Polymers containing backbone fluorescein, phenolphthalein and benzaurin. Synthesis and optical properties

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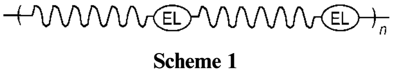
In order to utilize the prominent fluorescence ability of fluorescein in light emitting devices, we have synthesized a series of polymers that contain fluorescein in their backbones. The key step of the synthesis, in which the fluorescein unit and the polymer are created simultaneously, is the reaction of bis(2,4-dihydroxyphenyl)alkanes with phthalic anhydride. This new methodology was also used for the synthesis of polymers containing phenolphthalein and benzaurin. All the new polymers completely maintained the optical and chemical characteristics of the parent pigment.

Electroluminescence (EL) and fluorescence are related processes. Both involve the relaxation of a singlet exciton in a photon-releasing mechanism and thus both emit light at the same wavelength.[1] They differ, however, in the way the exciton is formed. In fluorescence this is achieved by photolytic excitation, usually in solution. In electroluminescence this is done by passing an electric current through a film with the excitons formed upon the meeting of electrons, from the cathode, and of holes, from the anode.[2] The required film form imperative for EL[3,4] can be attained mainly from polymers and indeed a large majority of the organic light emitting diodes (OLED) in use are based on polymers, usually fully conjugated ones.[5]

The most popular of these are polyphenylene vinylene (PPV)[6–8] and polythiophene (PT),[8–11] these however, display some critical faults, such as low quantum yields, very broad emission bands and high (red) emission wavelengths.[12,13] One possible way to avoid these shortcomings is the design of precisely structured polymers constructed of small chromophore units connected by saturated spacers (Scheme 1). Such polymers will retain the optical properties of the luminescent monomeric building blocks while possessing the physical properties of macromolecules such as film formation and thermal stability.[14] Arrangements of this kind will not only avert the flaws mentioned above but, considering the vast choice of available fluorescent materials, will allow fine tuning over the full range of luminescence.

Several polymers, synthesized in accord with this approach, have been described by us[15] and by others,[16–25] with most of them utilizing oligomeric sections of known electroluminescent polymers as the isolated chromophore. However, any strongly fluorescent molecule may be used, preferably incorporated in a polymer. Accordingly, this paper describes the incorporation of fluorescein (**1**) and some related compounds, with the aim of making use of its outstanding fluorescence in the electronic materials field.

Ever since its original synthesis by Baeyer in 1871 (Scheme 2),[26] fluorescein has been one of the standards of fluorescence. It has been commonly used, as the parent compound[27] or as the isothiocyanate or iodoacetyl derivatives,[28,29] as a fluorescent probe in biological studies. Fluorescein can exist in four different pH dependent states: cationic, neutral, anionic and dianionic (Scheme 3). In the dianionic state ($pK_a > 6.4$) it absorbs light at 492 nm and emits at 517 nm with a quantum yield of 0.9. At lower pH, in the neutral and monoanionic states, it exists mainly in a lactone form and therefore its fluorescence is much weaker.

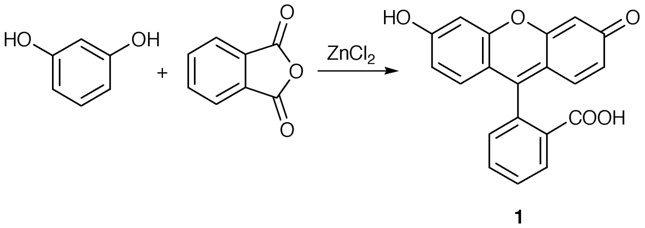


Scheme 1

Results and discussion

The target compounds consist of alternating copolymers of chromophore units and saturated spacers. The most apparent approach to the synthesis of this arrangement is the reaction of a suitable bifunctional chromophore with a counterpart bifunctional spacer (Scheme 4, method A).[30–32] We have used this route successfully in the synthesis of polymers with isolated thiophene oligomers as the chromophores.[15] It is, however, not operative in the case of fluorescein as any linking through its existing functional groups (hydroxy and carboxy) would dramatically change the optical and chemical properties. These groups will also interfere with most carbon–carbon bond-forming reactions.

Consequently another approach had to be devised, in which two components used in the synthesis of the chromophore are linked by the spacer and then allowed to react. The formation of the chromophore unit would thus simultaneously produce the polymer (Scheme 4, method B). The classical fluorescein synthesis by Baeyer involves a reaction of two molecules of resorcinol with one molecule of phthalic anhydride in a zinc chloride melt (Scheme 2). If this reaction is performed with two resorcinol moieties connected at position 4 by appropriate saturated chains, an intramolecular reaction would be geometrically very improbable and the reaction will afford the desired polymers (**3**) directly (Scheme 5). As in previous studies,[15] we made spacers of diverse chain lengths [–$(CH_2)_m$–,



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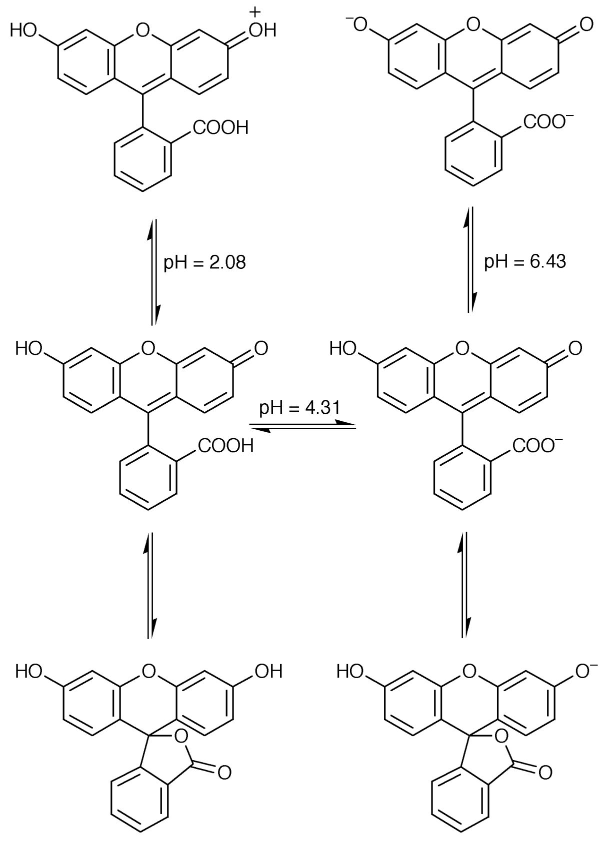
Scheme 2 The synthesis of fluorescein (**1**).

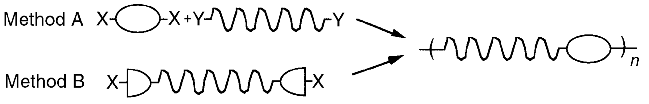


Scheme 3 The 6 different states of fluorescein (**1**).

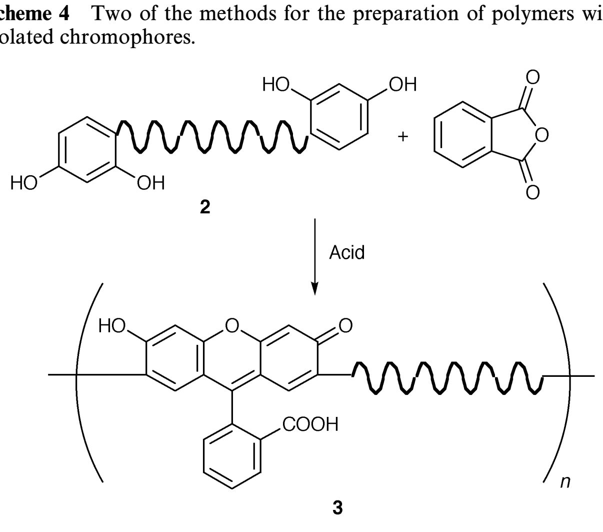
$m = 2, 6, 12$] in order to study the effects of this parameter on the optical properties of the polymers.

The initial synthetic goal, according to the strategy outlined above, would be a series of terminal bis(2,4-dihydroxyphenyl)-alkanes (**2**). The synthesis of **2a** was accomplished through McMurry coupling[33] of 2,4-dimethoxybenzaldehyde,[34] which yielded the tetramethoxystilbene **4a**. Catalytic hydrogenation to **5a** and removal of the methyl protecting groups from the phenolic oxygens with boron tribromide[35,36] yielded the required 1,2-bis(2,4-dihydroxyphenyl)ethane (**2a**) (Schemes 6 and 7).

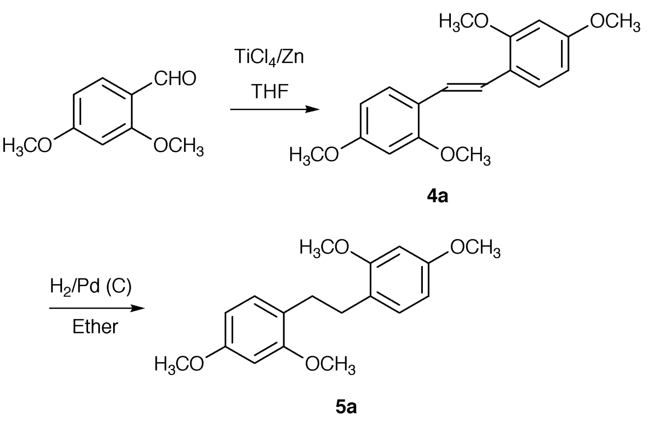
For the preparation of compounds **2** with longer tethers we have utilized Friedel–Crafts acylations of 1,3-dimethoxybenzene,[37] which occurred almost exclusively at the required position 4. Reactions with adipoyl chloride and with dodecanoyl chloride gave the diketones **6b** and **6c**, respectively. These were reduced *via* the Clemmensen reduction (Zn amalgam)[38] to 1,6-bis(2,4-dimethoxyphenyl)hexane (**5b**) and 1,12-bis(2,4-dimethoxyphenyl)dodecane (**5c**) (Scheme 8). Removal of the protecting methyls from **5b** gave 1,6-bis(2,4-dihydroxyphenyl)-hexane (**2b**) while **5c** gave, in the same manner, 1,12-bis(2,4-dihydroxyphenyl)dodecane (**2c**) (Scheme 7).



Scheme 4 Two of the methods for the preparation of polymers with isolated chromophores.

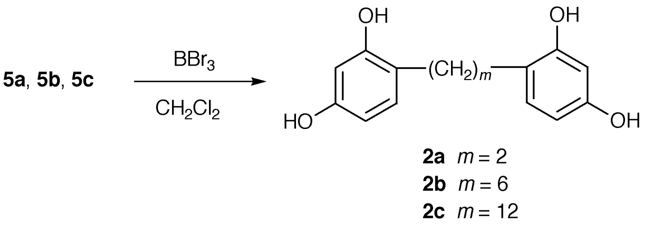


Scheme 5 The approach for the preparation of fluorescein containing polymers.

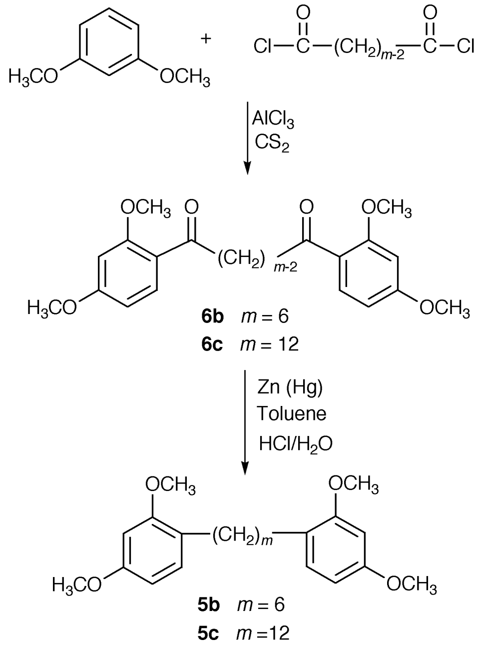


Scheme 6 Preparation of compound **5a**.

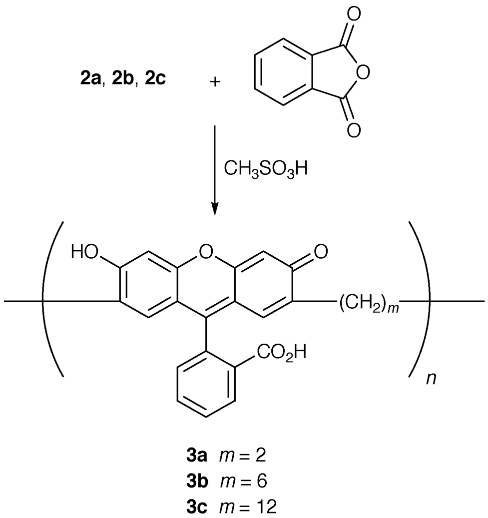
The polymerization step (**2** → **3**) proceeded smoothly upon heating the precursors **2a**, **2b** and **2c** with phthalic anhydride in methanesulfonic acid (Scheme 9).[35] Addition of water caused precipitation of the pure polymers **3a**, **3b**, and **3c** as pink powders. The intensity of the color was visibly inversely proportional to the length of the spacer. The polymers were all soluble in polar organic media (THF, alcohol, *etc.*) as well as in dilute caustic alkali aqueous solutions. The NMR



Scheme 7 Synthesis of precursors **2a–c** by the demethylation of compounds **5**.



Scheme 8 Preparation of compounds **5b** and **5c**.



Scheme 9 Polymerization of compounds **2a–c** with phthalic anhydride giving polymers **3a-c**.

spectra were as expected for such polymers and showed no trace of the starting materials, and the elemental analyses verified the purity. The molecular weights (determined by GPC, see Table 1) were in the range of 10 000–20 000, which are satisfactory as they are large enough to make sufficiently high quality films while not high enough to create problems with solubility.

The spectral properties, absorption and emission, of the polymers were as intended, very similar to those of fluorescein itself (Table 2), both as neutral species and as dianions. It is evident from the table that the change to a basic medium (pH >8) causes a bathochromic shift of *ca.* 50 nm in the absorptions, while the wavelength of the emissions remain almost unchanged. The reason for this unusual phenomenon is that the major tautomer in the neutral state is the nonfluorescent lactonic one. The fluorescence originates only from the minor carboxyquinone form whose absorption is hardly detectable. Hence the fluorescence of the dianion, which exists completely as a carboxyquinone, occurs at a wavelength close to that of the neutral state, but is much more intense. Solutions of the dianionic state of the fluorescein polymers showed high extinction coefficients similar to fluorescein *vis-à-vis* the number of fluorescein units. The pK_a of the dianion form was also determined from the absorption spectra for the polymers and was found to be equal to that of fluorescein (Table 3, Fig. 1). The effect of the change in pH was even more apparent in the emission (Fig. 2) spectra with a second pK_a at *ca.* 4.3 noticeable. This pK_a is in accord with the neutral to monoanion change in **1** (Scheme 3).

A major problem in the existing uses of fluorescein and its derivatives is photochemical instability (bleaching), which

Table 1 Molecular weight data for the polymers

	$M_w/10^4$	$M_n/10^4$	MWD
3a	1.69	1.03	1.64
3b	1.32	1.03	1.28
3c	1.73	1.15	1.51
12	1.79	1.41	1.27
13	1.66	1.17	1.42

Table 3 Photochemical data for polymers **3** relative to fluorescein (**1**)

	$\varepsilon^a/10^4\ M^{-1}\ cm^{-1}$	Bleaching (%)^b	$pK_a{}^c$
1	9.0	17	6.5
3a	8.2	11	6.6 ± 0.2
3b	8.4	10	6.5 ± 0.1
3c	8.4	8	6.5 ± 0.1

[a] Per repeating unit in the dianionic state. [b] Determined by the decrease in fluorescence of dilute (10^{-4}–10^{-6} M) MeOH solutions. [c] From the anionic to the dianionic state.

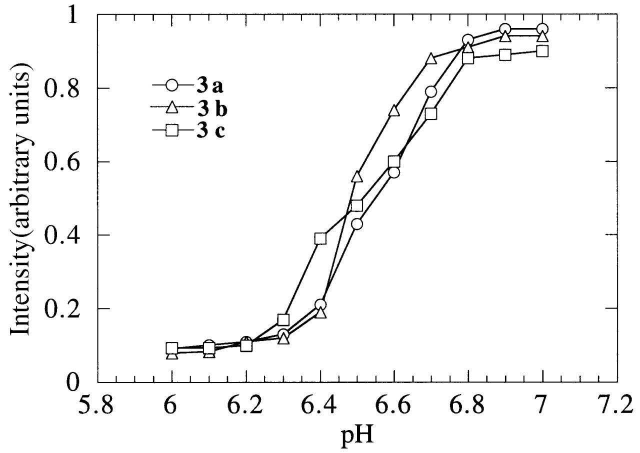


Fig. 1 The intensity of the absorption at *ca.* 500 nm as a function of pH for polymers **3a–c**.

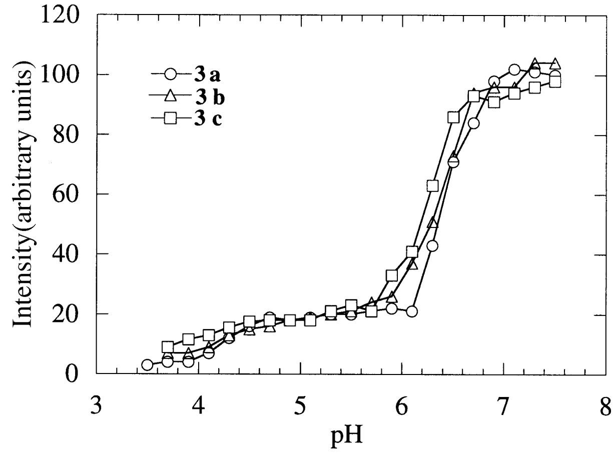


Fig. 2 The intensity of the emission at *ca.* 520 nm as a function of pH for polymers **3a–c**.

Table 2 Absorption and emission values for polymers **3** relative to fluorescein **1** [a]

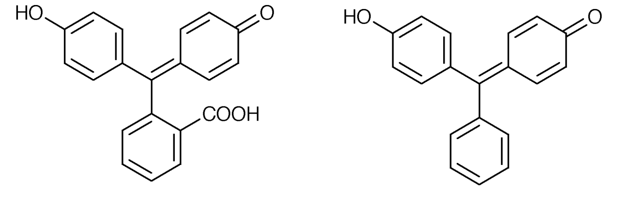
	Absorption/nm		Emission/nm	
	Neutral	Basic	Neutral	Basic
1	466	493	520	526
3a	455	502	515	518
3b	460	508	518	525
3c	454	510	513	518

[a] Methanolic solutions.

causes a decrease of the fluorescence in relation to radiation time. We found that the new polymers are photochemically more stable than fluorescein by a factor of 1.5–2 (Table 3). After 30 min of irradiation at 450 nm the polymers were bleached by only 8–11% while fluorescein was reported to bleach under identical conditions and irradiation time by 17%,[35] suggesting that the polymeric forms stabilize and lengthen the time of the optical activity of the fluorescein unit. Such bleaching does not occur at all during electroluminescence processes.

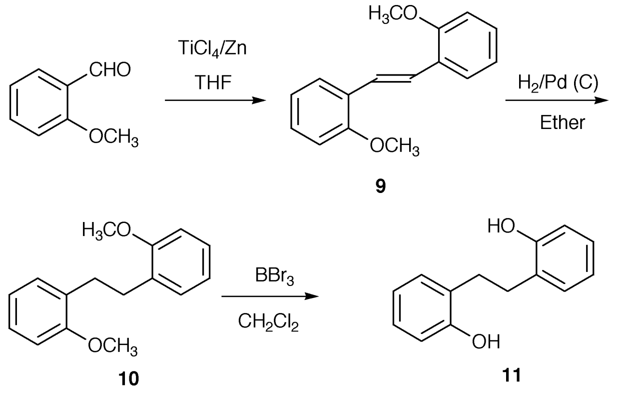
The synthetic approach presented above for the synthesis of fluorescein polymers can be extended to other structurally related dyes. We have used it for synthesis of polymers that contain phenolphthalein (**7**)[39] and benzaurin (phenolbenzene)[40] **8** (Scheme 10). Neither are fluorescent but are extensively used as indicators and the corresponding polymers may, therefore, be utilized as unusual pH sensory devices in the form of films. The McMurry coupling of 2-methoxybenzaldehyde[34] afforded the dimethoxystilbene **9**, which was hydrogenated to give 1,2-bis(2-methoxyphenyl) ethane (**10**) and then demethylated with BBr_3 to 1,2-bis(2-hydroxyphenyl)ethane (**11**) (Scheme 11). Reaction of **11** with phthalic anhydride or benzoic anhydride in methanesulfonic acid yielded polymeric phenolphthalein **12** and polymeric benzaurin **13**, respectively (Scheme 12).

The chemical and optical properties of the polymers **12** and **13** were, as anticipated, very close to those of the corresponding monomeric indicators **7** and **8** (Table 4). The most significant feature is the indicator function, which involves a reversible change of the color from colorless to deep purple over a very small range of pH. Optically there was a slight variation from the normal absorption of phenolphthalein and benzaurin. This is a common occurrence among polymers with short spacers and involves steric and other secondary interactions.



7 **8**

Scheme 10

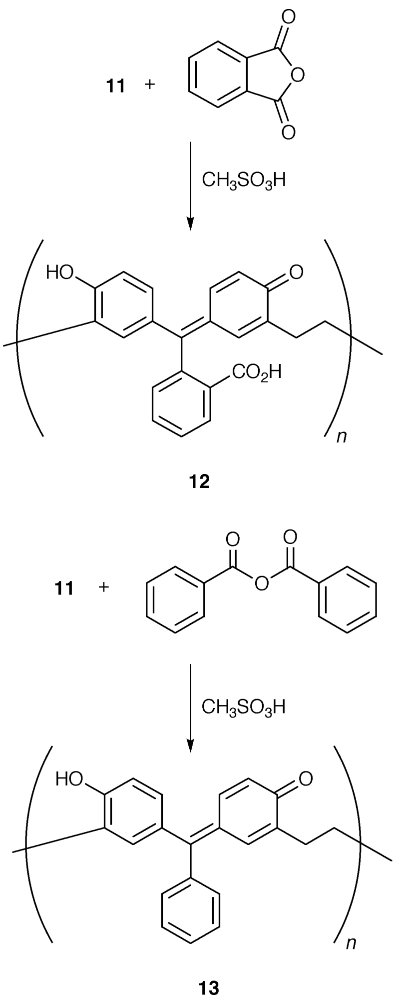


Scheme 11 Synthesis of precursor **11**.

Table 4 Absorption data for polymers **12** and **13** relative to the parent compounds[a]

	Absorption/nm		
	Neutral	Basic	pK_a
7	374	552	9.2
12	410	564	9.4 ± 0.3
8[40]	397	509	8.9
13	405	470	8.9 ± 0.4

[a] Methanolic solutions.



Scheme 12 Polymerization of **11** with phthalic anhydride or benzoic anhydride giving polymer **12** or polymer **13** respectively.

Conclusion

We have developed a new synthetic approach to polymers composed of triphenylmethane dye units interconnected by inert aliphatic chains. The method has been demonstrated by the successful syntheses of polymeric derivatives of fluorescein, phenolphthalein and benzaurin. The polymers display the same optical and chemical features as the dye components themselves, and therefore can accomplish their functions, such as use as light sources or as color change indicators. The polymeric structure and the physical properties it induces would, however, expand the number of possible utilizations, and indeed the construction of electro-optical devices based on the new polymers is underway.

Experimental

Instrumentation

NMR spectra were measured on either a Bruker DRX-400 or AMX-300 spectrometer. Melting points were determined using a Phillips Mel-TempII apparatus. UV-vis spectra were measured on a Kontron UVIKON 860 spectrophotometer. Fluorescence was measured on a Kontron SFM25 fluorimeter. Molecular weights of the polymers were estimated on a gel permeation chromatography (GPC) system consisting of a Spectra Physics P1000 pump, an Applied Bioscience 759A UV detector relative to polystyrene standards (Polyscience) with molecular weights of 4000, 5570, 9100 and 22000. Elemental analysis was performed by the Microanalysis Laboratory, the Hebrew University of Jerusalem.

Materials

All reagents were purchased from Aldrich Chemical Co. and were used as received. Solvents were purchased from Frutarom. THF was dried by distillation from sodium and benzophenone.

***E*-2,2′,4,4′-Tetramethoxystilbene (4a).** To a stirred solution of 2,4-dimethoxybenzaldehyde (3.32 g, 20 mmol) in dry THF (120 ml) in an atmosphere of nitrogen was added titanium(IV) chloride (4.75 g, 2.62 ml, 24 mmol) over 30 minutes at −10 °C and then stirred for an additional 30 min. Zinc dust (3.14 g, 48 mmol) was then added in portions over the next 30 min. The solution was allowed to warm to room temperature and then refluxed for 3.5 h. Water (≈500 ml) was added to the cooled mixture, which was then filtered. The solids were extracted with dichloromethane (≈200 ml), filtered and dried. Evaporation of the solvent gave the pure product (2.2 g, 14.6 mmol, 73%). Mp 142–5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 3.82 (s, 6H), 3.91 (s, 6H), 6.48 (d, $J = 8.1$ Hz, 2H), 6.57 (s, 2H), 7.31 (s, 2H), 7.57 (d, $J = 8.1$ Hz, 2H). Anal. calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.30; H, 6.62.

1,6-Bis(2,4-dimethoxyphenyl)hexane-1,6-dione (6b). To an ice-cold mixture of aluminum chloride (1.33 g, 10 mmol) in carbon disulfide (20 ml) was added a solution of 1,3-dimethoxybenzene (2.07 g, 15 mmol) in carbon disulfide (10 ml) over 15 min. To this mixture was added a solution of adipoyl chloride (0.46 g, 0.46 ml, 2.5 mmol) in carbon disulfide (20 ml) over 30 min. The mixture was allowed to warm to room temperature, refluxed for 2 h and then quenched with water (≈150 ml). The solids were separated and dissolved in chloroform (≈100 ml), filtered and evaporated to give the crude product, which was recrystallized from methanol to give pure **6b** (0.78 g, 2.0 mmol, 80%). Mp 140–3 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 1.76 (m, 4H), 2.97 (m, 4H), 3.87 (s, 6H), 3.89 (s, 6H), 6.45 (d, $J = 2.3$ Hz, 2H), 6.55 (dd, $J = 8.1$, 2.3 Hz, 2H), 7.74 (d, $J = 8.1$ Hz, 2H). Anal. calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 67.90; H, 6.64.

1,12-Bis(2,4-dimethoxyphenyl)dodecane-1,12-dione (6c). Prepared as compound **6b** with aluminum chloride (1.33 g, 10 mmol), 1,3-dimethoxybenzene (2.07 g, 15 mmol) and dodecanoyl chloride (0.67 g, 0.63 ml, 2.5 mmol) to give pure **6c** (0.95 g, 2.0 mmol, 80%). Mp 94–7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 1.29 (m, 12H), 1.72 (m, 4H), 2.96 (dd, $J = 6.7$, 6.4 Hz, 4H), 3.84 (s, 6H), 3.87 (s, 6H), 6.45 (s, 2H), 6.52 (d, $J = 8.7$ Hz, 2H), 7.71 (d, $J = 8.7$ Hz, 2H). Anal. calcd for $C_{28}H_{38}O_6$: C, 71.46; H, 8.14. Found: C, 71.05; H, 8.01.

1,2-Bis(2,4-dimethoxyphenyl)ethane (5a). A mixture of **4a** (1.5 g, 5 mmol) in ether (50 ml) and palladium on carbon (10% w/w, 0.1 g) was hydrogenated at a pressure of 4 atm for 4 h. The mixture was filtered and evaporated to give the crude product, which was recrystallized from ethanol to give pure **5a** (1.4 g, 4.6 mmol, 96%). Mp 82–85 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 2.90 (s, 4H), 3.83 (s, 6H), 3.89 (s, 6H), 6.49 (m, 4H), 7.56 (m, 2H). Anal. calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.39; H, 7.14.

1,6-Bis(2,4-dimethoxyphenyl)hexane (5b). An amalgam of zinc and mercury was prepared by mixing zinc (2.23 g, 34.1 mmol) and mercury(II) chloride (0.23 g, 0.84 mmol) in water (4 ml) and concentrated hydrochloric acid (0.15 ml) for 5 min. The liquids were poured out and to the amalgam was added **6b** (1 g, 2.6 mmol), water (2 ml), toluene (5 ml) and concentrated hydrochloric acid (3.25 ml). The mixture was refluxed for 24 h with concentrated hydrochloric acid (1 ml) being added every 6 h. The mixture was cooled, diluted with water (20 ml), extracted with ether and dried. Evaporation of the solvent gave pure **5b** (0.7 g, 1.95 mmol, 75%). Mp 131–2 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 1.30 (m, 4H), 1.56 (m, 4H), 2.51 (m, 4H), 3.77 (s, 6H), 3.81 (s, 6H), 6.42 (m, 4H), 6.93 (m, 2H). Anal. calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.41; H, 8.43.

1,12-Bis(2,4-dimethoxyphenyl)dodecane (5c). Prepared as compound **5b** with a Zn–Hg amalgam [zinc (2.23 g, 34.1 mmol) and mercury(II) chloride (0.23 g, 0.84 mmol)], **6c** (1.2 g, 2.6 mmol), water (2 ml), toluene (5 ml) and concentrated hydrochloric acid (3.25 ml) with concentrated hydrochloric acid (1 ml) being added every 6 h to give pure **5c** (1.05 g, 2.36 mmol, 91%). Mp 68 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 1.29 (m, 16H), 1.55 (m, 4H), 2.57 (m, 4H), 3.84 (s, 6H), 3.9 (s, 6H), 6.47 (d, $J = 8.2$ Hz, 2H), 6.52 (s, 2H), 7.08 (d, $J = 8.2$ Hz, 2H). Anal. calcd for $C_{28}H_{42}O_4$: C, 75.98; H, 9.56. Found: C, 76.20; H, 9.46.

1,2-Bis(2,4-dihydroxyphenyl)ethane (2a). A solution of boron tribromide (8.96 g, 3.4 ml, 36 mmol) in dichloromethane (35 ml) was added to a solution of **5a** (0.9 g, 3 mmol) in dichloromethane (30 ml) over 30 min in an atmosphere of nitrogen and stirred at room temperature for 4 days. The mixture was quenched with water (≈50 ml), the layers were separated and the aqueous layer extracted with ether. The combined organic fractions were dried and evaporated to give the crude product. Recrystallization from ethyl acetate–petroleum ether gave pure **2a** (0.55 g, 2.2 mmol, 74%). Mp 121 °C.[41] ^{1}H-NMR (300 MHz, D_6-DMSO, 25 °C) δ 2.87 (s, 4H), 6.19 (m, 4H), 6.86 (m, 2H). Anal. calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.99; H, 5.91.

1,6-Bis(2,4-dihydroxyphenyl)hexane (2b). Prepared as compound **2a** with boron tribromide (7.15 g, 2.7 ml, 27 mmol) in dichloromethane (30 ml) and **5b** (0.8 g, 2.23 mmol) in dichloromethane (20 ml). Recrystallization from methanol gave pure **2b** (0.61 g, 2.02 mmol, 89%). Mp 136–9 °C. ^{1}H-NMR (300 MHz, D_6-DMSO, 25 °C) δ 1.26 (m, 4H), 1.42 (m, 4H), 2.35 (t, $J = 6.5$ Hz, 4H), 6.09 (d, $J = 8.0$ Hz, 2H), 6.23 (s, 2H), 6.74 (d, $J = 8.0$ Hz, 2H). HR-MS calcd for $C_{18}H_{22}O_4$: 302.1518. Found: 302.1504.

1,12-Bis(2,4-dihydroxyphenyl)dodecane (2c). Prepared as compound **2a** with boron tribromide (7.15 g, 2.7 ml, 27 mmol) in dichloromethane (30 ml) and **5c** (1 g, 2.26 mmol) in dichloromethane (20 ml). Recrystallization from methanol gave pure **2c** (0.78 g, 2.02 mmol, 89%). Mp 96 °C. ^{1}H-NMR (300 MHz, D_6-DMSO, 25 °C) δ 1.25 (m, 16H), 1.48 (m, 4H), 2.50 (m, 4H), 6.37 (m, 4H), 6.97 (m, 2H). Anal. calcd for $C_{24}H_{34}O_4$: C, 74.61; H, 8.81. Found: C, 74.10; H, 8.96.

Polymer 3a. A mixture of **2a** (80 mg, 0.33 mmol), phthalic anhydride (49 mg, 0.33 mmol) and methanesulfonic acid (1 ml) under an atmosphere of nitrogen was stirred at 85 °C for 24 h. To the cooled mixture was added water (≈8 ml), the mixture was filtered and the filter cake was rinsed several times with cold water and air dried to give the polymer (93 mg). The polymer was further purified by dissolving in a saturated sodium bicarbonate solution and precipitating with a 10% HCl solution. Anal. calcd for $(C_{22}H_{14}O_5)_n$: C, 73.74; H, 3.91. Found: C, 73.65; H, 3.94.

Polymer 3b. Prepared as polymer **3a** using **2b** (0.65 g, 2.1 mmol), phthalic anhydride (0.32 g, 2.1 mmol) and methanesulfonic acid (2.5 ml) to give the pure polymer (0.81 g). Anal. calcd for $(C_{26}H_{22}O_5)_n$: C, 75.30; H, 5.31. Found: C, 75.28; H, 5.35.

Polymer 3c. Prepared as polymer **3a** using **3c** (0.7 g, 1.81 mmol), phthalic anhydride (0.28 g, 1.81 mmol) and methanesulfonic acid (2 ml) to give the pure polymer (0.9 g). Anal.

calcd for $(C_{32}H_{34}O_5)_n$: C, 77.11; H, 6.83. Found: C, 77.05; H, 6.87.

***E*-2,2′-Dimethoxystilbene (9).** Prepared as compound **4a** using 2-methoxybenzaldehyde (1.36 g, 1.2 ml, 10 mmol) in dry THF (60 ml), titanium(IV) chloride (2.25 g, 1.3 ml, 12 mmol) and zinc dust (1.57 g, 24 mmol) to give the pure product (0.9 g, 7.5 mmol, 75%). Mp 129–131 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 3.90 (s, 6H), 6.69 (d, $J = 8.0$ Hz, 2H), 7.02 (t, $J = 8.2$ Hz, 2H), 7.29 (t, $J = 8.2$ Hz, 2H), 7.54 (s, 2H), 7.73 (d, $J = 8.0$ Hz, 2H). Anal. calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.90; H, 6.55.

1,2-Bis(2-methoxyphenyl)ethane (10). Prepared as compound **5a** using **9** (0.55 g, 2.3 mmol) in ether (75 ml) and palladium on carbon (10% w/w, 0.1 g) at a hydrogen pressure of 4 atm for 4 h. The product was recrystallized from ethanol to give pure **10** (0.55 g, 2.3 mmol, 99%). Mp 78 °C (lit.[42] mp 80–82 °C). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 2.89 (s, 4H), 3.81 (s, 6H), 6.85 (m, 4H), 7.15 (m, 4H). Anal. calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.78; H, 7.65.

1,2-Bis(2-hydroxyphenyl)ethane (11). Prepared as compound **2a** using boron tribromide (2 g, 0.76 ml, 8 mmol) in dichloromethane (10 ml) and **10** (0.32 g, 1.32 mmol) in dichloromethane (30 ml). Recrystallization from ether–petroleum ether gave the pure **11** (0.22 g, 1.05 mmol, 80%). Mp 117–9 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 2.87 (s, 4H), 6.30 (m, 2H, O*H*), 6.85 (m, 4H), 7.17 (m, 4H). Anal. calcd for $C_{14}H_{14}O_2$: C, 74.48; H, 6.59. Found: C, 74.16; H, 6.73.

Polymer 12. Prepared as polymer **3a** using **11** (0.56 g, 2.6 mmol), phthalic anhydride (0.38 g, 2.6 mmol) and methanesulfonic acid (2 ml) to give the pure polymer (0.67 g). Anal. calcd for $(C_{21}H_{16}O_4)_n$: C, 75.90; H 4.82. Found: C, 75.95; H, 4.85.

Polymer 13. Prepared as polymer **3a** using **11** (0.54 g, 2.5 mmol), benzoic anhydride (0.57 g, 2.5 mmol) and methanesulfonic acid (4 ml) to give a polymer–benzoic acid mixture. The mixture was dissolved in ether (≈20 ml) and rinsed with a saturated bicarbonate solution. The organic layer was worked up in the usual manner to give the pure polymer (0.55 g). Anal. calcd for $(C_{21}H_{16}O_2)_n$: C, 84.00; H 5.33. Found: C, 83.90; H, 5.35.

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