, 6.2 mL, 9.9 mmol) was added dropwise to a stirred solution of bromide **9** (5.367 g, 6.42 mmol) in THF (120 mL) at −78 °C, and the resulting dark solution was stirred at −78 °C for 10 min. DMF (0.9 mL, 11.7 mmol) was then added dropwise and the resulting mixture was stirred at −78 °C for 30 min, then room temperature for 1.5 h. The reaction was then quenched with sat. aq $NaHCO_3$ (50 mL) and the THF removed under reduced pressure. The residue was taken up in ether and washed with H_2O (4 × 100 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the aldehyde as an orange oil (5.040 g, 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83−1.01 (18H, m), 1.28−1.39 (12H, m), 1.42−1.66 (12H, m), 1.75−1.87 (3H, m), 3.83 (3H, s), 3.85−4.01 (12H, m), 6.78 (1H, dd, J = 3.0, 8.9 Hz), 6.84 (1H, d, J = 8.9 Hz), 7.16 (1H, s), 7.17 (1H, s), 7.21 (1H, d, J = 3.0 Hz), 7.24 (1H, s), 7.34 (1H, s), 7.46−7.54 (3H, m), 7.65 (1H, d, J = 16.6 Hz), 10.46 (1H, s). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.4, 11.5, 14.21, 14.22, 14.24, 23.2, 23.3, 24.2, 24.4, 24.5, 29.29, 29.34, 30.9, 30.98, 31.02, 39.8, 39.9, 40.0, 56.0, 56.2, 56.6, 71.4, 71.7, 109.0, 109.6, 110.0, 110.1, 111.7, 113.6, 114.0, 122.2, 123.3, 124.1, 124.2, 126.2, 127.4, 128.0, 128.4, 135.3, 151.2, 151.4, 151.5, 151.8, 153.8, 156.8, 189.1. FT-IR (neat, cm^{-1}) 1675, 971. HRMS (ESI)$^+$ m/z 785.5353 ($C_{50}H_{73}O_7$ [M + H]$^+$ requires 785.5356).

(*E,E,E*)-1-Bromo-2-(2-ethylhexyloxy)-4-(2′-(2-ethylhexyloxy)-4′-(2″-(2-ethylhexyloxy)-4″-(2‴-(2-ethylhexyloxy)-5‴-methoxystyryl)-5″-methoxystyryl)-5′-methoxystyryl)-5-methoxybenzene, 11: A solution of aldehyde **10** (0.402 g, 0.512 mmol)

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and phosphonate **5** (0.382 g, 0.774 mmol) in THF (10 mL) was added to a stirred solution of potassium *tert*-butoxide (0.256 g, 2.28 mmol) in THF (10 mL) at 0 °C. The mixture was brought to room temperature and stirred for 3 h. The reaction was then quenched with sat. aq NH_4Cl (5 mL) and the THF removed under reduced pressure. Ether was added and the organic phase was washed with sat. aq NH_4Cl (2 × 50 mL) and sat. aq NaCl (2 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give an orange solid. The orange solid was purified by passing it through a plug of silica (CH_2Cl_2 as eluent) to give the product as a bright orange solid (0.494 g, 88%), mp 97−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84−1.01 (24H, m), 1.29−1.42 (16H, m), 1.43−1.67 (16H, m), 1.76−1.86 (4H, m), 3.83 (3H, s), 3.86 (3H, s), 3.89−3.99 (14H, m), 6.77 (1H, dd, J = 3.0, 8.9 Hz), 6.84 (1H, d, J = 8.9 Hz), 7.08 (1H, s), 7.16−7.18 (5H, m), 7.22 (1H, d, J = 3.0 Hz), 7.41 (1H, d, J = 16.6 Hz), 7.45−7.56 (5H, m). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.4, 11.5, 14.3, 23.2, 23.3, 24.1, 24.4, 24.5, 29.3, 29.4, 30.7, 31.0, 31.0, 39.8, 39.95, 40.03, 40.04, 56.0, 56.55, 56.62, 56.64, 71.4, 71.5, 71.7, 72.5, 109.3, 109.4, 110.0, 110.1, 111.1, 111.5, 111.6, 113.7, 113.9, 116.7, 122.5, 122.9, 123.5, 123.6, 123.8, 124.4, 126.8, 127.2, 127.25, 127.34, 127.6, 128.2, 150.3, 151.4, 151.45, 151.48, 151.5, 151.6, 153.9. FT-IR (neat, cm^{-1}) 968. HRMS (ESI)$^+$ m/z 1094.6206 ($C_{66}H_{95}BrO_8$ [M]$^+$ requires 1094.6210).

(*E*,*E*,*E*)-2-(2-Ethylhexyloxy)-4-(2′-(2-ethylhexyloxy)-4′-(2″-(2-ethylhexyloxy)-4″-(2‴-(2-ethylhexyloxy)-5‴-methoxystyryl)-5″-methoxystyryl)-5′-methoxystyryl)-5-methoxybenzaldehyde, 12: *n*-BuLi (1.6 M, 4.7 mL, 7.5 mmol) was added dropwise to a stirred solution of bromide **11** (4.626 g, 4.22 mmol) in THF (75 mL) at −78 °C, and the resulting dark solution was stirred at −78 °C for 10 min. DMF (0.7 mL, 9.1 mmol) was then added dropwise and the resulting mixture was stirred at −78 °C for 30 min, then room temperature for 1.5 h. The reaction was then quenched with sat. aq $NaHCO_3$ (50 mL) and the THF removed under reduced pressure. The residue was taken up in ether and washed with H_2O (3 × 80 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the aldehyde as an orange solid (4.371 g, 99%), mp 91−93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82−1.02 (24H, m), 1.28−1.42 (16H, m), 1.43−1.68 (16H, m), 1.74−1.86 (4H, m), 3.83 (3H, s), 3.86−4.02 (17H, m), 6.77 (1H, dd, J = 3.0, 8.9 Hz), 6.84 (1H, d, J = 8.9 Hz), 7.17−7.19 (4H, m), 7.22 (1H, d, J = 3.0 Hz), 7.24 (1H, s), 7.35 (1H, s), 7.46−7.53 (4H, m), 7.57 (1H, d, J = 16.4 Hz), 7.66 (1H, d, J = 16.5 Hz), 10.47 (1H, s). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.4, 11.5, 14.2, 23.2, 23.3, 24.2, 24.4, 24.5, 29.3, 29.4, 30.8, 30.97, 31.02, 39.8, 39.9, 40.0, 56.0, 56.2, 56.6, 71.35, 71.43, 71.7, 109.0, 109.3, 109.5, 109.9, 110.1, 111.5, 111.6, 112.2, 112.5, 113.6, 113.9, 114.6, 122.1, 122.7, 122.9, 123.2, 123.4, 123.5, 123.6, 123.7, 124.0, 124.18, 124.23, 126.1, 127.0, 127.17, 127.23, 127.3, 127.4, 127.5, 128.0, 128.1, 128.2, 128.5, 135.3, 151.2, 151.4, 151.46, 151.50, 151.6, 151.8, 153.8, 156.8, 189.1. FT-IR (neat, cm^{-1}) 1676, 967. HRMS (ESI)$^+$ m/z 1044.7041 ($C_{67}H_{96}O_9$ [M]$^+$ requires 1044.7054).

(*E*,*E*)-1′-(2-Ethylhexyloxy)-5′-(2″-(2-ethylhexyloxy)-5″-methoxystyryl)-4′-methoxy-2′-(4-methylstyryl)benzene, 1: A solution of aldehyde **8** (0.286 g, 0.545 mmol) and phosphonate **13** (0.273 g, 1.311 mmol) in THF (7 mL) was added to a stirred solution of potassium *tert*-butoxide (0.288 g, 2.54 mmol) in THF (8 mL) at 0 °C. The mixture was brought to room temperature and stirred for 24 h. The reaction was then quenched with sat. aq NH_4Cl (5 mL) and the THF was removed under reduced pressure. Ether was added and the organic phase was washed with sat. aq NH_4Cl (2 × 50 mL) and sat. aq NaCl (2 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a yellow oil. The yellow oil was purified by flash chromatography (CH_2Cl_2/*n*-pentane as eluent) to give the product as a bright yellow oil (0.255 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83−1.00 (12H, m), 1.26−1.42 (8H, m), 1.43−1.65 (8H, m), 1.75−1.84 (2H, m), 2.37 (1H, s), 3.83 (3H, s), 3.84−3.90 (2H, m), 3.91 (3H, s), 3.94 (2H, d, J = 5.6 Hz), 6.77 (1H, dd, J = 3.0, 8.9 Hz), 6.83 (1H, d, J = 8.9 Hz), 7.11−7.18 (5H, m), 7.21 (1H, d, J = 3.0 Hz), 7.39−7.52 (5H, m). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.4, 11.5, 14.3, 21.4, 23.25, 23.26, 24.39, 24.42, 29.35, 29.40, 31.0, 31.1, 39.9, 40.0, 56.0, 56.5, 71.7, 71.8, 109.3, 110.3, 111.6, 113.6, 113.9, 122.7, 123.5, 123.6, 126.5, 126.9, 127.2, 128.1, 128.7, 129.2, 129 0.5, 129.7, 135.4, 137.4, 151.38, 151.40, 151.6, 153.8. FT-IR (neat, cm^{-1}) 966. HRMS (ESI)$^+$ m/z 612.4173 ($C_{41}H_{56}O_4$ [M]$^+$ requires 612.4179).

(*E*,*E*,*E*)-2″-(2-Ethylhexyloxy)-1″-(2′-(2-ethylhexyloxy)-5′-methoxy-1′-(1-methylstyryl)styryl)-4″-(2‴-(2-ethylhexyloxy)-5‴-methoxystyryl)-5″-methoxybenzene, 2: A solution of aldehyde **10** (0.228 g, 0.290 mmol) and phosphonate **13** (0.169 g, 0.625 mmol) in THF (5 mL) was added to a stirred solution of potassium *tert*-butoxide (0.130 g, 1.16 mmol) in THF (5 mL) at 0 °C. The mixture was brought to room temperature and stirred for 3 h. The reaction was then quenched with sat. aq NH_4Cl (5 mL) and the THF removed under reduced pressure. Ether was added and the organic phase was washed with sat. aq NH_4Cl (2 × 30 mL) and sat. aq NaCl (2 × 30 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a light brown solid. The light brown solid was purified by flash chromatography (ether/*n*-pentane as eluent) to give the product as a bright yellow oil (0.126 g, 50%), mp 101−103 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88−1.01 (18H, m), 1.28−1.42 (12H, m), 1.43−1.68 (12H, m), 1.75−1.88 (3H, m), 2.37 (3H, s), 3.83 (3H, s), 3.85−3.99 (12H, m), 6.77 (1H, dd, J = 3.0, 8.9 Hz), 6.84 (1H, d, J = 8.9 Hz), 7.13 (1H, m), 7.15−7.18 (6H, m), 7.22 (1H, d, J = 3.0 Hz), 7.42−7.53 (6H, m), 7.54 (1H, d, J = 16.6 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.45, 11.53, 14.3, 21.4, 23.25, 23.26, 24.40, 24.42, 24.5, 29.36, 29.42, 30.98, 31.02, 31.1, 39.96, 40.01, 40.1, 56.0, 56.5, 56.6, 71.5, 71.7, 71.8, 109.2, 109.3, 110.1, 110.2, 111.6, 113.7, 113.9, 122.7, 122.9, 123.53, 123.56, 123.7, 126.5, 126.9, 127.2, 127.28, 127.31, 128.2, 128.7, 129.5, 135.4, 137.4, 151.39, 151.44, 151.47, 151.52, 151.6, 153.9. FT-IR (neat, cm^{-1}) 969. HRMS (ESI)$^+$ m/z 872.5949 ($C_{58}H_{80}O_6$ [M]$^+$ requires 872.5955).

(*E*,*E*,*E*,*E*)-2″-(2-Ethylhexyloxy)-1″-(2′-(2-ethylhexyloxy)-5′-methoxy-1′-(1-methylstyryl)styryl)-4″-(2‴-(2-ethylhexyloxy)-4‴-(2⁗-(2-ethylhexyloxy)-5⁗-methoxystyryl)-5‴-methoxystyryl)-5″-methoxybenzene, 3: A solution of aldehyde **12** (0.423 g, 0.405 mmol) and phosphonate **13** (0.168 g, 0.622 mmol) in THF (15 mL) was added to a stirred solution of potassium *tert*-butoxide (0.097 g, 0.864 mmol) in THF (15 mL) at 0 °C. The mixture was brought to room temperature and stirred for 19 h. The reaction was then quenched with sat. aq NH_4Cl (10 mL) and the THF removed under reduced pressure. Ether was added and the organic phase was washed with H_2O (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give an orange solid. The orange solid was purified by flash chromatography (ether/*n*-hexane as eluent) to give the product as an orange solid (0.418 g, 91%), mp 149−150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88−1.02 (24H, m), 1.29−1.43 (16H, m), 1.44−1.70 (16H, m), 1.75−1.86 (4H, m), 2.37 (3H, s), 3.83 (3H, s), 3.85−4.02 (17H, m), 6.77 (1H, dd, J = 3.0, 8.9 Hz), 6.84 (1H, d, J = 8.9 Hz), 7.13 (1H, m), 7.16−7.19 (7H, m), 7.22 (1H, d, J = 3.0 Hz), 7.42−7.46 (3H, m), 7.48−7.56 (7H, m). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.4, 11.5, 14.2, 21.4, 23.3, 24.4, 24.5, 29.34, 29.36, 29.40, 29.41, 30.97, 31.02, 31.11, 39.94, 40.0, 40.05, 56.0, 56.5, 56.6, 71.4, 71.5, 71.7, 71.8, 109.19, 109.23, 110.0, 110.1, 110.2, 111.5, 113.6, 113.8, 122.7, 122.8, 122.9, 123.50, 123.54, 123.60, 123.63, 126.5, 126.9, 127.2, 127.26, 127.29, 127.4, 128.2, 128.7, 129.5, 135.4, 137.4, 151.37, 151.43, 151.46, 151.49, 151.51, 151.56, 151.60, 153.8. FT-IR (neat, cm^{-1}) 968. HRMS (ESI)$^+$ m/z 1132.7729 ($C_{75}H_{104}O_8$ [M]$^+$ requires 1132.7731).

Synthesis of *n*-Hexyl Derivatives

2-Bromo-1-hexyloxy-4-methoxybenzene, 16: KOH (14.34 g, 255.6 mmol) was added to a stirred solution of 2-bromo-4-methoxyphenol (26.02 g, 128 mmol) and 1-bromohexane (27.0 mL, 31.7 g,

192 mmol) in acetone (125 mL) at room temperature. The reaction mixture was then stirred at reflux for 70 h. After 70 h, the acetone was removed under reduced pressure and the dark residue was taken up in ether. The organic layer was washed with H_2O (1 × 80 mL), 10% KOH (2 × 80 mL), and sat. aq $NaHCO_3$ (2 × 80 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a dark brown oil. Excess 1-bromohexane was removed by Kugel−Rohr distillation (0.6 mbar, 155 °C) to give a light brown residue. Subsequent Kugel−Rohr distillation of the light brown residue (0.6 mbar, 190 °C) gave the product as a pale yellow oil (34.831 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89−0.93 (3H, m), 1.32−1.38 (4H, m), 1.46−1.52 (2H, m), 1.77−1.83 (2H, m), 3.76 (3H, s), 3.96 (2H, t, J = 6.5 Hz), 6.79 (1H, dd, J = 2.9, 8.9 Hz), 6.84 (1H, d, J = 9.0 Hz), 7.11 (1H, d, J = 2.9 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.2, 22.7, 25.8, 29.4, 31.7, 56.0, 70.4, 113.0, 113.9, 114.9, 118.9, 150.1, 154.2. HRMS (ESI)$^+$ m/z 392.9613 ($C_{13}H_{19}AgBrO_2$ [M + Ag]$^+$ requires 392.9619).

2-Hexyloxy-5-methoxybenzaldehyde, 17: *n*-BuLi (1.5 M, 9.0 mL, 13.5 mmol) was added dropwise to a stirred solution of bromide **16** (2.595 g, 9.04 mmol) in THF (50 mL) at −78 °C, and the resulting solution was stirred at −78 °C for 15 min. DMF (1.3 mL, 16.9 mmol) was then slowly added and the resulting mixture was stirred at −78 °C for 45 min, then room temperature for 15 min. The reaction was then quenched with sat. aq $NaHCO_3$ (15 mL) and the THF was removed under reduced pressure. The residue was taken up in ether and washed with H_2O (3 × 80 mL) and sat. aq NaCl (1 × 80 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a yellow oil. The yellow oil was purified by automated column chromatography (SNAP 50G cartridge, ether/petroleum spirit as eluent) to give the product as a light brown oil (1.494 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89−0.92 (3H, m), 1.33−1.38 (4H, m), 1.45−1.51 (2H, m), 1.79−1.85 (2H, m), 3.80 (3H, s), 4.03 (2H, t, J = 6.5 Hz), 6.93 (1H, d, J = 9.1 Hz), 7.12 (1H, dd, J = 3.3, 9.0 Hz), 7.32 (1H, d, J = 3.3 Hz), 10.48 (1H, s). ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.1, 22.7, 25.9, 29.3, 31.7, 55.6, 69.4, 110.2, 114.6, 123.8, 125.3, 153.7, 156.6, 189.8. FT-IR (neat, cm^{-1}) 1682. HRMS (ESI)$^+$ m/z 237.1485 ($C_{14}H_{21}O_3$ [M + H]$^+$ requires 237.1491).

Diisopropyl 4-bromo-5-hexyloxy-2-methoxybenzylphosphonate, 18: A solution of bromide **16** (24.64 g, 85.80 mmol), *p*-formaldehyde (10.31 g, 343.3 mmol), concentrated HCl (32%, 34 mL, 347 mmol), and glacial acetic acid (30.0 mL, 31.5 mmol) was heated at 80 °C for 23 h. After 23 h the solution was cooled to room temperature and the mixture was taken up in *n*-hexane (100 mL). The organic layer was washed with sat. aq $NaHCO_3$ (3 × 100 mL) and sat. aq NaCl (3 × 100 mL) and the combined aqueous layers were re-extracted with additional *n*-hexane (2 × 100 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a 3:1 mixture of the desired product and its 6-chloromethyl regioisomer as a dark brown oil (28.75 g, 100%). ^{1}H NMR of the desired 4-chloromethyl regioisomer (500 MHz, $CDCl_3$) δ 0.90−0.92 (3H, m), 1.33−1.37 (4H, m), 1.47−1.52 (2H, m), 1.77−1.86 (2H, m), 3.83 (3H, s), 3.98 (2H, t, J = 6.5 Hz), 4.59 (2H, s), 6.94 (1H, s), 7.08 (1H, s). The isomeric mixture in triisopropyl phosphite (35.7 g, 39.4 mL, 171.4 mmol) was then stirred at reflux for 19 h. Removal of the excess triisopropyl phosphite by Kugel−Rohr distillation gave a mixture of 4- and 6-diisopropyl phosphonates as a brown oil. The brown oil was purified by flash chromatography (EtOAc/*n*-hexane as eluent) to give the desired product as a light brown oil (22.72 g, 57% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, t, J = 7.1 Hz), 1.19 (6H, d, J = 6.2 Hz), 1.27 (6H, d, J = 6.2 Hz), 1.32−1.36 (4H, m), 1.45−1.50 (2H, m), 1.76−1.82 (2H, m), 3.13 (2H, d, J = 21.8 Hz), 3.77 (3H, s), 3.97 (2H, t, J = 6.6 Hz), 4.57−4.67 (2H, m), 7.01 (1H, d, J = 2.7 Hz), 7.03 (1H, d, J = 1.0 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.1, 22.6, 23.7 (d, J = 5.1 Hz), 23.9 (d, J = 5.0 Hz), 24.1 (d, J = 3.7 Hz), 25.7, 27.4 (d, J = 142 Hz), 29.3, 31.6, 56.3, 70.2, 70.6 (d, J = 6.8 Hz), 110.6 (d, J = 4.6 Hz), 116.0, 117.0 (d, J = 4.9 Hz), 120.8 (d, J = 9.1 Hz), 149.4 (d, J = 3.4 Hz), 151.7 (d, J = 7.5 Hz). FT-IR (neat, cm^{-1}) 1211. HRMS (ESI)$^+$ m/z 487.1219 ($C_{20}H_{34}BrNaO_5P$ [M + Na]$^+$ requires 487.1225).

(*E*)-1-Bromo-2-hexyloxy-4-(2′-hexyloxy-5′-methoxystyryl)-5-methoxybenzene, 19: A solution of aldehyde **17** (1.199 g, 5.07 mmol) and phosphonate **18** (3.554 g, 7.64 mmol) in THF (15 mL) was added to a stirred solution of potassium *tert*-butoxide (2.275 g, 20.27 mmol) in THF (10 mL) at 0 °C. The mixture was brought to room temperature and stirred for 3 h. The reaction was then quenched with sat. aq NH_4Cl (10 mL) and the THF removed under reduced pressure. Ether was added and the organic phase was washed with H_2O (3 × 50 mL) and sat. aq NH_4Cl (1 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a yellow solid. The yellow solid was purified by automated column chromatography (SNAP 50G cartridge, ether/petroleum spirit as eluent) to give the product as a yellow solid (2.507 g, 95%), mp 53−55 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88−0.93 (6H, m), 1.30−1.41 (8H, m), 1.49−1.56 (4H, m), 1.79−1.86 (4H, m), 3.82 (3H, s), 3.83 (3H, s), 3.97 (2H, t, J = 6.4 Hz), 4.03 (2H, t, J = 6.5 Hz), 6.77 (1H, dd, J = 3.0, 8.9 Hz), 6.83 (1H, d, J = 8.9 Hz), 7.07 (1H, s), 7.16 (2H, m), 7.38 (1H, d, J = 16.6 Hz), 7.43 (1H, d, J_{trans} = 16.6 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.2, 22.7, 22.8, 25.8, 26.0, 29.4, 29.6, 31.7, 31.8, 55.9, 56.5, 69.6, 70.4, 111.7, 111.8, 111.9, 114.0, 116.6, 123.3, 124.4, 127.2, 127.9, 150.0, 151.2, 151.6, 153.9. FT-IR (neat, cm^{-1}) 971. HRMS (ESI)$^+$ m/z 519.2110 ($C_{28}H_{40}BrO_4$ [M + H]$^+$ requires 519.2110).

(*E*)-2-Hexyloxy-4-(2′-hexyloxy-5′-methoxystyryl)-5-methoxybenzaldehyde, 20: *n*-BuLi (1.6 M, 6.4 mL, 10.3 mmol) was added dropwise to a stirred solution of bromide **19** (3.540 g, 6.814 mmol) in THF (95 mL) at −78 °C, and the resulting dark solution was stirred at −78 °C for 10 min. DMF (1.1 mL, 14.2 mmol) was then added dropwise and the resulting solution was stirred at −78 °C for 45 min, then room temperature for 15 min. The reaction was quenched with sat. aq $NaHCO_3$ (25 mL) and the THF removed under reduced pressure. The residue was taken up in ether and washed with H_2O (3 × 50 mL), and the aqueous layer was extracted with additional ether. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give an orange solid. The orange solid was purified by flash chromatography (ether/*n*-hexane as eluent) to give the aldehyde as a yellow solid (2.450 g, 77%), mp 66−67 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88−0.93 (6H, m), 1.32−1.38 (8H, m), 1.47−1.56 (4H, m), 1.81−1.88 (4H, m), 3.82 (3H, s), 3.88 (3H, s), 3.98 (2H, t, J = 6.4 Hz), 4.11 (2H, t, J = 6.4 Hz), 6.81 (1H, dd, J = 2.9, 8.9 Hz), 6.85 (1H, d, J = 8.9 Hz), 7.18 (1H, d, J = 2.9 Hz), 7.21 (1H, s), 7.33 (1H, s), 7.48 (1H, d, J = 16.6 Hz), 7.56 (1H, d, J = 16.6 Hz), 10.45 (1H, s). ^{13}C NMR ($CDCl_3$, 500 MHz) δ 14.1, 14.2, 22.7, 22.8, 25.9, 26.1, 29.4, 29.6, 31.7, 31.8, 56.0, 56.2, 69.3, 69.6, 109.0, 110.7, 112.1, 114.0, 114.8, 123.2, 124.2, 127.38, 127.43, 135.1, 151.3, 151.5, 153.9, 156.5, 189.2. FT-IR (neat, cm^{-1}) 1668, 983. HRMS (ESI)$^+$ m/z 469.2948 ($C_{29}H_{41}O_5$ [M + H]$^+$ requires 469.2954).

(*E*,*E*)-1′-Hexyloxy-5′-(2″-hexyloxy-5″-methoxystyryl)-4′-methoxy-2′-(4-methylstyryl)benzene, 15: A solution of aldehyde **20** (0.210 g, 0.448 mmol) and phosphonate **13** (0.193 g, 0.714 mmol) in THF (7 mL) was added to a stirred solution of potassium *tert*-butoxide (0.104 g, 0.927 mmol) in THF (3 mL) at 0 °C. The mixture was brought to room temperature and stirred for 5 h. The reaction was then quenched with sat. aq NH_4Cl (20 mL) and the THF removed under reduced pressure. Ether was added and the organic phase was washed with H_2O (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a yellow solid. The yellow solid was purified by flash chromatography (ether/*n*-hexane as eluent) to give the product as a yellow solid (0.203 g, 81%), mp 70−72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87−0.94 (6H, m), 1.31−1.44 (8H, m), 1.51−1.58 (4H, m), 1.81−1.89 (4H, m), 2.37 (3H, s), 3.83 (3H, s), 3.92 (3H, s), 3.97 (2H, d, J = 6.4 Hz), 4.04 (2H, d, J = 6.5 Hz), 6.77 (1H,

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dd, J = 3.0, 8.9 Hz), 6.84 (1H, d, J = 8.9 Hz), 7.11−7.14 (2H, m), 7.16 (2H, s), 7.18 (1H, s), 7.20 (1H, d, J = 3.0 Hz), 7.43−7.50 (5H, m). ^{13}C NMR ($CDCl_3$, 500 MHz) δ 14.17, 14.20, 21.4, 22.8, 29.08, 29.12, 29.62, 29.66, 31.8, 55.9, 56.5, 69.7, 69.8, 109.2, 111.0, 111.7, 113.8, 114.1, 122.7, 123.7, 123.8, 127.1, 127.2, 128.3, 128.8, 129.5, 135.4, 137.4, 151.2, 151.7, 153.9. FT-IR (neat, cm^{-1}) 965. HRMS $(ESI)^+$ m/z 556.3546 ($C_{37}H_{48}O_4$ $[M]^+$ requires 556.3553).

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic information file for **15**, details of the molecular mechanics calculations for the rotamer and twistomer conformations of **14**, and ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic coordinates for **15** have been deposited with the Cambridge Crystallographic Data Centre; deposition no. 818656. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK or via www.ccdc.cam.ac.uk/conts/retrieving.html.

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