Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Quantitative Investigation of Surface Functionalization on Cylindrical Nanopores Derived from Polystyrene-Poly(methylmethacrylate) Diblock Copolymers

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(13 pages)

Synthesis Procedures

Chemicals and Materials. Ferrocene (Aldrich), aluminum chloride ($AlCl_3$, Acros), 16-bromohexadecanoic acid (Aldrich), 6-bromohexanoic acid (Aldrich), ferrocene carboxaldehyde (Aldrich), hydroxylamine (Aldrich), magnesium sulfate (Fisher), lithium aluminum hydride ($LiAlH_4$, Aldrich), ethanol (Fisher) and potassium acetate (Aldrich) were used as received. Tetrahydrofuran (THF, Fisher) was dried by distillation from Na, and dichloromethane (Fisher) was dried by distillation from CaH_2.

Synthesis. ^{1}H- and ^{13}C-NMR spectra were measured on a Varian INOVA 400 Fourier transform NMR spectrometer, and chemical shifts were reported in δ values in ppm downfield of tetramethylsilane. IR spectra were measured on a Nicolet Protege 640 spectrophotometer. Exact MS data were measured at the Mass Spectroscopy Laboratory, University of Kansas.

Synthesis of Ferrocenylmethylamine. Ferrocenylmethylamine was synthesized according to reported procedure.[1] A mixture of ferrocene carboxaldehyde (0.50 g, 2.34 mmol) and hydroxylamine (0.165 g, 5.00 mmol) in ethanol (25 mL) was stirred at reflux for 3 h. After cooling to room temperature, the mixture was poured to 50 mL water, and then extracted by dichloromethane (3 × 30 mL). The organic phase was washed by brine, and then dried over $MgSO_4$. The solvent was evaporated to give ferrocenylcarboxaldehyde oxime as an orange solid. The solid was dried, and then dissolved in anhydrous THF (20 mL) without purification. This solution was dropped to $LiAlH_4$ (0.37 g, 9.30 mmol) in anhydrous THF (20 mL). The mixture was stirred under reflux overnight. After cooling to room temperature, the mixture was poured to 30 mL water, and then extracted by diethyl ether (3 × 100 mL). The organic phase was

washed by brine, and then dried over $MgSO_4$. The solvent was removed, and purified by silica gel column chromatography (elution with ethyl acetate) to give ferrocenylmethylamine as an orange oil (0.44 g, 89%). ^{1}H-NMR ($CDCl_3$): δ 4.16 (t, J = 2.0 Hz, 2H, C_p), 4.14 (s, 5H, $C_{p'}$), 4.11 (t, J = 2.0 Hz, 2H, C_p), 3.53 (s, J = 6.2 Hz, 2H, CH_2).

Synthesis of 16-Bromo-1-Oxohexadecylferrocene. 16-Bromo-1-oxohexadecylferrocene was synthesized following the same procedure reported for 6-bromo-1-oxohexylferrocene.[2] 16-Bromohexadecanoic acid (0.50 g, 1.49 mmol) and oxalyl chloride (3 mL, 35 mmol) were mixed together and stirred at room temperature for overnight. The extra oxalyl chloride was removed under vacuum to obtain a colorless solid. Anhydrous dichloromethane (5 mL) was added to the flask to dissolve the solid, and then anhydrous $AlCl_3$ (0.2 g, 1.5 mmol) was added to the solution and stirred for 20 min at 0 °C under argon. In a separate flask, ferrocene (0.28 g, 1.5 mmol) was dissolved in 5 mL of anhydrous dichloromethane. The acid-chloride-containing solution was transferred to the ferrocene-containing solution via cannula over a period of 5 min. The solution turned purple during this addition. After stirring for 2 h, 5 mL of water was added slowly. After additional stirring for 10 min, the solution was diluted with 25 mL dichloromethane. The organic layer was collected, washed with water until the pH of the aqueous phase became neutral, and dried over $MgSO_4$. The solvent was removed, and then purified by silica gel column chromatography (eluent: dichloromethane) to give 16-bromo-1-oxohexadecylferrocene as an orange solid (0.65 g, 87%). ^{1}H-NMR ($CDCl_3$): δ 4.79 (t, J = 1.6 Hz, 2H, C_p), 4.50 (t, J = 1.6 Hz, 2H, C_p), 4.21 (s, 5H, $C_{p'}$), 3.42 (t, J = 6.8 Hz, 2H, CH_2Br), 2.70 (t, J = 7.4 Hz, 2H, $COCH_2$), 1.88 (m, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.56-1.27 (m, 22H, $(CH_2)_{11}$). ^{13}C-NMR ($CDCl_3$) δ 205.06, 79.36, 72.31, 69.93, 69.53, 39.98, 34.37, 33.03, 29.85, 29.82, 29.74, 29.65, 28.98, 28.38, 24.86.

Synthesis of 6-Bromo-1-Oxohexylferrocene. 6-Bromo-1-oxohexylferrocene as an orange oil was prepared from bromohexadecanoic acid by following the same procedure as 16-bromo-1-oxohexadecylferrocene (yield: 79%). ^{1}H-NMR ($CDCl_3$): δ 4.79 (t, J = 2.0 Hz, 2H, C_p), 4.50 (t, J = 2.0 Hz, 2H, C_p), 4.20 (s, 5H, $C_{p'}$), 3.43 (t, J = 6.8 Hz, 2H, CH_2Br), 2.75 (t, J = 7.2 Hz, 2H, $COCH_2$), 1.97 (m, 2H, CH_2), 1.75 (m, 2H, CH_2), 1.58 (m, 2H, CH_2).

Synthesis of 16-Acetyl-1-Oxohexadecylferrocene. 16-Bromo-1-oxohexadecylferrocene (0.45 g, 0.89 mmol) was dissolved in 6 mL of ethanol, followed by addition of potassium acetate (3.51 g, 35 mmol) to the solution. The mixture was refluxed for 48 hours with stirring. The solvent was removed, and then purified by silica gel column chromatography (eluent: dichloromethane) to give 16-acetyl-1-oxohexadecylferrocene as an orange solid (0.31 g, 71%). ^{1}H-NMR ($CDCl_3$): δ 4.78 (t, J = 2.0 Hz, 2H, C_p), 4.49 (t, J = 1.8 Hz, 2H, C_p), 4.20 (s, 5H, $C_{p'}$), 4.05 (t, J = 7.0 Hz, 2H, CH_2O), 2.69 (t, J = 7.6 Hz, 2H, $COCH_2$), 2.05 (s, 3H, CH_3), 1.71 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.35-1.27 (m, 22H, $(CH_2)_{11}$). ^{13}C-NMR ($CDCl_3$) δ ($CDCl_3$) δ 204.92, 171.46, 79.44, 72.28, 69.94, 69.55, 64.89, 39.99, 29.86, 29.78, 29.76, 29.47, 28.82, 26.13, 24.87, 21.24.

Synthesis of 6-Acetyl-1-Oxohexylferrocene. 6-Acetyl-1-oxohexylferrocene as an orange oil was prepared from 6-bromo-1-oxohexylferrocene by following the same procedure as 16-acetyl-1-oxohexadecylferrocene (yield: 75%). ^{1}H-NMR ($CDCl_3$): δ 4.79 (t, J = 2.0 Hz, 2H, C_p), 4.51 (t, J = 1.6 Hz, 2H, C_p), 4.20 (s, 5H, $C_{p'}$), 4.09 (t, J = 6.8 Hz, 2H, CH_2O), 2.72 (t, J = 7.2 Hz, 2H,

$COCH_2$), 2.06 (s, 3H, CH_3), 1.75-1.46 (m, 6H, $(CH_2)_3$). ^{13}C-NMR ($CDCl_3$) δ 204.45, 171.44, 79.31, 72.38, 69.97, 69.53, 64.64, 39.70, 28.81, 26.14, 24.37, 21.25.

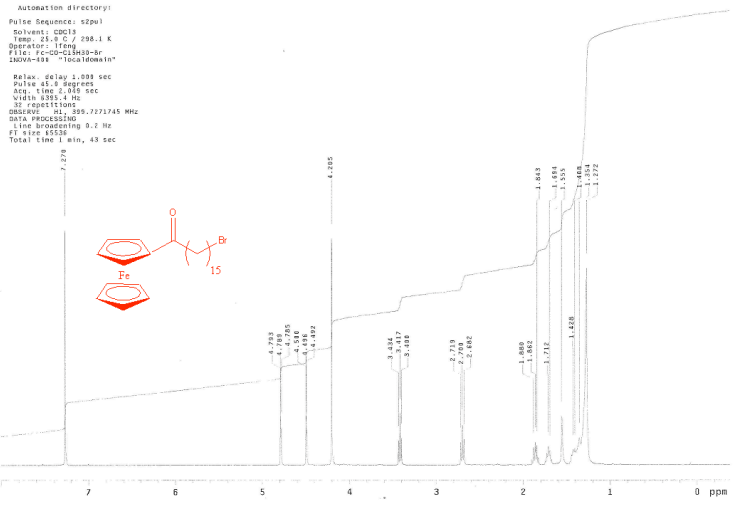
Synthesis of 16-Hydroxy-1-Oxohexadecylferrocene. 16-Acetyl-1-oxohexadecylferrocene (0.30 g, 0.62 mmol) was mixed with sodium hydroxide solution (3 M, 15 mL), then refluxed for 48 h. The mixture was extracted by ethyl acetate (3 × 30 mL). The organic phase was washed by brine, and then dried over $MgSO_4$. The solvent was removed, and then purified by silica gel column chromatography (eluent: dichloromethane: ethyl acetate = 7:3) to give 16-hydroxy-1-oxohexadecylferrocene as an orange solid (0.26 g, 98%). ^{1}H-NMR ($CDCl_3$): δ 4.79 (t, J = 2.0 Hz, 2H, C_p), 4.49 (t, J = 1.8 Hz, 2H, C_p), 4.20 (s, 5H, $C_{p'}$), 3.65 (t, J = 6.4 Hz, 2H, CH_2OH), 2.70 (t, J = 7.4 Hz, 2H, $COCH_2$), 1.71 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.35-1.27 (m, 22H, $(CH_2)_{11}$). ^{13}C-NMR ($CDCl_3$) δ 205.02, 79.45, 72.31, 69.96, 69.78, 69.58, 63.34, 40.02, 33.05, 30.20, 29.86, 29.82, 29.81, 29.76, 29.65, 25.97, 24.90. FTIR (cm^{-1}): 3097, 2920, 2850, 1661, 1473, 1461, 1105, 836, 823, 719. Exact MS: *m/z* calculated for $C_{26}H_{41}O_2Fe$ (M + Na), 463.2290; found, 463.2275

Synthesis of 6-Hydroxy-1-Oxohexylferrocene. 6-Hydroxy-1-oxohexylferrocene as an orange oil was prepared from 6-acetyl-1-oxohexylferrocene by following the same procedure as 16-hydroxy-1-oxohexadecylferrocene (yield: 99%). ^{1}H-NMR ($CDCl_3$): δ 4.79 (t, J = 1.8 Hz, 2H, C_p), 4.50 (t, J = 1.6 Hz, 2H, C_p), 4.20 (s, 5H, $C_{p'}$), 3.70 (t, J = 6.4 Hz, 2H, CH_2O), 2.74 (t, J = 7.4 Hz, 2H, OCH_2), 1.75 (m, 2H, CH_2) , 1.65 (m, 2H, CH_2) , 1.47 (m, 2H, CH_2). ^{13}C-NMR ($CDCl_3$) δ 204.79, 79.32, 72.40, 69.99, 69.55, 62.93, 45.03, 39.79, 32.74, 25.83, 24.32. FTIR (cm^{-1}): 3343,

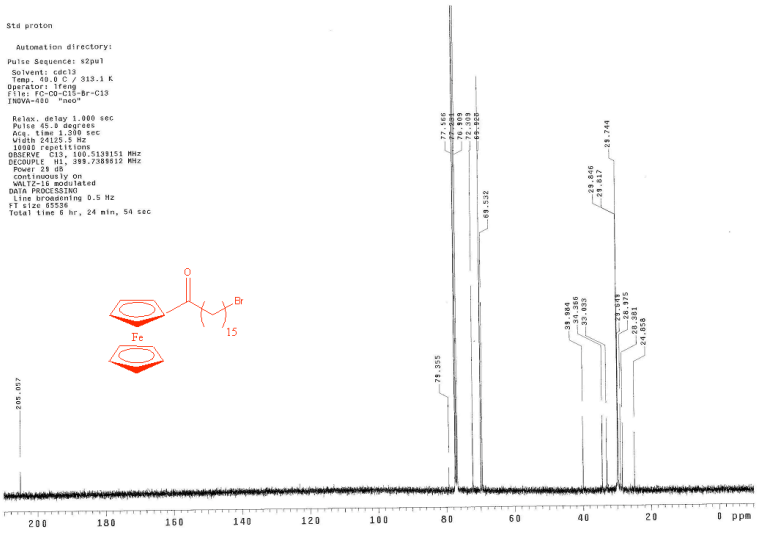
3095, 2917, 2848, 1661, 1470, 1462, 1377, 1105, 820, 718. Exact MS: *m*/*z* calculated for $C_{16}H_{20}O_2Fe$ (M + Na), 323.0715; found, 323.0710.

^{1}H- and ^{13}C-NMR, and FTIR spectra are shown below.

^{1}H-NMR Spectrum of 16-Bromo-1-Oxohexadecylferrocene

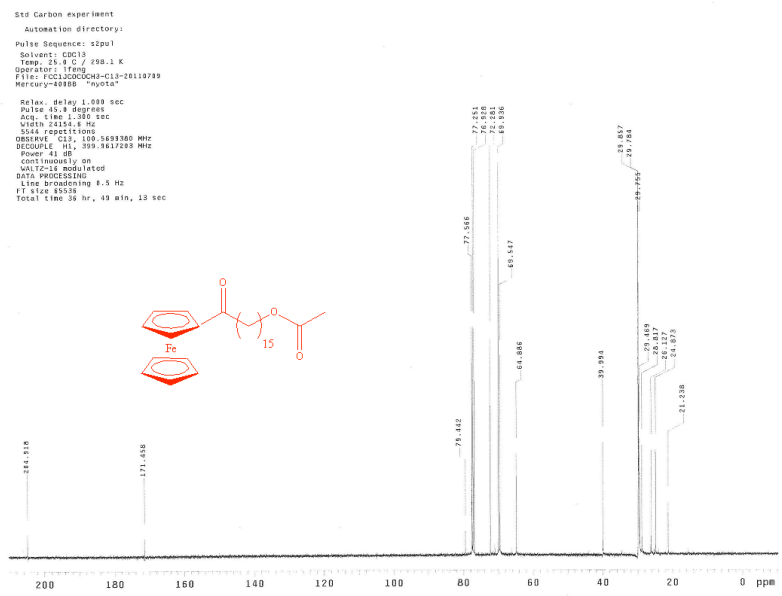


^{13}C-NMR Spectrum of 16-Bromo-1-Oxohexadecylferrocene



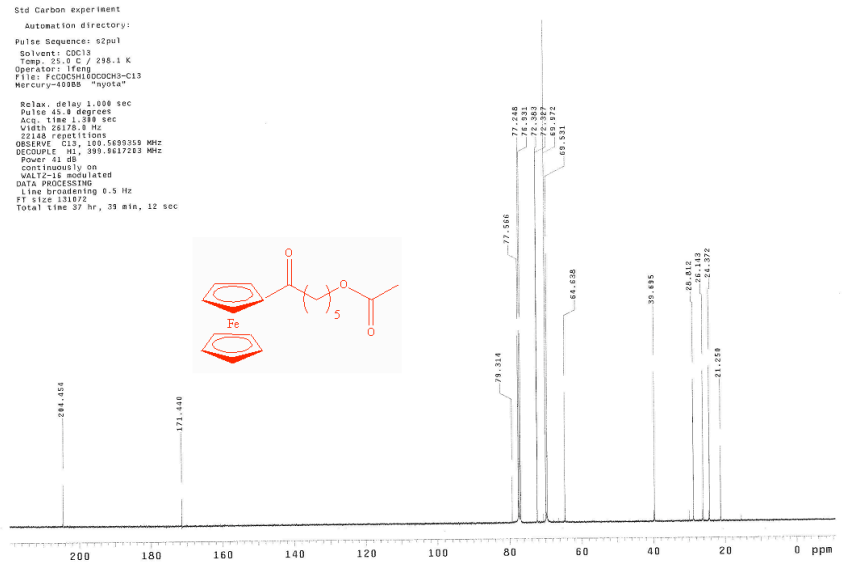
^{1}H-NMR Spectrum of 16-Acetyl-1-Oxohexadecylferrocene

^{13}C-NMR Spectrum of 16-Acetyl-1-Oxohexadecylferrocene

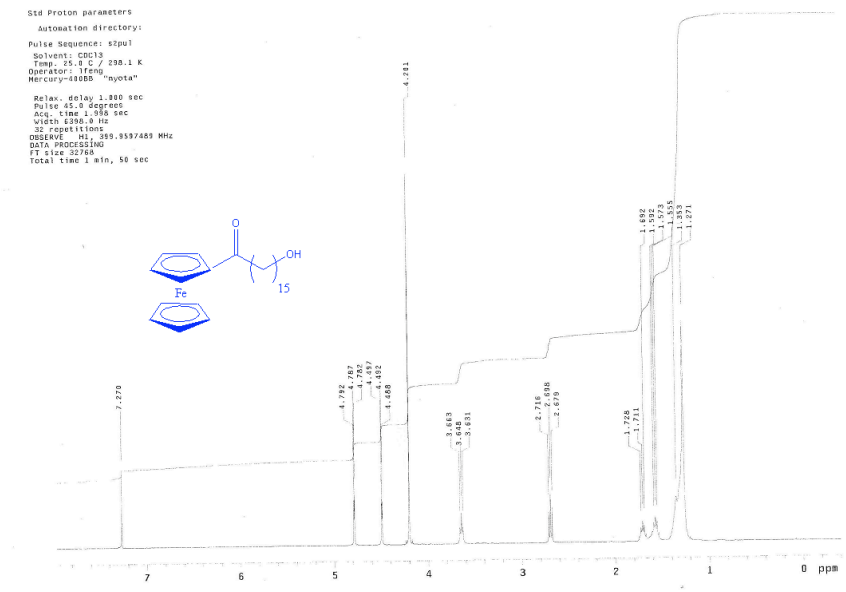


^{1}H-NMR Spectrum of 6-Acetyl-1-Oxohexylferrocene

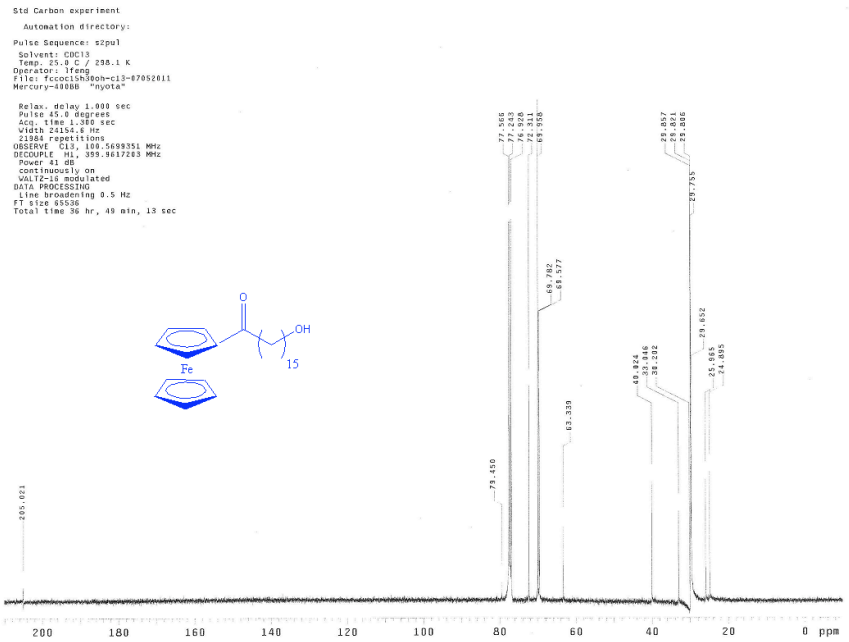
^{13}C-NMR Spectrum of 6-Acetyl-1-Oxohexylferrocene



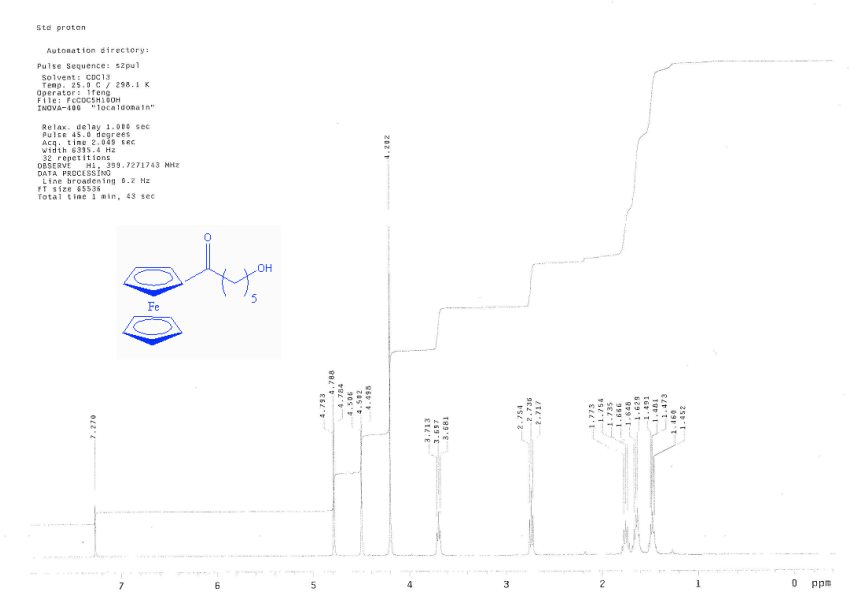
^{1}H-NMR Spectrum of 16-Hydroxy-1-Oxohexadecylferrocene



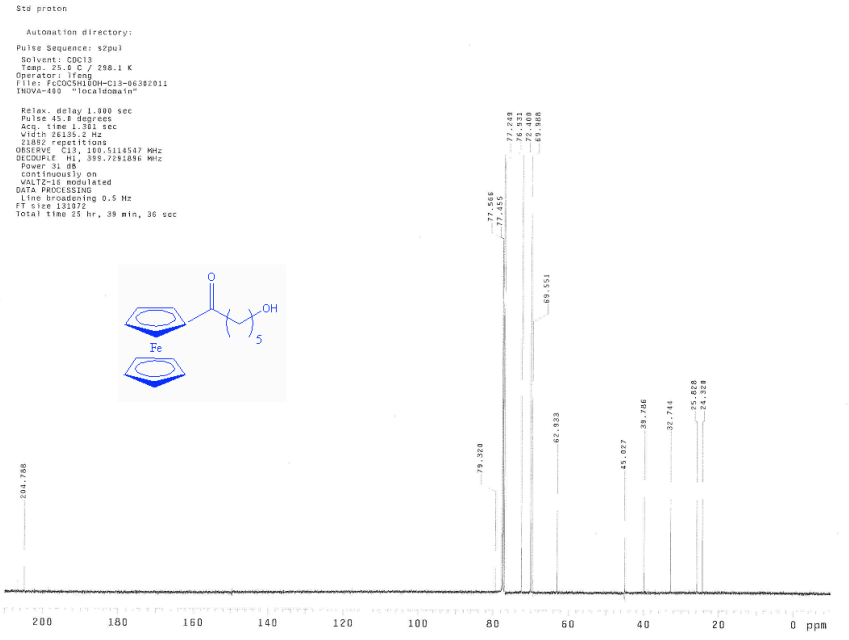
^{13}C-NMR Spectrum of 16-Hydroxy-1-Oxohexadecylferrocene



^{1}H-NMR Spectrum of 6-Hydroxy-1-Oxohexylferrocene



^{13}C-NMR Spectrum of 6-Hydroxy-1-Oxohexylferrocene



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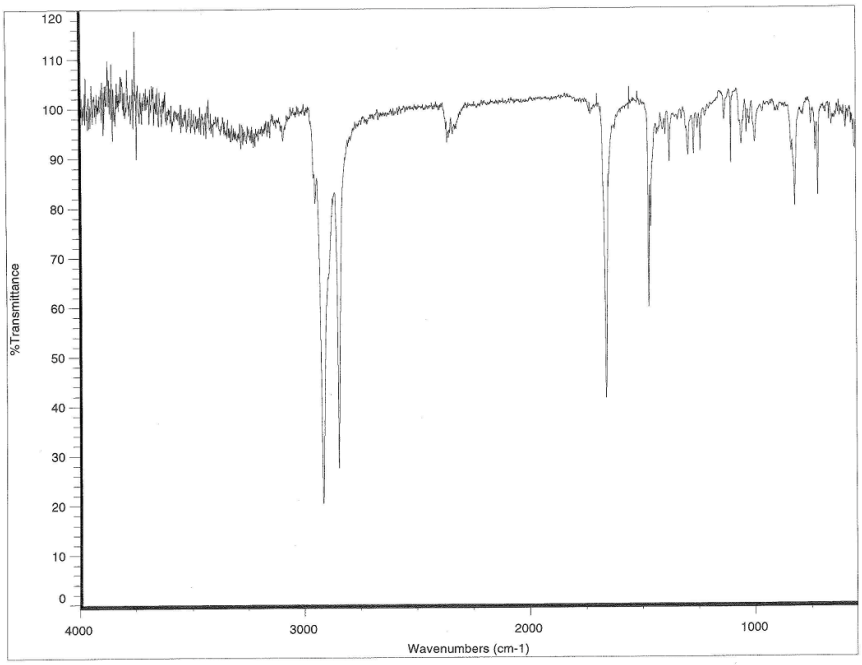
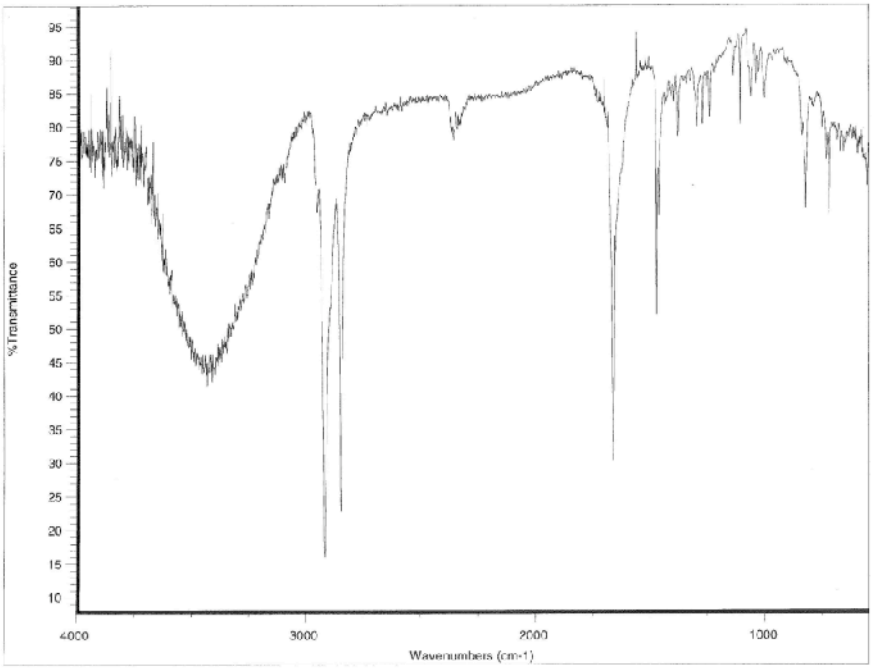
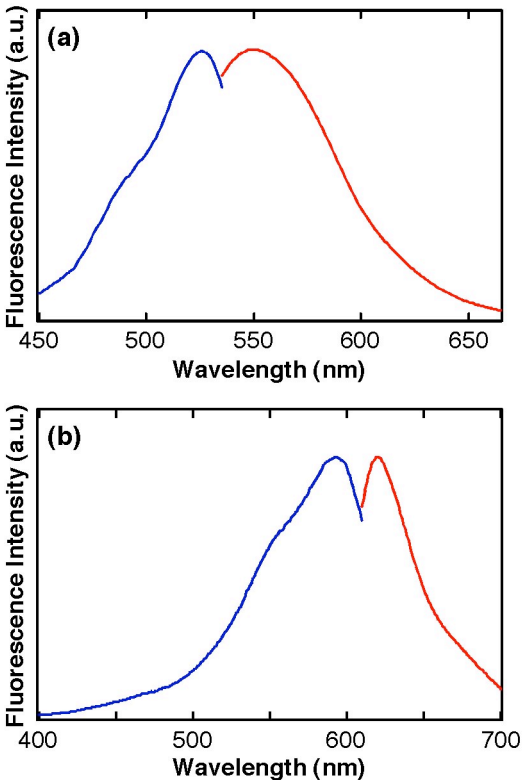
FTIR Spectrum of 16-Hydroxy-1-Oxohexadecylferrocene



FTIR Spectrum of 6-Hydroxy-1-Oxohexylferrocene



Fluorescence Spectra of Rhodamine 6G and Thionine Acetate



Excitation (blue) and emission (red) spectra of (a) Rhodamine 6G (100 nM, in 0.01 M HCl) and (b) thionine acetate (100 nM, in 0.01 M HCl in a 1:1 mixture of ethanol and water). The excitation spectra were measured at 550 nm (Rhodamine 6G) or 620 nm (thionine) as emission wavelength, and the emission spectra were obtained at 525 nm (Rhodamine 6G) or 594 nm (thionine) as excitation wavelength.

References

1. A. Baramee, A. Coppin, M. Mortuaire, L. Pelinski, S. Tomavo and J. Brocard, *Bioorg. Med. Chem.*, 2006, **14**, 1294-1302.
2. S. E. Creager and G. K. Rowe, *J. Electroanal. Chem.*, 1994, **370**, 203-211.