Conglomerate stabilization by chiral self assembled monolayers†

Michal Ejgenberg* and Yitzhak Mastai

S-LMHA (L-Leucine methyl ester covalently attached to 6-mercaptophexanoic acid): 6-Trityl-mercaptophexanoic acid and L-Leucine methyl ester were coupled using PyBOP. The subsequent removal of the trityl protecting group using TFA afforded S-LMHA.

1) Coupling of 6-Tritylmercaptohexanoic acid and L-Leucine methyl ester: Trityl-mercaptophexanoic acid (2.56 mmol), L-Leucine methyl ester (2.82 mmol), PyBOP (2.82 mmol), dichloromethane (20 ml) and triethyl amine (1.1 ml) were added to a 50 ml flask. The contents of the flask were stirred overnight. The solution was washed with potassium hydrogen sulphate (0.5M, 20 ml), sodium hydrogen carbonate (saturated solution, 3*20 ml) and brine (2*20 ml). The solution was then dried with magnesium sulphate and the solvent was evaporated, affording a yellow oil. The product (S-LTMHA) (white solid) was isolated by column chromatography (silica column, 70% ether/30% hexane).

Removal of the trityl protecting group: S-LTMHA and dichloromethane (20 ml) were added to a 50 ml flask. TFA (1 ml) and triisopropylsilane (1 ml) were then added and the solution turned bright yellow. The contents of the flask were stirred overnight and the yellow color dissapeared with time. The solvent was evaporated and the crude product was cleaned using column chromatography (silica column, a) 100% hexane (to remove the trityl group) and b) 70% ether/30% hexane (to afford the desired product, S-LMHA.).
1H NMR (CDCl3) δ 6.41 (d, 1H, H-14, J = 7.5 Hz), 4.64 (m, 1H, H-10), 3.7 (s, 3H, H-8), 2.51 (q, 2H, H-6, J = 10.5 Hz), 2.23 (t, 2H, H-2, J = 10.5 Hz), 1.62, 1.43 (m, 10H, H-3,4,5,7,11,12), 0.94 (d, 6H, H-13, J= 12 Hz); 13C NMR (CDCl3) δ 173.89 (C-1), 172.94 (C-9), 52.17 (C-10), 50.61 (C-8), 41.50 (C-11), 36.13 (C-2), 33.63 (C-5), 24.99 (C-3), 24.89 (C-12), 24.37 (C-6), 22.80 (C-4), 21.90 (C-13); MS (TOF ES) m/z, 276 (MH⁺, 100%), 549 (2MH⁺ (disulfide), 64.8%)

Figure 1-ESI: AFM images of the ultra flat gold covered mica surface.
Figure 2-ESI: X-ray diffraction spectrum of the gold-covered mica surface (red) showing the preferred orientation of the gold along the (111) plane.
Figure 3-ESI: XPS spectral peaks of S- LMHA.
Figure 4-ESI: X-ray diffraction spectra of (A) L-glutamic acid, (C) DL-glutamic acid monohydrate and (B) DL-glutamic acid monohydrate after loss of water (the crystals were heated to 130°C in an oven). It is clearly evident that upon loss of water, DL-glutamic acid monohydrate transforms into anhydrous DL-glutamic acid conglomerate (the spectral peaks are not well defined, but it is clear that they correspond to the L-glutamic acid spectral peaks).