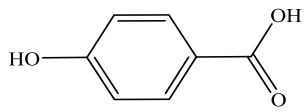
CHAPTER 3 EXPERIMENTAL

3.1 Materials

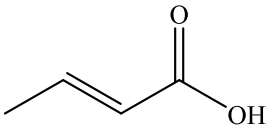
The main objectives of this research project were to synthesise and characterize stable low-temperature ionic copper(II) mixed carboxylates as hybrid heat-light solar-cell materials. The general formula of the complexes are $K_n[Cu_2(p\text{-}OC_6H_4COO)_n(RCOO)_{4-n}]$, where n = 1-3, and R = saturated or unsaturated alkyl group.

The carboxylic acids used were *p*-hydroxybenzoic acid (*p*-HOC_6H_4COOH; FW = 138.12 g mol^{-1}), 2-butenoic acid ($CH_3CH{=}CHCOOH$; FW = 86.09 g mol^{-1}), 2-methylpropenoic acid ($CH_2{=}C(CH_3)COOH$; FW = 86.09 g mol^{-1}), octadec-9-enoic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$; FW = 283.47 g mol^{-1}), 2,2-dimethylpropanoic acid ($(CH_3)_3CCOOH$; FW = 102.13 g mol^{-1}), 2-ethylhexanoic acid ($CH_3(CH_2)_3CH(C_2H_5)COOH$; FW = 145.22 g mol^{-1}), 2-hexyldecanoic acid ($CH_3(CH_2)_7CH((CH_2)_5CH_3)COOH$); FW = 256.43 g mol^{-1}). The structural formulas of the carboxylates are shown in **Figure 3.1**.

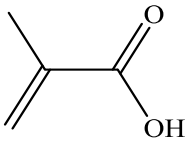
The complexes were analysed by CHN elemental analyses, FTIR spectroscopy, UV-vis spectroscopy (solid and solution), TGA, DSC, room-temperature magnetic susceptibility, cyclic voltammetry (CV), and for suitable complexes, by photoluminescence spectroscopy (PL). Crystalline complexes were analysed by single-crystal X-ray crystallography.



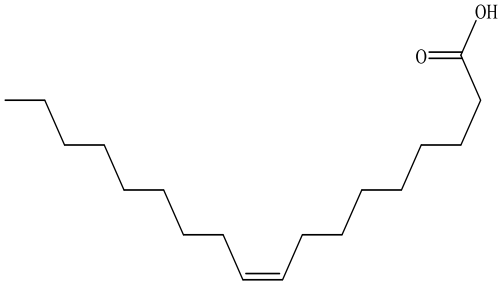
p-hydroxybenzoic acid



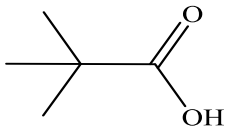
2-butenoic acid



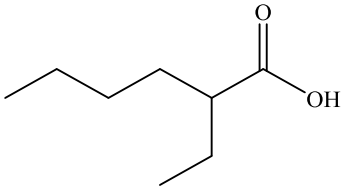
2-methylpropenoic acid



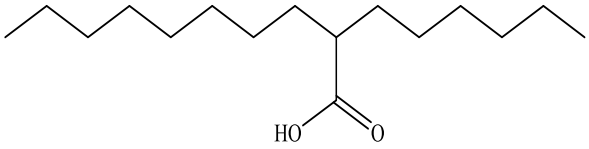
octadec-9-enoic acid



2,2-dimethylpropanoic acid



2-ethylhexanoic acid



2-hexyldecanoic acid

Figure 3.1 Structural formulas of the carboxylic acids used for the synthesis of ionic copper(II)

3.2 Synthesis

The methods used intended to synthesize these complexes involved one-pot and ligand-exchange reactions.

3.2.1 One-pot reaction

The one-pot reaction was used to synthesize six (6) ionic complexes of general formula $K_n[Cu_2(p\text{-}OC_6H_4COO)_n(CH_3CH=CHCOO)_{4-n}]$ and $K_n[Cu_2(p\text{-}OC_6H_4COO)_n(CH_2=C(CH_3)COO)_{4-n}]$, where n = 1-3.

(a) $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3CH=CHCOO)_2]$

p-HOC_6H_4COOH (2.69 g; 0.02 mol) and $CH_3CH=CHCOOH$ (1.6895 g; 0.02 mol) were mixed in an aqueous ethanolic solution of KOH (0.06 mol; 100 mL). The mixture was magnetically stirred and heated until all solids dissolved. $CuCl_2.2H_2O$ (3.33 g; 0.02 mol) was dissolved in distilled water (20 mL) and the solution was added to the hot solution. The mixture was further stirred and gently heated for 30 minutes. The green solid formed (**Complex 1**) was filtered from the warm reaction mixture, washed with water, and dried in a warm oven (60^{o}C). The yield was 3.73 g.

The blue filtrate (**Complex 2**) was left standing at room temperature for about one week. The blue small needles formed was filtered and dried in a warm oven (60^{o}C). The yield was 2.82 g.

(b) $K[Cu_2(p\text{-}OC_6H_4COO)(CH_3CH=CHCOO)_3]$

The method was the same as for $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3CH=CHCOO)_2]$ (**Section 3.2.1(a)**), using *p*-HOC_6H_4COOH (2.69 g; 0.02 mol), $CH_3CH=CHCO_2H$ (5.07 g; 0.06 mol), KOH (0.10 mol; 100 mL), and $CuCl_2.2H_2O$ (3.33 g; 0.02 mol). The product obtained from the residue was a green powder (**Complex 3**; 3.62 g) and that obtained from the filtrate was a blue powder (**Complex 4**; 2.85 g).

(c) $K_3[Cu_2(p\text{-}OC_6H_4COO)_3(CH_3CH{=}CHCOO)]$

The method was the same as for $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3CH{=}CHCOO)_2]$ (**Section 3.2.1(a)**), using *p*-HOC_6H_4COOH (8.09 g; 0.06 mol), $CH_3CH{=}CHCOOH$ (1.70 g; 0.02 mol), KOH (0.15 mol; 100 mL), and $CuCl_2.2H_2O$ (3.35 g; 0.02 mol). The product deposited out from the filtrate was a dark brown powder (2.10 g). This complex was not isolated as it was actually **Complex 1**.

(d) $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_2{=}C(CH_3)COO)_2]$

The method was the same as for $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3CH{=}CHCOO)_2]$ (**Section 3.2.1(a)**), using *p*-HOC_6H_4COOH (2.73 g; 0.02 mol), $CH_2{=}C(CH_3)COOH$ (1.65 ml; 0.02 mol), KOH (0.06 mol; 100 mL), and $CuCl_2.2H_2O$ (3.36 g; 0.02 mol). The product obtained was the residue was a green powder (**Complex 5**; 4.78 g).

(e) *$K[Cu_2(p\text{-}OC_6H_4COO)(CH_2{=}C(CH_3)COO)_3]$*

The method was the same as for $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3CH{=}CHCOO)_2]$ (**Section 3.2.1(a)**), using *p*-HOC_6H_4COOH (2.70 g; 0.02 mol), $CH_2{=}C(CH_3)COOH$ (5.00 ml; 0.06 mol), KOH (0.10 mol; 100 mL), and $CuCl_2.2H_2O$ (3.33 g; 0.02 mol). The product obtained as the residue was a green powder (**Complex 6**; 5.41 g).

(f) *$K_3[Cu_2(p\text{-}OC_6H_4COO)_3(CH_2{=}C(CH_3)COO)]$*

The method was the same as for $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3CH{=}CHCOO)_2]$ (**Section 3.2.1(a)**), using *p*-HOC_6H_4COOH (8.09 g; 0.06 mol), $CH_2{=}C(CH_3)COOH$ (1.65 ml; 0.02 mol), KOH (0.15 mol; 100 mL), and $CuCl_2.2H_2O$ (3.33 g; 0.02 mol). The product obtained as the residue was a green powder (**Complex 7**; 5.47 g).

3.2.2 Ligand-exchange reaction

The ligand-exchange reaction was used to synthesize seven (7) ionic complex precursors: $[Cu_2(RCOO)_n(CH_3CH=CHCOO)_{4-n}])$, $[Cu_2(RCOO)(CH_3(CH_2)_7CH=CH(CH_2)_7COO)_3]$, $[Cu_2(RCOO)((CH_3)_3CCOO)_3]$, $[Cu_2(RCOO)(CH_3(CH_2)_3CH(C_2H_5)COO)_3]$, and $[Cu_2(RCOO)(CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_3]$, where R = *p*-$HOC_6H_4$, and *n* = 1-3.

(a) *Synthesis of $[Cu_2(p\text{-}HOC_6H_4COO)_n(CH_3CH=CHCOO)_{4-n}]$*

The ligand-exchange reaction involved syntheses of $[Cu_2(p\text{-}HOC_6H_4COO)_4]$ and $[Cu_2(CH_3CH=CHCOO)_4]$, and then reacting the two complexes in the correct mole ratios.

(i) $[Cu_2(p\text{-}HOC_6H_4COO)_4]$

p-HOC_6H_4COOH (34.51 g; 0.25 mol) was dissolved in ethanol (100 mL). The solution was magnetically stirred and gently heated. $[Cu(CH_3COO)_2].H_2O$ (26.23 g; 0.13 mol) was added to the solution portion wise. The reaction mixture was further heated for 30 minutes, and then left to cool to room temperature overnight. The green solid formed was filtered and dried in a warm oven (60^oC). The yield was 53.40 g.

(ii) $[Cu_2(CH_3CH=CHCOO)_4]$

The synthesis involved two steps.

Step 1: Synthesis of $CH_3CH=CHCOONa$

Na_2CO_3 (5.12 g; 0.05 mol) and $CH_3CH=CHCOOH$ (8.38 g; 0.10 mol) were separately dissolved in distilled water (50 mL). The sodium carbonate solution was added portion wise to the $CH_3CH=CHCOOH$ solution. The reaction mixture was magnetically stirred and gently heated at about 30 minutes and then left to cool to room temperature

overnight. The white solid deposited was filtered and dried in a warm oven (60^{o}C). The yield was 9.91 g (94.5%).

Step 2: Synthesis of [$Cu_2(CH_3CH=CHCOO)_4$]

$CH_3CH=CHCOONa$ (2.92 g; 0.027 mol) was dissolved in distilled water (50 mL). $CuCl_2.2H_2O$ (2.36 g; 0.014 mol) was dissolved in a minimum volume of distilled water. The solutions were mixed, magnetically stirred and gently heated for 30 minutes. The green powder formed was left to cool to room temperature overnight. It was then filtered and dried in a warm oven (60^{o}C). The yield was 4.01 g.

(iii) [$Cu_2(p\text{-}HOC_6H_4COO)_2(CH_3CH=CHCOO)_2$]

An ethanolic solutions of [Cu_2[*p*-$HOC_6H_4COO)_4$] (3.38 g; 0.01 mol; **Section 3.2.2** (a) (i)) and [$Cu_2(CH_3CH=CHCOO)_4$] (2.34 g; 0.01 mol; **Section 3.2.2** (a) (ii)) were mixed in a conical flask. The mixture was magnetically stirred and gently heated for about 5 minutes. A few drops of pyridine were added to the warm reaction mixture, and the dark green solution formed was further gently heated for 30 minutes. It was left to cool overnight, and the purple solid (**Complex 8**) formed was filtered and dried in a warm oven (60^{o}C). The yield was 2.42 g

On standing at room temperature for one week, a green solid (**Complex 9**) deposited from the green filtrate was filtered and dried in a warm oven (60^{o}C). The yield was 3.57 g.

(iv) [$Cu_2(p\text{-}HOC_6H_4COO)(CH_3CH=CHCOO)_3$]

The method was the same as for [Cu_2*(p*-$HOC_6H_4COO)_2(CH_3CH=CHCOO)_2$] (**Section 3.2.2** (a) (iii)) using [Cu_2(*p*-$HOC_6H_4COO)_4$] (1.69 g; 0.003 mol) (**Section 3.2.2** (a) (i)) and [$Cu_2(CH_3CH=CHCOO)_4$] (3.51 g; 0.008 mol) (**Section 3.2.2** (a) (ii)). The product

deposited out was blue powder from the residue (**Complex 10**; 0.72 g) and a green powder from the filtrate (**Complex 9**; 3.34 g).

(v) [Cu_2(p-$HOC_6H_4COO)_3(CH_3CH$=CHCOO)]

The method was the same as for [Cu_2(*p*-$HOC_6H_4COO)_2(CH_3CH$=CHCOO)$_2$] (**Section 3.2.2** (a) (iii)) using [Cu_2(*p*-$HOC_6H_4COO)_4$] (4.71 g; 0.007 mol) (**Section 3.2.2** (a) (i)) and [$Cu_2(CH_3CH$=CHCOO)$_4$] (1.17 g; 0.003 mol) (**Section 3.2.2** (a) (ii)). The product deposited out was purple powder from the residue (**Complex 8**; 4.63 g) and a green powder from the filtrate (**Complex 9**; 3.34 g).

(b) *[Cu_2(p-$HOC_6H_4COO)(CH_3(CH_2)_7CH$=$CH(CH_2)_7COO)_3$]*

The ligand-exchange reaction involved the synthesis of [$Cu_2(CH_3(CH_2)_7CH$=$CH(CH_2)_7COO)_4$], and then reacting it with [Cu_2(*p*-$HOC_6H_4COO)_4$] (prepared in **Section 3.2.2** (a) (i)) in the correct mole ratio.

(i) *[$Cu_2(CH_3(CH_2)_7CH$=$CH(CH_2)_7COO)_4$]*

The method was the same as for [$Cu_2(CH_3CH$=CHCOO)$_4$] (**Section 3.2.2** (a) (ii)), using Na_2CO_3 (2.65 g; 0.03 mol), $CH_3(CH_2)_7CH$=$CH(CH_2)_7COOH$ (14.2 g; 0.05 mol) and $CuCl_2.2H_2O$ (4.37 g; 0.03 mol). The product was obtained as a dark green semi-solid from the residue (14.58 g).

(ii) *[Cu_2(p-$HOC_6H_4COO)(CH_3(CH_2)_7CH$=$CH(CH_2)_7COO)_3$]*

The method was the same as for [Cu_2(*p*-$HOC_6H_4COO)_2(CH_3CH$=CHCOO)$_2$] (**Section 3.2.2** (a) (iii)) using [Cu_2(*p*-$HOC_6H_4COO)_4$] (2.03 g; 0.003 mol) (**Section 3.2.2** (a) (i)) and [$Cu_2(CH_3(CH_2)_7CH$=$CH(CH_2)_7COO)_4$] (11.29 g; 0.009 mol) (**Section 3.2.2** (b) (i)). The product was obtained as a dark green semi-solid from the residue (**Complex 11**; 9.23 g).

(c) *[Cu_2(p-HOC_6H_4COO)($(CH_3)_3CCOO$)$_3$]*

The ligand-exchange reaction involved the synthesis of [$Cu_2((CH_3)_3CCOO)_4$], and then reacting it with [Cu_2(*p*-$HOC_6H_4COO)_4$] (prepared in **Section 3.2.2** (a) (i)) in the correct mole ratio.

(i)*[$Cu_2((CH_3)_3CCOO)_4$]*

The method was the same as for [$Cu_2(CH_3CH=CHCOO)_4$] (**Section 3.2.2** (a) (ii)), using Na_2CO_3 (5.09 g; 0.05 mol) $(CH_3)_3CCOOH$ (9.98 g; 0.10 mol) and $CuCl_2.2H_2O$ (8.20 g; 0.05 mol). The product was obtained from the residue as a green powder (10.05 g).

(ii)*[Cu_2(p-HOC_6H_4COO)($(CH_3)_3CCOO$)$_3$]*

The method was the same as for [Cu_2(*p*-$HOC_6H_4COO)_2(CH_3CH=CHCOO)_2$] (**Section 3.2.2** (a) (iii)) using [Cu_2(*p*-$HOC_6H_4COO)_4$] (1.69 g; 0.003 mol) (**Section 3.2.2** (a) (i)) and [$Cu_2((CH_3)_3CCOO)_4$] (4.07 g; 0.008 mol) (**Section 3.2.2** (c) (i)). The product was obtained as a greenish brown solid from the residue (**Complex 12**; 0.82 g) and a green crystal from the filtrate (**Complex 13**; 1.15 g).

(d) *[Cu_2(p-HOC_6H_4COO)($CH_3(CH_2)_3CH(C_2H_5)COO$)$_3$]*

The ligand-exchange reaction involved the synthesis of [$Cu_2(CH_3(CH_2)_3CH(C_2H_5)COO)_4$], and then reacting it with [Cu_2(*p*-$HOC_6H_4COO)_4$] (prepared in **Section 3.2.2** (a) (i)) in the correct mole ratio.

(i)*[$Cu_2(CH_3(CH_2)_3CH(C_2H_5)COO)_4$]*

The method was the same as for [$Cu_2(CH_3CH=CHCOO)_4$] (**Section 3.2.2** (a) (ii)), using Na_2CO_3 (2.66 g; 0.03 mol), $CH_3(CH_2)_3CH(C_2H_5)COOH$ (7.26 g; 0.05 mol) and $CuCl_2.2H_2O$ (4.28 g; 0.03 mol). The product was obtained as a green powder from the residue (14.79 g).

(ii) *[Cu_2(p-HOC_6H_4COO)($CH_3(CH_2)_3CH(C_2H_5)COO)_3$]*

The method was the same as for [Cu_2(*p*-$HOC_6H_4COO)_2(CH_3CH$=$CHCOO)_2$] (**Section 3.2.2** (a) (iii)) using [Cu_2(*p*-$HOC_6H_4COO)_4$] (3.38 g; 0.005 mol) (**Section 3.2.2** (a) (i)) and [$Cu_2(CH_3(CH_2)_3CH(C_2H_5)COO)_4$] (10.51 g; 0.015 mol) (**Section 3.2.2** (d) (i)). The product was obtained as a green powder from the residue (**Complex 14**; 3.28 g).

(e) *[Cu_2(p-$HOC_6H_4COO)(CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_3$]*

The ligand-exchange reaction involved the syntheses of [$Cu_2(CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_4$], and then reacting it with [Cu_2(*p*-$HOC_6H_4COO)_4$] (prepared in **Section 3.2.2** (a) (i)) in the correct mole ratio.

(i)[$Cu_2(CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_4$]

The method was the same as for [$Cu_2(CH_3CH$=$CHCOO)_4$] (**Section 3.2.2** (a) (ii)), using Na_2CO_3 (5.09 g; 0.05 mol), $CH_3(CH_2)_7CH((CH_2)_5CH_3)COOH$ (25.64 g; 0.10 mol) and $CuCl_2.2H_2O$ (8.21 g; 0.05 mol). The product was obtained as a dark green powder from the residue (17.74 g).

(ii) *[Cu_2(p-$HOC_6H_4COO)(CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_3$]*

The method was the same as for [Cu_2(*p*-$HOC_6H_4COO)_2(CH_3CH$=$CHCOO)_2$] (**Section 3.2.2** (a) (iii)), using [Cu_2(*p*-$HOC_6H_4COO)_4$] (3.38 g; 0.005 mol) (**Section 3.2.2** (a) (i)) and [$Cu_2(CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_4$] (17.24 g; 0.015 mol) (**Section 3.2.2** (e) (i)). The products were a dark turquoise solid (**Complex 15**; 8.12 g) and a green liquid (**Complex 16**; 5.30 g).

3.2.3 K[Cu_2(p-OC_6H_4COO)($CH_3(CH_2)_7CH=CH(CH_2)_7COO)_3$]

[Cu_2(*p*-HOC_6H_4COO)($CH_3(CH_2)_7CH=CH(CH_2)_7COO)_3$] (0.68 g; 0.0006 mol; **Section 3.2.2.2**) was suspended in 50 ml absolute ethanol. The complex was magnetically stirred and gently heated until it dissolved. An ethanolic solution of KOH (0.04 g; 0.0006 mol) was added to the hot solution. The mixture was further gently heated for 30 minutes. It was left to cool overnight and the green solid formed (**Complex 17**) was filtered. The yield was 0.08 g.

3.3 Instrumental Analyses

3.3.1 Elemental analyses

The elemental analyses were recorded on a Perkin Elmer CHNS/O analyser 2400 Series II. The sample was weighed (1 – 2 mg) in a tin capsule (5 x 8 mm). The capsule containing the sample was folded into a tiny piece. Then it was placed inside the analyzer to be heated to a maximum temperature of 1000 ^{o}C.

3.3.2 Fourier transform infrared spectroscopy

The Fourier Transform Infrared spectra (FTIR) were recorded as potassium bromide (KBr) discs from 4000 – 400 cm^{-1} on a FT-IR spectrum RX 1 spectrometer.

For the preparation of KBr disc, KBr was dried in an oven at 120 ^{o}C for 12 hours and left to cool in a desiccator. Tthe sample was finely grinded and then mixed with KBr in the mass ratio of about 1:9. The mixture was compressed to a transparent thin disc, and the disc was inserted into the spectrometer cell holder. The spectrum obtained was calibrated against KBr as a blank. The peaks were identified by comparison with the corresponding wavenumber from the literature.

3.3.3 Ultraviolet-visible spectroscopy

The ultraviolet-visible spectra (UV-vis), for both solid and solution samples, were recorded from 1000 – 300 nm on a SHIMADZU UV-vis-NIR 3600 spectrophotometer.

For a solid sample, the powder was grinded to a very fine powder and compressed onto the sample holder. Then the sample was inserted into the cell holder. The spectrum obtained was calibrated against barium sulphate ($BaSO_4$) as the background.

For solution sample, an exactly known mass of the solid was dissolved in a suitable organic solvent in a 10-mL volumetric flask. The solution was introduced into a

1-cm quartz cuvette. Then the cuvette was inserted into the sample holder. The spectrum obtained was recorded against the solvent as the background.

3.3.4 Thermogravimetric analysis

The thermogravimetric analysis (TGA) was recorded from 50–900 ^{o}C on a Pyris Diamond TG/DTA Perkin Elmer instrument with the scan rate of 20 ^{o}C min^{-1}. The sample was analysed under nitrogen at a flow rate of 10 cm^{3} min^{-1}. An empty alumina pan was placed in the holder and tared. Then the sample (4 - 5 mg) was loaded onto the pan and the weight recorded.

3.3.5 Differential scanning calorimetry

Differential scanning calorimetry (DSC) was recorded from 35–300 ^{o}C on a Perkin Elmer DSC 6 calorimeter. The analysis was performed under nitrogen gas at a flow rate of 10 cm^{3} min^{-1} and scan rate of 10 ^{o}C min^{-1}. The weight of the sample (3 – 4 mg) was initially recorded on a microbalance. The sample was transferred into an aluminium crucible and placed inside the DSC instrument.

3.3.6 Room-temperature magnetic susceptibility

Room-temperature magnetic susceptibility was recorded on a Sherwood Auto Magnetic Susceptibility Balance. An empty tube was tared on the analytical balance and then placed in the instrument. The exponent of the reading was changed to 10^{-5} and tared. The finely ground sample was packed into the tube to the calibrated mark (length 5 cm) and the mass was recorded. The tube containing the sample was then placed in the instrument and the χ_g was recorded.

3.3.7 Cyclic voltammetry

The cyclic voltammograms (CV) were recorded on a Gamry Potentiostat/Galvanostat/ ZRA Reference 600 Instruments, using a standard three-electrode assembly (glassy carbon working electrode, platinum counter electrode, and saturated calomel reference electrode). The supporting electrolyte was 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBATFB) dissolved in a suitable organic solvent. The scan range was from -2.5 V to +2.5 V, starting at and back to 0 V, the scan rate was 100 mV s^{-1}, and the quoted E values are *vs* saturated calomel electrode.

3.3.8 Photoluminescence spectroscopy

The photoluminescence spectra (PL) were measured on a PL-Raman (Horiba Jobin Yvon) at room temperature using a He-Cd lamp. The excitation wavelength was at 325 nm.

3.3.9 Single crystal X-ray crystallography

Single crystal X-ray diffraction was performed on a Bruker SMART APEX diffractometer operating with graphite-monochromator Mo Kα radiation (λ = 0.71073Å) at 100K. The intensities were collected using the ω -2θ scan mode, in the range $2.0^o < \theta < 27.5^o$. All structures were solved by direct method using SHELXS-97 and refined by full matrix least-square methods on F^2 with the use of the SHELXL-97 program package.