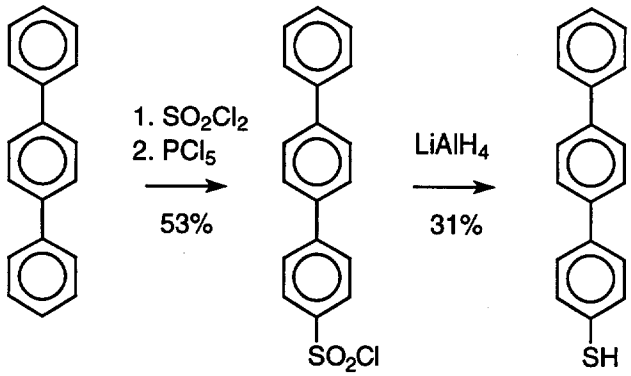
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
J. Am. Chem. Soc., 1998, 120(46), 12069-12074, DOI:10.1021/ja981872s

Synthesis of the thiols used in this study

All solvents were dried according to standard procedures. All other reagents were used as received. 4-Methylterphenyl and ethyl 4'-bromobiphenyl-4-carboxylate were prepared by published procedures. ^{1}H-NMR and ^{13}C-NMR were recorded on a Bruker AM 360 and a Varian Gemini 200, respectively. IR spectra were recorded in KBr pellets on a FT-IR-apparatus 1720 (Perkin-Elmer).



4 **1**

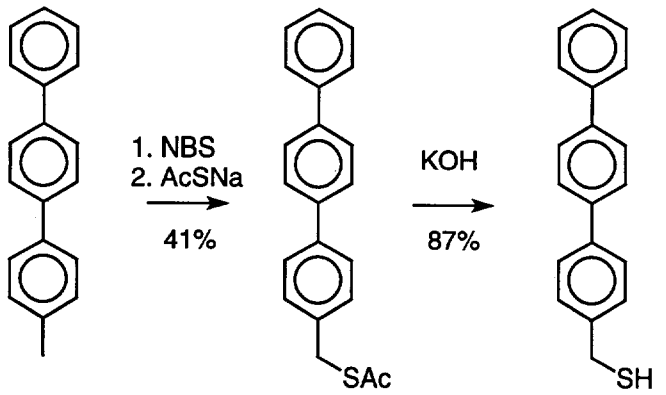
4-Terphenylsulfonyl chloride (**4**)
A solution of $ClSO_3H$ (1.6 ml, 24 mmol) in tetrachloroethane (60 ml) was added dropwise to a solution of terphenyl (4.6 g, 20 mmol) in the same solvent (130 ml) at 40-50°C. After heating to 60°C for 5 h, PCl_5 (5.0 g, 24 mmol) was added and heating to 70°C was continued for another 2 h. The solvent was removed and the residue was taken up in CH_2Cl_2 (50 ml) and C_6H_{12} (200 ml) and chromatographed on silica using a gradient C_6H_{12}/CH_2Cl_2 (6:1 -> 1:1). After drying *in vacuo* a colorless powder (3.5 g, 53%) was obtained.

4-Terphenylthiol (**1**)
4 (2.0 g, 6.1 mmol) in THF (30 ml) was added dropwise to a suspension of $LiAlH_4$ (0.65 g, 17 mmol) in THF (70 ml) under N_2. The mixture was heated to reflux for 2 h, cooled, and H_2O was added, followed by HCl. The aqueous phase was extracted several times with CH_2Cl_2 and the combined organic phase was evaporated onto silica. Chromatography on silica using a gradient of petroleum ether/CH_2Cl_2 (9:1 -> 1:1) yielded off-white leaflets (0.5 g, 31%), m.p. 236-240°C.

^{1}H ($CDCl_3$): 3.61 (s, 1 H, SH), 7.32 - 7.73 (m, 13 H, arom. H).

^{13}C ($CDCl_3$): 127.0, 127.2, 127.4, 127.5, 127.6, 128.8, 129.8, 129.9, 138.2, 139.2, 139.2, 140.2, 140.6.

IR: 1482, 1397, 816, 763, 691 cm^{-1}.



5 **2**

4-(Thioacetylmethyl)terphenyl (**5**)
4-(Bromomethyl)terphenyl: A solution of 4-methylterphenyl (3.7 g, 15 mmol) and NBS (3.1 g, 17 mmol) in acetone (500 ml) was irradiated under N_2 for 4.5 h, with more NBS (0.5 g, 2.8 mmol) being added after 3 h. After evaporation to dryness, the remainder was taken up in CH_2Cl_2 and washed three times with H_2O. Filtration through silica (CH_2Cl_2) yielded an off-white solid (4.2 g) which was used directly for the next step.
4-(Thioacetylmethyl)terphenyl: Sodium ethanolate, made by reacting sodium (0.5 g, 22 mmol) with ethanol (20 ml) followed by removal of the solvent, was dissolved in DMF (10 ml). To this CH_3COSH (3.0 ml, 42 mmol) and then a suspension of the bromomethyl compound (4.2 g, 13 mmol) in DMF (80 ml) was added. The mixture was heated to 80°C for 30 min, then the solvent was removed, and the remainder was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed twice with H_2O and concentrated. Chromatography on silica with a gradient C_6H_{12}/CH_2Cl_2 (33% -> 100% CH_2Cl_2), followed by two crystallizations from AcOH yielded brownish leaflets (2.0 g, 42%), m.p. ~195°C.

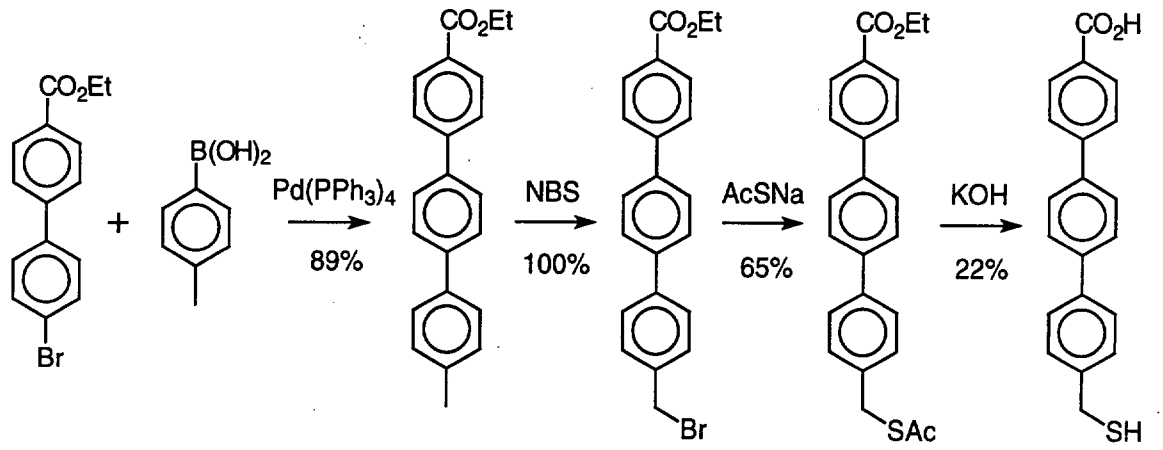
^1H ($CDCl_3$): 2.38 (s, 3 H, $COC\underline{H}_3$), 4.18 (s, 2 H, $ArC\underline{H}_2S$), 7.38 (d, J = 8 Hz, 2 H, H-3, H-5), 7.47 (t, J = 8 Hz, 1 H, H-4''), 7.58 (d, J = 8 Hz, 2 H, H-2, H-6), 7.61 - 7.69 (m, 8 H, H-2' - H-6', H-2'', H-6'').

Terphenylmethanethiol (**2**)
To a suspension of **5** (2.0 g, 6.3 mmol) in EtOH (50 ml) was added solid KOH (1.25 g, 26 mmol) and the mixture was heated to 70°C for 3 h. After cooling, conc. HCl (4 ml, 48 mmol) and H_2O (30 ml) were added and the precipitate was filtered off and washed with H_2O. After drying *in vacuo* the solid was crystallized from n-butanol to yield an off-white powder (1.5 g, 87%), m.p. 205 - 207°C.

^1H ($CDCl_3$): 1.82 (t, J = 7.7 Hz, 1 H, S$\underline{H}$), 3.81 (d, J = 7.6 Hz, 2 H, $ArC\underline{H}_2S$), 7.35 - 7.49 (m, H, arom. H), 7.57 - 7.67 (m, H, arom. H).

^{13}C ($CDCl_3$): 28.7, 127.0, 127.3, 127.4, 127.5, 128.5, 128.8, 139.5, 139.6, 140.2, 140.3, 140.7.

IR: 1485, 1400, 824, 762, 691 cm^{-1}.



6 **7** **8** **3**

Ethyl 4''-methylterphenyl-4-carboxylate (**6**)
A degassed mixture of Na_2CO_3 (2.2 g, 21 mmol), tris(4-methylphenyl)boroxin (1.3 g, 3.7 mmol), $Pd(PPh_3)_4$ (0.35 g, 0.30 mmol), ethyl 4'-bromobiphenyl-4-carboxylate (3.1 g, 10 mmol), H_2O (8 ml), EtOH (8 ml), and toluene (30 ml) was stirred under N_2 at 80°C for 16 h. After cooling, the aqueous layer was removed and the organic phase was evaporated to dryness. Chromatography on silica (CH_2Cl_2) yielded a reddish solid, which was crystallized from methylcyclohexane to give a colorless solid (2.3 g), m.p. 252°C. Work up of the mother liquors yielded another 0.5 g with slightly lower m.p. (overall yield 89%).

^1H ($CDCl_3$): 1.42 (t, J = 7 Hz, 3 H, $OCH_2C\underline{H}_3$), 2.41 (s, 3 H, $ArC\underline{H}_3$), 4.40 (q, J = 7 Hz, 2 H, $OC\underline{H}_2CH_3$), 7.28 (d, J = 8 Hz, 2 H, H-3'', H-5''), 7.55 (d, J = 8 Hz, 2 H, H-2'', H-6''), 7.69 (s, 4 H, H-2' - H-6'), 7.72 (d, J = 8 Hz, 2 H, H-2, H-6), 8.13 (d, J = 8 Hz, 2 H, H-3, H-5).

^{13}C ($CDCl_3$): 14.3, 21.1, 60.9, 126.8, 127.4, 127.6, 129.6, 130.1, 137.4, 139.2, 140.9, 166.4 (not all carbon atoms were found!).

IR: 2982, 1715, 1277, 1110, 812, 772 cm^{-1}.

Ethyl 4''-(bromomethyl)terphenyl-4-carboxylate (**7**)
6 (2.5 g, 7.9 mmol), NBS (1.5 g, 8.4 mmol), and a few mg of AIBN were heated to reflux in CCl_4 for 1 h. After 30 min, some more AIBN was added. Removal of the solvent, followed by filtration through silica (CH_2Cl_2) yielded a colorless solid (3.1 g, 100%), m.p. ~227°C, which was pure enough for the next step.
^1H ($CDCl_3$): 1.42 (t, J = 7.2 Hz, 3 H, $OCH_2C\underline{H}_3$), 4.41 (q, J = 7.2 Hz, 2 H, $OC\underline{H}_2CH_3$), 4.56 (s, 2 H, $ArC\underline{H}_2Br$), 7.49 (d, J = 8 Hz, 2 H, H-3'', H-5''), 7.62 (d, J = 8 Hz, 2 H, H-2'', H-6''), 7.65 - 7.73 (m, 6 H, H-2' - H-6', H-2, H-6), 8.13 (d, J = 8 Hz, 2 H, H-3, H-5).

^{13}C ($CDCl_3$): 14.3, 33.2, 61.0, 126.8, 127.2, 127.5, 129.6, 130.1, 137.1, 139.2, 140.1, 140.5, 144.8, 166.4.

IR: 2983, 1715, 1281, 1112, 772, 740, 607 cm^{-1}.

Ethyl 4''-(thioacetylmethyl)terphenyl-4-carboxylate (**8**)
To a solution of potassium t-butanolate (1.1 g, 9.8 mmol) in DMF (30 ml) under N_2, CH_3COSH (1.6 ml, 23 mmol) was quickly added, followed by a solution of **7** (3.1 g, 7.8 mmol) in DMF (30 ml). The resulting mixture was stirred at r.t. for 2 h before the solvent was removed at the same temperature. Chromatography on silica with a gradient toluene -> CH_2Cl_2, followed by two crystallizations from toluene/methylcyclohexane 1:1, yielded an off-white powder (2.0 g, 65%), m.p. 224 - 225°C.

^1H ($CDCl_3$): 1.42 (t, J = 7.2 Hz, 3 H, $OCH_2C\underline{H}_3$), 2.37 (s, 3 H, $COC\underline{H}_3$), 4.17 (s, 2 H, $ArC\underline{H}_2S$), 4.41 (q, J = 7.2 Hz, 2 H, $OC\underline{H}_2CH_3$), 7.39 (d, J = 8 Hz, 2 H, H-3'', H-5''), 7.57 (d, J = 8 Hz, 2 H, H-2'', H-6''), 7.63 - 7.73 (m, 6 H, H-2' - H-6', H-2, H-6), 8.13 (d, J = 8 Hz, 2 H, H-3, H-5).

^{13}C ($CDCl_3$): 14.4, 30.4, 33.1, 61.0, 126.8, 127.3, 127.5, 127.6, 129.3, 130.1, 137.1, 138.9, 139.4, 140.4, 144.9, 166.5.

IR: 1709, 1690, 1274, 1107, 819, 773 cm^{-1}.

4-Carboxyterphenyl-4''-methanethiol (**3**)
To a suspension of **8** (1.85 g, 4.7 mmol) in degassed EtOH (50 ml) was added KOH (1.5 g, 23 mmol). The mixture was kept at 70-80°C under N_2 for 18 h, cooled, and conc. HCl (5 ml, 60 mmol), followed by H_2O (50 ml) was added. The precipitate was filtered off, washed with H_2O and dried. Crystallisation from DMF in the presence of charcoal yielded an off white powder (0.36 g, 22%), m.p. > 300°C.

^1H (DMSO-D_6): 2.91 (t, J = 7 Hz, 1 H, SH), 3.78 (d, J = 7 Hz, 2 H, $ArC\underline{H}_2S$), 7.44 (d, J = 8 Hz, 2 H, H-3'', H-5''), 7.68 (d, J = 8 Hz, 2 H, H-2'', H-6''), 7.82 (s, 4 H, H-2' - H-6'), 7.83 (d, J = 8 Hz, 2 H, H-2, H-6), 8.02 (d, J = 8 Hz, 2 H, H-3, H-5).

^{13}C (DMSO-D_6): 28.7, 126.7, 127.2, 127.5, 128.9, 129.6, 130.0, 137.7, 137.8, 139.7, 141.2, 143.8, 167.1.

IR: 2668, 2547, 1683, 1606, 1430, 1298, 822, 774 cm^{-1}.

Results from thermal desorption spectroscopy

Fig.1 Thermal desorption spectrum of TFA adsorbed on a CTPMT-monolayer recorded with a heating rate of 1.3 K/s. Adsorption was carried out by exposing the substrate to 100 L (1L = $1x10^{-6}$ mbar s) at a surface temperature of 150 K.