SUPLEMENTARY MATERIAL

SYNTHETIC STRATEGY

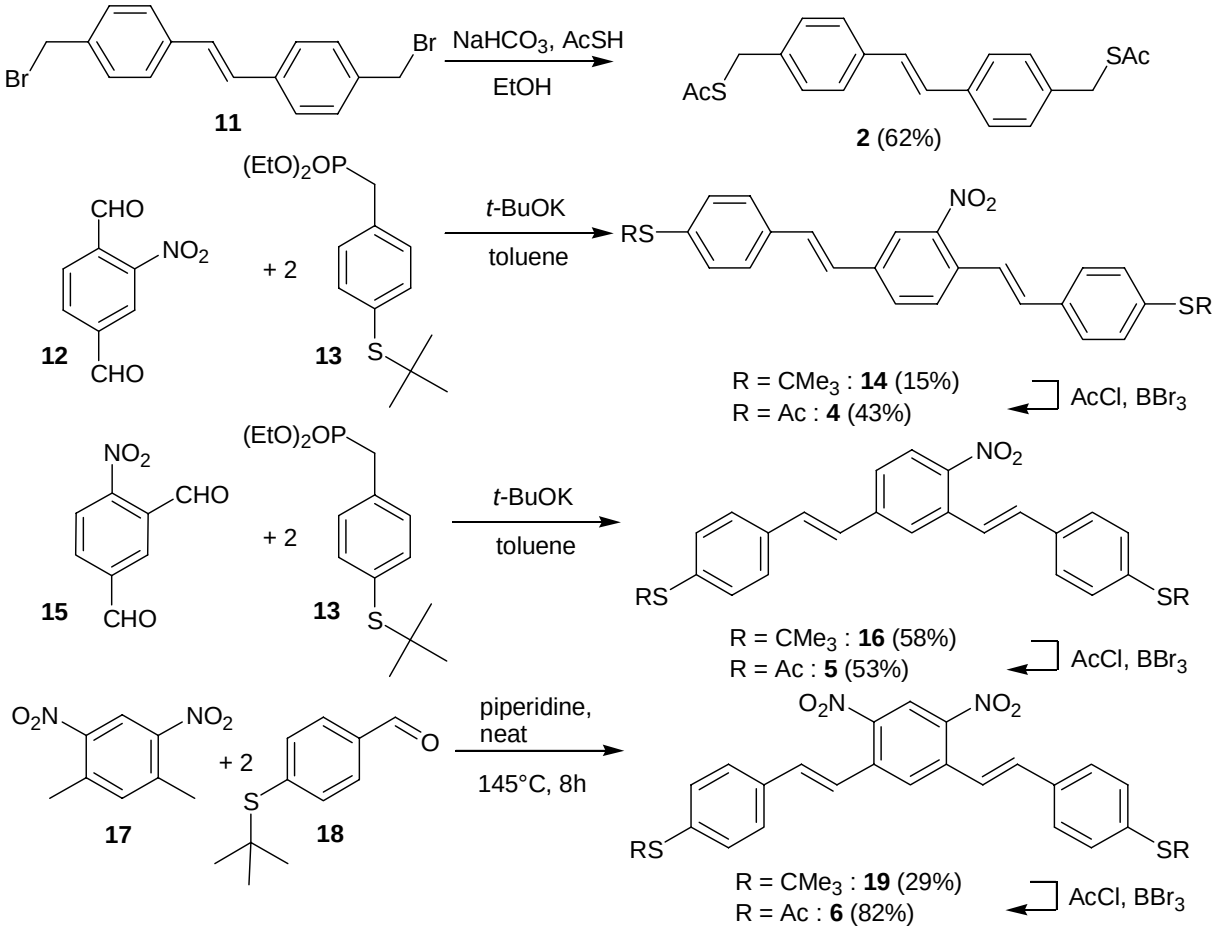

Figure 1 *shows the synthesis of the molecules (**2**,**4**,**5** and **6**). The thiol end-capped phenylenevinylenes (**4** and **5**) were synthesised via HWE type condensations of the corresponding aldehydes (**12** and **15**) with4-(tert-butylthio)benzyl phosphonate **13**.*[1,2] *Molecule **6** were synthesised via Siegrist type condensation of dinitroxylene **17** with p-(tert-butylthio) benzaldehyde **18** under conditions similar to* [3].

EXPERIMENTAL

Melting Points were recorded on a hot stage calibrated using a set of Reichert calibration substances. NMR spectra were recorded on a Bruker AM250 or a Varian Unity 400 spectrometer. Mass spectra were recorded on a 4 sector Jeol HX110/HX110. CHN analysis was recorded on a Carlo Elba FLASH 1112 apparatus.

***trans*-4,4'-Bis-(*S*-acetylthiomethyl)stilbene (2).** To a mixture of thiolacetic acid (3.8 g, 50 mmol) and ethanol (100 mL) was added sodium hydrogencarbonate (4.6 g, 55 mmol) in small portions during ten minutes. Trans-4,4'-dibromomethylstilbene[4] (**11**) (3.67 g, 10 mmol) was added in one portion. The colorless reaction mixture was stirred at room temperature for 12 hours and then poured into water (300 mL). After extraction with ether (3 x 40 mL) the pooled extracts were washed with sodium hydrogencarbonate (2 M aq., 30 mL), dried with magnesium sulfate, and concentrated *in vacuo*. The white crystalline material was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Evaporation and recrystallization from heptane gave the stilbene **2** (2.20 g, 62%) as small white plates. Mp: 153-154˚C. Anal. Calcd for $C_{20}H_{20}O_2S_2$: C, 67.38; H, 5.65; S, 17.99. Found: C, 67.09; H, 5.78; S, 18.17. ^{1}H NMR (400 MHz, $CDCl_3$): δ2.36 (s, 6H), 4.12 (s, 4H), 7.04 (s, 2H), 7.27 (d, J = 8.4 Hz, 4H), 7.16 (d, J = 8.4 Hz, 4H). ^{13}C NMR (400 MHz, $CDCl_3$): δ30.25, 33.19, 126.60, 128.13, 129.06, 136.25, 136.92, 194.92. MS: EI (m/z, relative intensity): 356 (M^+, 15), 296 (8), 282 (48), 239 (6), 221 (12), 207 (100).

Aldehydes**, 12** and **15** are all known in the litterature, they were prepared as described for **2a,** from their methyl esters.

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(15) 4-nitroisophtalic aldehyde

The Etard type oxidation procedure from 4-nitro m-xylene as reported by Doleib and Iskander[5] is of no preparative use since 4-nitroisophtalic aldehyde (**15**) can only be isolated as a by product in very low yields.

The DIBALH reduction of 4-nitroisophtalic acid methyl ester[6,7] (**20**) gave **15** in acceptable yield (65%).

The reaction was run under nitrogen atmosphere, glassware dried in the oven and assembled hot. 4-nitro isophtalic acid methyl ester **20** (8,5g,35,6mmol) and toluene (65mL) were mixed in a three neck flask equipped with a rubber septum, nitrogen bubbler and an internal thermometer. The reaction was cooled on an acetone/dry ice bath to -70°C. DIBALH (65mL, 1,2M in dichloromethane) was added with a syringe over 1h so that the temperature did not exceed -65°C. The white slurry was stirred for 4h. Methanol (30mL) was added slowly through the septum so that the temperature did not exceed -65°C). Finally the reaction mixture was poured into a mixture of ice (200mL) and hydrochloric acid (2M, 200mL). The aqueous solution was extracted with dichloromethane, the organic phase dried with $MgSO_4$ and evaporated to yield 5g of crude material. Recrystalisation from heptane gave 4-nitro isophtalic aldehyde **15** (4.11g, 23mmol≈65%) as white crystals.

Mp 78,7-82,2°C (litt.[5] 98,5-100°C)

GC-MS, EI (m/z, relative intensity): 162 (0,2), 149 (100) ^{1}H NMR (250MHz, $CDCl_3$): δ 8,25 (s, 2H) 8,44 (s, 1H) 10,18 (s, 1H), 10,43 (s, 1H) ^{13}C NMR (62,8Hz, $CDCl_3$) 125,3, 131,2, 131,7, 133,3, 139,4, 152,0, 186,6, 189,0 Anal. Calcd. for $C_8H_5NO_4$, C 53,64; H 2,81; N 7,82 found C 53,73; H 2,88, N 7,78.

(16) (*E,E*)-1,3-Bis[4-(tert-butylthio)styryl]-4-nitrobenzene

A mixture of diethyl 4-(tert-butylthio)benzylphosphonate **13** (1.27 g, 4mmol) and 4-nitroisophthalic aldehyde **15** (0.36 g, 2mmol) in THF (20 mL) was cooled on an ice bath and added t-BuOK (0.49 g, 4.4mmol) in small portions during a 10 minutes period. The reaction mixture was stirred at room temperature for 1h then poured into water (100 mL). The phases were separated and the water phase was further extracted with toluene (2 x 25 mL). The pooled organic phases were washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1mM). Reflux was maintained for 12h and the reaction mixture allowed to cool slowly, yielding (E,E)-1,3-Bis[4-(tert-butylthio)styryl]-4-nitrobenzene **16** (yield 0.29g, 58%) as yellow crystals. Mp: 154-156 ˚C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (s, 18H), 7.03 (d, J = 16 Hz, 1H), 7.10 (d, J = 16 Hz, 1H), 7.20 (d, J = 16 Hz, 1H), 7.43-7.50 (m, 9H), 7.64 (d, J = 16 Hz, 1H), 7.71 (d, J = 2 Hz, 1H), 7.96 (d, J =8 Hz, 1H) . ^{13}C NMR (100.57MHz, $CDCl_3$) 30.91, 46.29, 120.81, 122.33, 123.76, 126.49, 126.59, 126.86, 128.10, 129.47, 130.36, 130.55, 130.82, 131.222, 132.17, 132.72, 133.11, 133.28, 136.48, 136.66, 137.48, 137.59, 137.63, 148.27. EIMS: (m/z, relative intensity): 503 (M^+, 100), 482 (6), 471 (5), 447 (32). Anal. Calcd. for $C_{30}H_{33}NO_2S_2$: C, 71.53; H, 6.60; S, 12.73. Found: C, 71.81; H, 6.68; S, 12.49. UV-VIS (acetonitrile): $\varepsilon_{318}=3.95\cdot10^4 mol^{-1}cm^{-1}$.

(5) (*E,E*)-1,3-Bis[4-(acetylthio)styryl]-4-nitrobenzene

A solution of (E,E)-1,3-bis[4-(tert-butylthio)styryl]-4-nitrobenzene **16** (0.50 g, 1mmol) and AcCl (1 mL) in CH_2Cl_2 (20 mL) was cooled on an ice bath under nitrogen. BBr_3 (1.0 M solution in CH_2Cl_2, 2.2 mL) was added stirring was maintained for 30 min. and the ice bath removed. The reaction mixture was further stirred for 90min at room temperature, until the conversion was complete. The

dark reaction mixture was poured into ice (100 g), the phases were separated and the water phase was further extracted with Et_2O/heptane (1:2, 2 x 20 mL). The pooled extracts were washed with water (40 mL), dried with magnesium sulphate, and concentrated. The residual material was boiled for 12 h in a solution of iodine in toluene (0.1mM, 5 mL). After evaporation of the solvent, recrystallization from heptane gave (E,E)-1,3-Bis[4-(acetylthio)styryl]-4-nitrobenzene **5** (0.25 g, 53%) as yellow crystals.

Mp: 127-128 ˚C.

MS: EI (m/z, relative intensity): 475 (M^+, 29), 253 (100) ^{1}H NMR (250 MHz, $CDCl_3$): □ 2.38 (s, 6H), 7.01-7,24 (several peaks, 3H), 7.37 (d, J = 8 Hz, 4H), 7.45-7,55 (m, 5H), 7.66 (d, J = 16 Hz, 1H), 7.72 (d, J = 1.5 Hz, 1H), 7.98 (d, J =9 Hz, 1H)

^{13}C NMR (100,57MHz, $CDCl_3$) 30,19, 122,46, 124,48, 127,11, 127,33, 127,60, 127,86, 128,03, 128,24, 130,41, 130,50, 131,29, 132,53, 134,65, 134,67, 137,33, 137,51, 148,32, 193,66 (17 of 22 expected signals between 120 and 150ppm)

Anal. Calcd. for $C_{26}H_{21}NO_4S_2$: C, 65.66; H, 4.45; N, 2.95; S, 13.48. Found: C, 65.65; H, 4.35 N, 2.75; S, 13.19.

UV-VIS (acetonitrile): $\varepsilon_{318}=4.1\cdot10^4 mol^{-1}cm^{-1}$.

(14) (*E*,*E*)-1,4-Bis[4-(tert-butylthio)styryl]-2-nitrobenzene.

(*E*,*E*)-1,4-Bis[4-(tert-butylthio)styryl]-2-nitrobenzene (**14**) were prepared, following the procedure for (E,E)-1,3-Bis[4-(tert-butylthio)styryl]-4-nitrobenzene (**16**).

Yellow powder, yield 15%.

Mp 146.2-148.8°C.

EI^+ (m/z, relative intensity): 503 (M^+ 2), 313 (23), 257 (100).

^1H NMR (400MHz, $CDCl_3$): δ 1.19 (s, 18H), 7.16 (d, J=16, 2H), 7.85 (d, J=16Hz, 1H), 7.46-7.58 (several multplets, 8H), 7.62 (d, J=16Hz,1H), 7.72 (dd, J_a=11Hz, J_b=2Hz, 1H), 7.78 (d, J=11Hz, 1H), 8.08 (d, J=2Hz, 1H) ^{13}C NMR (100.57MHz, $CDCl_3$): δ 30.90, 46.29, 122.32, 123.76, 126.49, 126.59, 126.86, 128.10, 130.36, 130.55, 131.22, 132.72, 133.11, 133.28, 136.48, 136.66, 137.48, 137.59, 137.63, 148.27 (20 signals).

Anal. Calcd. for $C_{30}H_{33}NO_2S_2$, C 71.53; H 6.60; N 2.78; S 12.73; found C 71.14; H 6.55; N 2.86; S 12.72.

UV-VIS (acetonitrile): $\varepsilon_{346}=5.5\cdot10^4 mol^{-1}cm^{-1}$.

(4) (*E,E*)-1,4-Bis[4-(acetylthio)styryl]-2-nitrobenzene.

(*E,E*)-1,4-Bis[4-(acetylthio)styryl]-2-nitrobenzene (**4**) were prepared, following the procedure for (E,E)-1,3-Bis[4-(tacetylthio)styryl]-4-nitrobenzene (**5**).

(Yellow powder, yield 43%).

Mp 178.1-179.0 °C.

EI^+ (m/z, relative intensity) 475 (M^+ 2), 324(48), 243(57), 28(100):

^1H NMR (400MHz, $CDCl_3$): δ 2.44 (s, 6H), 7.12 (d, J=16Hz, 1H), 7.14 (d, J=16Hz, 1H), 7.22 (d, J=16Hz, 1H), 7.43 (d, J=12Hz, 4H), 7.56-7.66 (two doublets J=12Hz, 4H), 7.64 (d, J=16Hz, 1H), 7.72 (dd, J_a=8Hz, J_b=2Hz, 1H), 7.78 (d, J=8Hz, 1H), 8.10 (d, J=2Hz, 1H) ^{13}C NMR (100.57MHz, $CDCl_3$): δ 30.19, 122.46, 124.48, 127.11, 127.33, 127.60, 127.86, 128.03, 128.24, 130.41, 130.50, 131.29, 132.53, 134.65, 134.67, 137.33, 137.51, 148.32, 193.66 (only 19 out of 20 expected signals were observed due to overlapping signals).

Anal. Calcd. for $C_{26}H_{21}NO_4S_2$, C 65.66; H 4.45; N 2.95; S 13.48; found C 65.64; H 4.31; N 3.01; S 13.55.

UV-VIS (acetonitrile): $\varepsilon_{344}=5.1\cdot10^4 mol^{-1}cm^{-1}$.

(19) (*E,E*)-1,3-Bis[4-(tert-butylthio)styryl]-4,6-dinitrobenzene

4,6-dinitro-m-xylene **17**[3] (0.98g, 5mmol), p-tert-butylthio benzaldehyde prepared according to ref. 2 (**18**) (1.94g, 10mmol) and piperidine (2 drops) were heated neat for 4 hours at 150°C, 2 additional drops of piperidine were added and the mixture was heated for another 4 hours. Cooling to room temperature gave the raw material which was boiled twice with 25mL of abs. ethanol. Recrystalisation from toluene (20mL) followed by recrystallisation from a mixture 4 mL chloroform and 100 mL ethanol gave (E,E)-1,3-Bis[4-(tert-butylthio)styryl-4,6-dinitrobenzene **19** (0.702g ≈26%) as a yellow powder. The ^{1}H NMR indicated that the compound was pure trans (J=16.1).

Mp 184.1-186.0°C.

MS EI$^+$ (m/z, relative intensity): 548(M^+ 25), 437(20), 154(100).

^{1}H NMR (400MHz, $CDCl_3$) δ 1.32 (s, 18H), 7.26 (d, J=16,1, 2H), 7.55 (d, J=8,2, 4H), 7.59 (d, J=8.2, 4H), 7.74 (d, J=16.1, 2H), 8.07 (s, 1H), 8.75 (s, 1H). ^{13}C NMR (62.9MHz, $CDCl_3$): δ 30.94, 46.53, 122.66, 122.83, 127.31, 128.02, 134.74, 135.78, 136.37, 137.56, 137.70, 145.24.

UV-VIS(acetonitrile): $\varepsilon_{347}=3.3\cdot10^4\ mol^{-1}cm^{-1}$

Anal. Calcd. for $C_{30}H_{32}N_2O_4S_2$, C 65.67; H 5.88; N 5.11, S 11.69 found C 65.44; H 5.83 N 5.19 S 11.42.

For the conversion of tert. Butyl sulphides to the corresponding acetylthioesters, the procedure for (E,E)-1,3-Bis[4-(acetylthio)styryl]-4-nitrobenzene are representative.

(6) (*E,E*)-1,3-Bis[4-(acetylthio)styryl]-4,6-dinitrobenzene orange powder, yield 82%

Mp 221°C.

MS EI^+ (m/z, relative intensity): 520 (M^+, 30), 478 (11), 28 (100) ^{1}H NMR (250MHz, $CDCl_3$): δ 2.47 (s, 6H), 7.26 (d, J=16.45, 2H), 7.47 (d, J=8.23, 4H), 7.64 (d, J=8.23, 4H), 7.76 (d, J=16.45, 2H), 8.07 (s, 1H) 8.78 (s, 1H) ^{13}C NMR (62.9MHz, $CDCl_3$): δ 30.23, 122.66, 123.43, 127.98, 128.15, 129.33, 134.76, 136.08, 136.54, 137.44, 145.37, 193.35.

Anal. Calcd. for $C_{26}H_{20}N_2O_6S_2$, C 59.99; H 3.87; N 5.38, S 12.32 found C 60.35; H 3.89 N 5.29 S 11.97.

UV-VIS (acetonitrile): $\varepsilon_{337}= 3.4 \cdot 10^4\ mol^{-1}cm^{-1}$.

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