Electronic Supplementary Material (ESI) for Polymer Chemistry

Biological surface modification by 'thiol-ene' addition of polymers synthesised by catalytic chain transfer polymerisation (CCTP)

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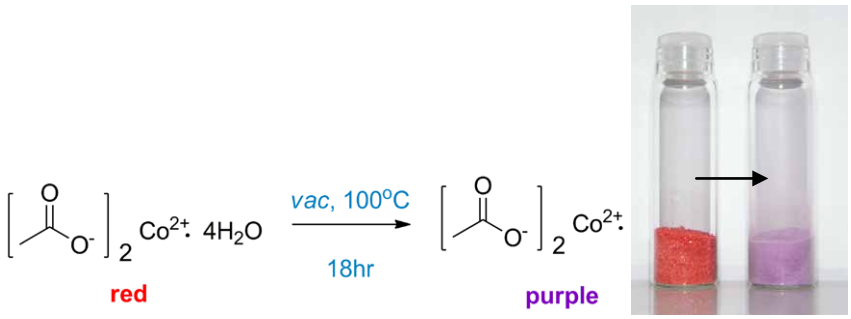
Supplementary Information

CoBF Synthesis

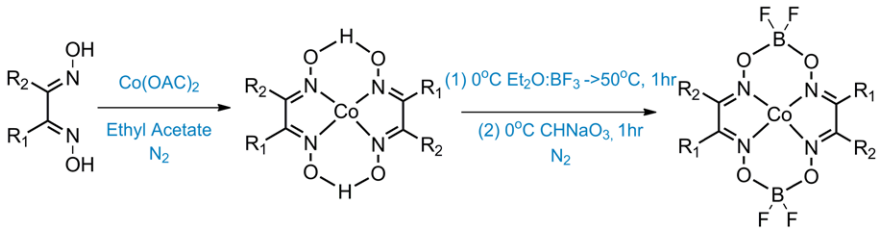
Preparation of anhydrous cobalt acetate



S1 Reaction scheme for anhydrous cobalt acetate preparation

Cobalt (II) acetate tetrahydrate was dehydrated to keep the water content in the synthesis of CoBF to a minimum. The red/pink powder changed to a purple colour once dehydration was complete.

Synthesis of CoBF (dimethanol complex)



S2 Reaction scheme for CoBF synthesis

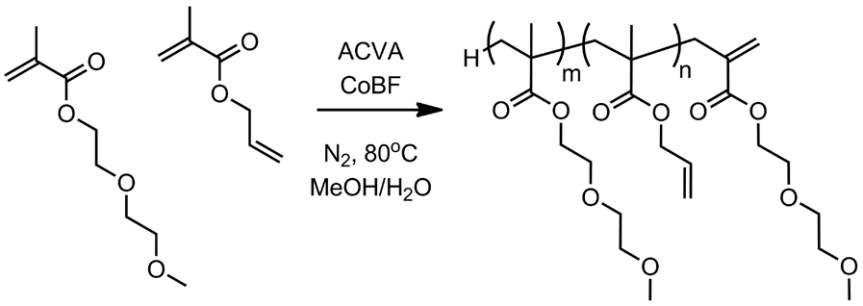
The reaction was kept under a dinitrogen atmosphere throughout preparation and isolation. Purification was not carried out under nitrogen therefore the time that the catalyst remained wet from solvents was kept to a minimum. Solvents were purged with nitrogen prior to use.

Dimethyl glyoxime (2.02 g, 17.3 mmol) and anhydrous cobalt acetate (2.16 g, 8.7 mmol) were placed in a round bottom flask with a magnetic stirrer bar and purged with nitrogen. 100 mL deoxygenated ethyl acetate was cannulated into the round bottom flask and cooled to

0 °C. Boron trifluoride diethyl etherate (5.89 mL, 47.8 mmol) was added slowly using a degassed syringe. The resulting brown solution was heated to 50 °C for 1 hour. Sodium hydrogen carbonate (1.61 g, 19.1 mmol) was added under a flow of nitrogen and the reaction was stirred for 1 hour at 0 °C. The brown solution was then filtered, washed with water (2 x 50 mL), methanol (2 x 15 mL) and dried under vacuum. The filtrate was refrigerated to obtain crystals as the product is readily soluble in water and methanol. Yield= 1.64 g (42 %)

IR ν (cm^{-1}): 3591 + 3521 O-H (from Ligand), 1623 (C=N), 1172 (N-O), 1094 (N-O), 946 (B-F), 825 (B-O), 730 (C=N-O), 506 (Co-N). Mass spectroscopy (m/z): 407.9 Da (Na+).

Polymer synthesis example: CCTP of di(ethylene glycol) methyl ether methacrylate-co-allyl methacrylate (5% AMA incorporation)



S3 Polymerisation reaction scheme

10 % incorporation

The same reaction procedure was carried out as explained above with the only changes shown in the table below:

Compound	Mass (g)	Moles (M)	MW (g. mol^{-1})
Allyl methacrylate	2.016	0.016	126

M_n (GPC) = 2400 g. mol^{-1}, M_w (GPC) = 6200 g. mol^{-1}, PDi = 2.58, DP (NMR) = 12, M_n (NMR) = 3800 g. mol^{-1}, conversion (NMR) = 81 %

20 % incorporation:

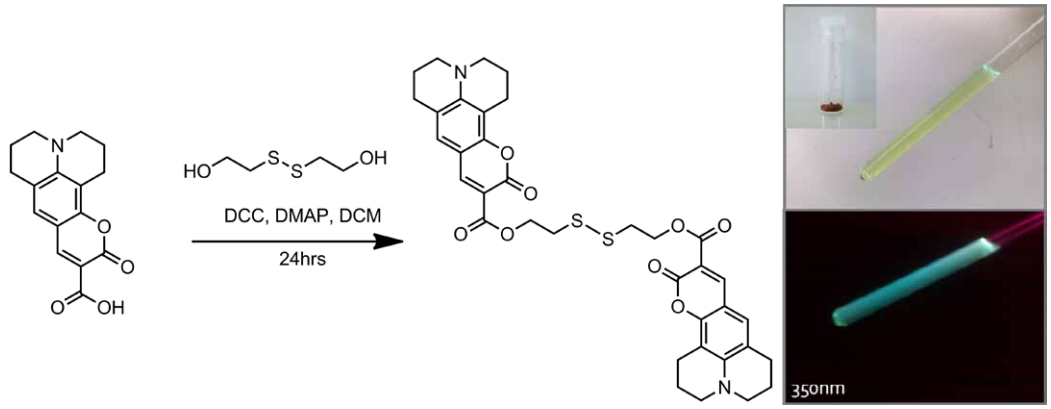
Compound	Mass (g)	Moles (M)	MW (g. mol^{-1})
Allyl methacrylate	4.032	0.032	126

M_n (GPC) = 6100 g. mol^{-1}, M_w (GPC) = 14 500 g. mol^{-1}, PDi = 2.36, DP (NMR) = 14 , M_n (NMR)= 4400 g. mol^{-1}, conversion (NMR) = 94 %

No LCST as the polymer was not water soluble.

With targeted AMA incorporation of 5, 10 and 20%, the obtained copolymers contained 2, 5 and 14% respectively, as determined *via* ^{1}H NMR.

Synthesis of coumarin disulfide dye



S4 Reaction scheme for coumarin disulfide synthesis