Functionalisation of the 1,3-bis(2-pyridylimino)isoindole (*BPI*) ligand *via* esterification

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1,3-bis(2-pyridylimino)isoindolines (*BPI*) with N-donor groups and long alkyl chains were synthesised by DCC-activated esterification of mercaptoethanol-substituted bis(pyridylimino)isoindole with carboxylic acid derivatives (pyridine-4-carboxylic acid, nonanoic acid). Homoleptic iron(II) complex was synthesised by reaction of *BPI* with $Fe(ClO_4)_2$ in acetone: chloroform. The new compounds were characterised by elemental analyses, FT-IR, ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data.

Keywords bis(pyridylimino)isoindole; N-donor ligands; iron complex; esterification

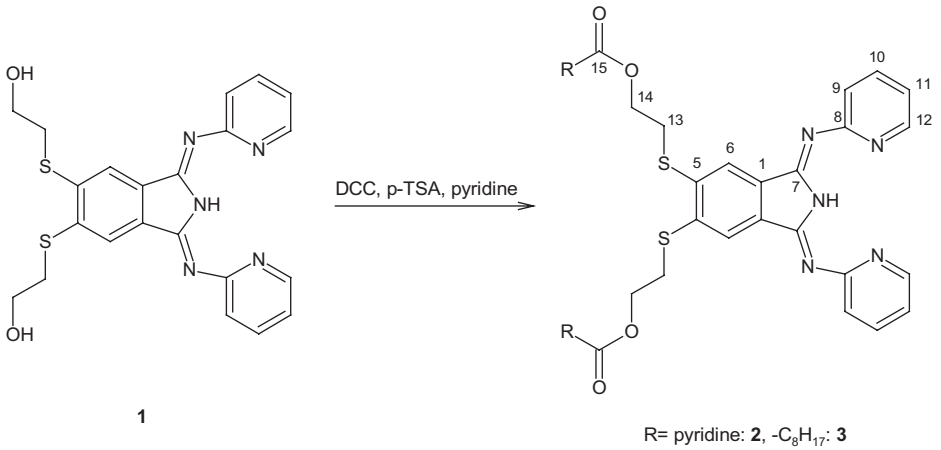
Nitrogen donor ligands have been widely used in the transition metal catalysed oxidation of hydrocarbons.[1] Among the acyclic polydentate ligands, bis(pyridylimino)isoindole (*BPI*) derivatives have been the focus of interest in oxidation chemistry.[2-7] The *BPI*-transition metal catalysed oxidations generally tend to be unselective and it is therefore of interest whether the modification of the ligands by variation of their peripheral substitution pattern[8-11] and the variation of the oxidising agent may enable more selective transformations.[12] Recently, DNA-binding properties of the cobalt(III) complex of 1,3-bis(2-pyridylimino)isoindoline have been investigated as an example of biological application as well as catalytic properties.[13]

*BPI*s have been shown to function as neutral, non-deprotonated and also as uninegative ligands. The ligands are capable of occupying three sites about a metal ion and forming either 1:1 or 2:1 (ligand:metal) complexes depending on the coordination number and geometry of the metal ion.[14-18] We herein described the synthesis of *BPI* derivatives containing N-donor groups and long alkyl chains. Complexation of the ligand containing N-donor groups with iron(II) was also studied. The new compounds were characterised by elemental analysis, FT-IR, ^{13}C NMR, ^{1}H NMR and UV-Vis spectral data.

Results and discussion

The synthesis of bis(2-pyridylimino)isoindole ligand **1** was achieved by refluxing 1,2-bis(hydroxyethylmercapto)-4,5-dicyanobenzene with two molar equivalents of 2-aminopyridine in the presence of $CaCl_2$ in hexanol for 20 h to give the ligand precursor as yellow crystalline solid.[19] Reaction of the mercaptoethanol-functionalised *BPI* derivative **1** with the carboxylic acid derivatives (pyridine-4-carboxylic acid, nonanoic acid) using dicyclohexylcarbodiimide (DCC) and p-toluenesulfonic acid as catalyst in pyridine for 4 days at room temperature yielded **2** and **3** (Scheme 1). The function of DCC was to facilitate the formation of the ester bond by forming an activated ester. Dicyclohexylurea by-product was separated from the crude product by treatment with ethanol several times at 0°C and was then filtered off. Conversion of bis(2-pyridylimino)isoindole derivative **2** into its corresponding homoleptic iron(II) complex was accomplished by reaction with $Fe(ClO_4)_2$ in acetone: chloroform according to the published procedure with some minor modifications (Fig. 1).[20]

The new compounds were characterised by elemental analysis, FT-IR, ^{13}C NMR, ^{1}H NMR, and UV-Vis spectrophotometry. The analyses, shown in the experimental section, are consistent with the predicted structures. The sharp peak in the IR spectra for the C=O stretching of *BPI* derivatives **2** and **3** at *ca* 1730 cm^{-1}, is indicative of ester bond formation (Fig. 2). The characteristic NH stretching band was observed at *ca* 3260 cm^{-1}. Aromatic and aliphatic CH stretching vibrations were observed at 2850–3050 cm^{-1}. The IR spectrum of **3** clearly proved the presence of the long alkyl chain by the intense absorption peak for aliphatic group at around 2900 cm^{-1}. In the ^{1}H NMR spectrum of **2**, the resonances belonging to aromatic protons were observed between δ 7.14 and 8.72 ppm and integrated for 18 protons. CH_2 protons were observed at δ 4.65 and 3.50 ppm as triplets. For ligand **3**, the aromatic protons, integrating for a total of 10, were observed between δ 7.05 and 8.53 ppm. CH_2 and CH_3 protons, which integrated for 42 protons, were observed



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R= pyridine: **2**, -C_8H_{17}: **3**

Scheme 1 Synthesis of *BPI*s.

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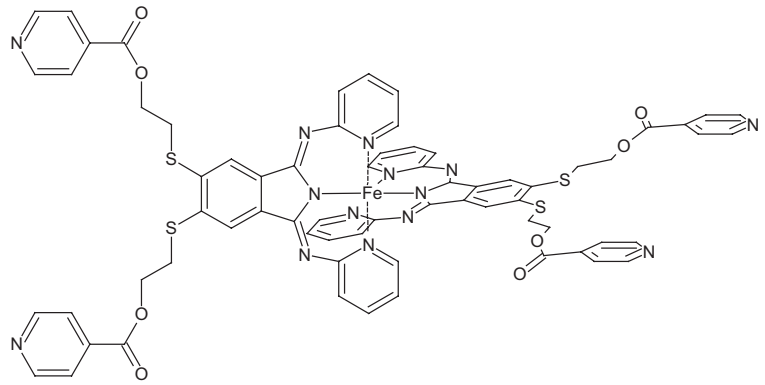

Fig. 1 Proposed structure for $[Fe(BPI)_2]$.

between δ 0.76 and 4.34 ppm. ^{13}C NMR data of ligands confirmed the result of ^{1}H NMR spectra.

The complex **4** was stable in air and analysed satisfactorily for C, H, and N. Infrared spectra of metal complexes with deprotonated ligand vs. non-deprotonated ligand show substantial differences in the region 1450–1650 cm^{-1}. Complexes with the deprotonated isoindoline ligand exhibit weak bands above 1600 cm^{-1}, while those with neutral non-deprotonated ligand have two strong absorptions in the range 1600–1660 cm^{-1} and also a strong band at 1100 cm^{-1}.[20-22] In the IR spectrum of the complex **4**, the absorptions at 1628, 1567 and *ca* 1100 cm^{-1} indicate that the complex contains the deprotonated isoindoline ligand. Due to the presence of ester groups, the characteristic absorption of the complex containing deprotonated isoindoline ligand at 1100 cm^{-1} overlapped with the C–O–C stretching bands at the same region.[23,24] In addition, after conversion of ligand **2** into the iron(II) complex, the strong peak for the NH vibration around 3260 cm^{-1} disappeared. The IR spectrum of the iron(II) complex showed aromatic C–H, aliphatic C–H and C=O peaks at around 3030, 2950 and 1725 cm^{-1}, respectively (Fig. 3). In the electronic spectrum, the band at *ca*. 439 nm can be assigned to a ligand-to-iron charge transfer transition and the bands between 210 and 410 nm can be assigned to ligand-based transitions.[21,22] In conclusion, we have showed that DCC-activated esterification is an applicable synthetic route for the derivatisation of suitably substituted *BPI* ligands. As an initial demonstration, we have succeeded in obtaining iron(II) complex **4** with moderate yield.

Experimental

IR spectra were recorded on Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-V_X 400 MHz spectrometer using TMS as internal reference. Elemental analyses were performed on a Thermo Flash EA 1112. Melting points were determined on an Electrothermal Gallenkamp apparatus. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC (SiO_2). 4,5-Bis(hydroxyethylmercapto)-*BPI* (**1**) was prepared according to the published procedure.[19]

Caution! Metal complexes containing organic ligands and perchlorate ion are potentially explosive and should be handled with care.

General procedure for the preparation of the BPI ligands **2–3**

A mixture of **1** 0.2 mmol (0.100 g), DCC 1.2 mmol (0.274 g), *p*-TSA 0.2 mmol (0.042 g) and carboxylic acid derivative 1.2 mmol (0.163 g pyridine-4-carboxylic acid, 0.230 ml nonanoic acid) was stirred in 15 ml dry pyridine for about 4 days at ambient temperature under a nitrogen atmosphere. Dicyclohexylurea by-product was precipitated and filtered off and the yellow filtrate was evaporated to dryness under reduced pressure. The crude product was stirred in ethanol several times at 0°C to remove the remaining dicyclohexylurea. Further purification was achieved for **2** by column chromatography on silica gel with chloroform/methanol (5/1) as eluent. **2.** Yield 0.051 g (35%), m.p. 146°C, FT-IR (KBr): ν_{max}, cm^{-1} 3266 (NH), 3040 (CH, aromatic), 2994–2922 (CH, aliphatic), 1720 (C=O) 1123 (C–O–C). ^{1}H NMR ($CDCl_3$): δ, ppm 8.72–7.14 (m, 18H, aromatic H), 4.65 (t, 4H, –O–C$\underline{H}_2$–), 3.50 (t, 4H, –C$\underline{H}_2$–S–). ^{13}C NMR ($CDCl_3$): δ, ppm 165 (C=O, C-15), 160.2 (C-8), 150.8 (C-7), 148.1 (C-18, C-12), 141.7 (C-16, C-10), 138.5 (C-5), 137,09 (C-1), 123.09 (C-6), 122.8 (C-17, C-11), 121 (C-9), 64.1 (–O–$\underline{C}H_2$, C-14), 32.3 (-$\underline{C}H_2$–S–, C-13). Anal. Calc. for $C_{34}H_{27}N_7O_4S_2$: C, 61.7; H, 4.1; N, 14.8. Found: C, 61.6; H, 4.1; N, 14.7. **3.** Yield 0.070 g (43%), m.p. 67°C, FT-IR (KBr): ν_{max}, cm^{-1} 3259 (NH), 3046 (CH, aromatic), 2926–2854 (CH, aliphatic), 1737 (C=O) 1158 (C–O–C). ^{1}H NMR ($CDCl_3$): δ, ppm 8.53–7.05 (m, 10H, aromatic H), 4.34–0.76 (m, 42H, aliphatic H). ^{13}C NMR ($CDCl_3$): δ, ppm 173.8 (C=O, C-15), 160.1 (C-8), 153.2 (C-7), 148 (C-12), 141.5 (C-10), 138.4 (C-5), 133,3 (C-1), 123.2 (C-6), 122.3 (C-11), 120.8 (C-9), 62.5 (–O–$\underline{C}H_2$, C-14), 34.4, 32.3, 32, 29.4,

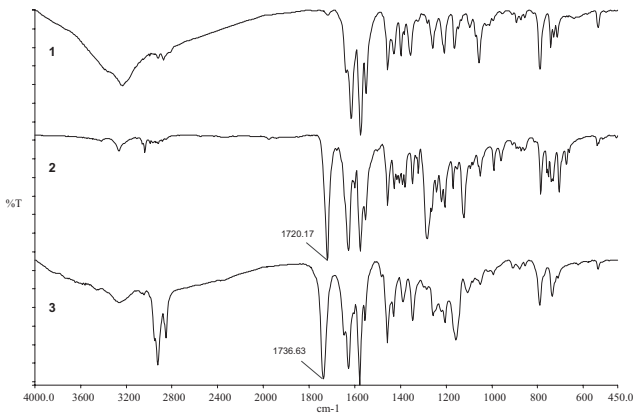

Fig. 2 FT-IR spectra of *BPI*s.

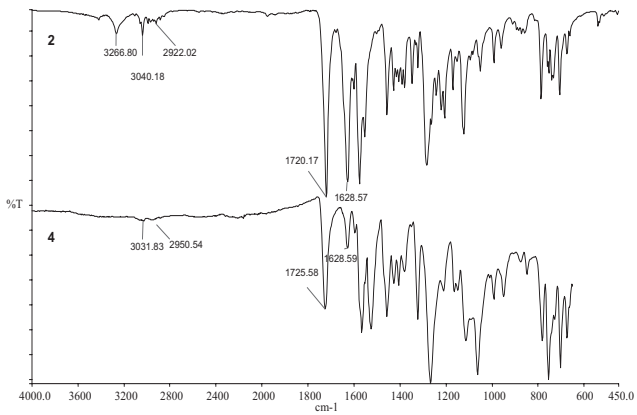

Fig. 3 FT-IR spectra of **2** and its iron(II) complex.

29.37, 29.32, 25.1, 22.8, 14.2 (CH_3). Anal. Calc. for $C_{40}H_{53}N_5O_4S_2$: C, 65.6; H, 7.3; N, 9.6. Found: C, 65.0; H, 7.3; N, 9.5.

Preparation of [Fe(BPI)$_2$] complex

A solution of 1,3-bis(2-pyridylimino)isoindoline derivative **2** (0.15 mmol, 0.100 g) in acetone: chloroform (3 ml) was stirred at room temperature for 4 h with $Fe(ClO_4)_2.6H_2O$ (0.075 mmol, 0.027 g). After addition of Et_3N (0.15 mmol), the reaction mixture was stirred for 2 h and a dark green solid precipitated upon standing for a day. The product was collected by filtration, washed with acetone and dried in vacuum. Yield 0.012 g (52%), FT-IR (KBr): ν_{max}, cm^{-1} 3031 (CH, aromatic), 2951 (CH, aliphatic), 1725 (C=O), 1628, 1596, 1567, 1526, 1457, 1427, 1114 (C–O–C). UV-Vis (CH_3CN): λ_{max}, nm 439, 413, 388, 368, 311, 210. Anal. Calc. for $C_{68}H_{52}N_{14}O_8S_4Fe$: C, 59.3; H, 3.8; N, 14.2. Found: C, 59.7; H, 3.8; N, 14.1.

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