Alkyl chain self ordering, induction and suppression of mesophase by Cu(II) containing [1,2,3]-triazole-based bidentate salicylaldimine ligands: Synthesis, characterization and X-ray diffraction studies.

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Content:

1. The percentage yields and analytical datas for ligands **4** are summarized as below:

4aF: yellow, yield 53%. Elemental analysis/% : Found C 69.36, H 6.50, N 9.75; calculated (C₃₃H₃₇FN₄O₄), C 69.21, H 6.51, N 9.78;. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1253 (C-O ether), 1291 (C-O phenolic), 1606 (C=C), 1626 (C=N), 1735 (C=O ester), 2918-2848 (C-H alkyl), 3452 (O-H). ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, 3H, CH₃), δ 1.34-1.94 (m, 16H, CH₂), δ 4.38 (t, 2H, OCH₂), δ 5.32 (s, 2H, OCH₂), δ 6.84 (d, 1H, Ar-H), δ 6.90 (s, 1H, Ar-H), δ 7.13 (m, 4H, Ar-H), δ 7.30 (d, 2H, Ar-H), δ 7.44 (d, 1H, Ar-H), δ 7.65 (s, 1H, N-CH), δ 8.17 (d, 2H, Ar-H), 8.62 (s, 1H, N=CH), 13.46 (s, 1H, Ar-OH). ¹³C NMR (75 MHz, CDCl₃) δ 14.25 (CH₃), δ 22.92-32.19 (C_{aliphatic}), δ 50.87, δ 62.84 (OCH₂), δ 110.94, δ 113.39, δ 115.32, δ 116.69, 117.45, δ 122.70, δ 122.94, δ 132.80, δ 132.91, δ 133.41, δ 145.02, δ 155.46, δ 162.91, δ 163.18, δ 164.38 (C_{aromatic}), δ 122.83, δ 143.87 (C_{triazole}), δ 161.95 (HC=N).

4bF: yellow, yield 51%. Elemental analysis/% : Found C 69.78, H 6.89, N 9.35; calculated (C₃₅H₄₁FN₄O₄), C 69.98, H 6.88, N 9.33;. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1254 (C-O ether), 1291 (C-O phenolic), 1606 (C=C), 1626 (C=N), 1735 (C=O ester), 2916-2848 (C-H alkyl), 3452 (O-H). ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, 3H, CH₃), δ 1.35-1.95 (m, 20H, CH₂), δ 4.37 (t, 2H, OCH₂), δ 5.32 (s, 2H, OCH₂), δ 6.84 (d, 1H, Ar-H), δ 6.90 (s, 1H, Ar-H), δ 7.12 (m, 4H, Ar-H), δ 7.30 (d, 2H, Ar-H), δ 7.44 (d, 1H, Ar-H), δ 7.65 (s, 1H, N-CH), δ 8.18 (d, 2H, Ar-H), 8.62 (s, 1H, N=CH), 13.45 (s, 1H, Ar-OH). ¹³C NMR (75 MHz, CDCl₃) δ 14.25 (CH₃), δ 22.91-32.21 (C_{aliphatic}), δ 50.86, δ 62.84 (OCH₂), δ 110.92, δ 113.38, δ 115.32, δ 116.69, 117.46, δ 122.70, δ

122.94, δ 132.81, δ 132.93, δ 133.41, δ 145.02, δ 155.45, δ 162.91, δ 163.18, δ 164.38 (C_{aromatic}), δ 122.82, δ 143.88 (C_{triazole}), δ 161.95 ($H\text{C}=\text{N}$).

4cF: yellow, yield 53%. Elemental analysis/% : Found C 70.81, H 7.26, N 8.93; calculated ($C_{37}H_{45}FN_4O_4$), C 70.68, H 7.21, N 8.91 ;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1254 (C-O ether), 1291 (C-O phenolic), 1605 (C=C), 1625 (C=N), 1734 (C=O ester), 2918-2848 (C-H alkyl), 3450 (O-H). ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, 3H, CH_3), δ 1.34-1.94 (m, 24H, CH_2), δ 4.37 (t, 2H, OCH_2), δ 5.33 (s, 2H, OCH_2), δ 6.83 (d, 1H, Ar-H), δ 6.91 (s, 1H, Ar-H), δ 7.12 (m, 4H, Ar-H), δ 7.31 (d, 2H, Ar-H), δ 7.44 (d, 1H, Ar-H), δ 7.64 (s, 1H, N-CH), δ 8.18 (d, 2H, Ar-H), 8.62 (s, 1H, N=CH), 13.46 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.25 (CH_3), δ 22.91-32.19 ($C_{\text{aliphatic}}$), δ 50.87, δ 62.84 (OCH_2), δ 110.92, δ 113.39, δ 115.33, δ 116.68, 117.45, δ 122.70, δ 122.92, δ 132.79, δ 132.91, δ 133.42, δ 145.02, δ 155.47, δ 162.91, δ 163.17, δ 164.38 (C_{aromatic}), δ 122.83, δ 143.85 (C_{triazole}), δ 161.95 ($H\text{C}=\text{N}$).

4dF: yellow, yield 56%. Elemental analysis/% : Found C 71.40, H 7.55, N 8.50; calculated ($C_{39}H_{49}FN_4O_4$), C 71.31, H 7.52, N 8.53 ;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1253 (C-O ether), 1292 (C-O phenolic), 1606 (C=C), 1627 (C=N), 1735 (C=O ester), 2918-2849 (C-H alkyl), 3450 (O-H). ^1H NMR (300 MHz, CDCl_3) δ 0.88 (t, 3H, CH_3), δ 1.33-1.93 (m, 28H, CH_2), δ 4.38 (t, 2H, OCH_2), δ 5.33 (s, 2H, OCH_2), δ 6.83 (d, 1H, Ar-H), δ 6.91 (s, 1H, Ar-H), δ 7.12 (m, 4H, Ar-H), δ 7.30 (d, 2H, Ar-H), δ 7.44 (d, 1H, Ar-H), δ 7.64 (s, 1H, N-CH), δ 8.17 (d, 2H, Ar-H), 8.63 (s, 1H, N=CH), 13.46 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.25 (CH_3), δ 22.92-32.19 ($C_{\text{aliphatic}}$), δ 50.87, δ 62.84 (OCH_2), δ 110.96, δ 113.40, δ 115.32, δ 116.69, 117.45, δ 122.70, δ 122.93, δ 132.79, δ 132.91, δ 133.42, δ 145.02, δ 155.44, δ 162.91, δ 163.18, δ 164.38 (C_{aromatic}), δ 122.83, δ 143.87 (C_{triazole}), δ 161.96 ($H\text{C}=\text{N}$).

4eF: yellow, yield 55%. Elemental analysis/% : Found C 72.04, H 7.82, N 8.17; calculated ($C_{41}H_{53}FN_4O_4$), C 71.90, H 7.80, N 8.18 ;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1252 (C-O ether), 1291 (C-O phenolic), 1605 (C=C), 1627 (C=N), 1733 (C=O ester), 2918-2848 (C-H alkyl), 3450 (O-H). ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, 3H, CH_3), δ 1.34-1.94 (m, 32H, CH_2), δ 4.38 (t, 2H, OCH_2), δ 5.33 (s, 2H, OCH_2), δ 6.83 (d, 1H, Ar-H), δ 6.92 (s, 1H, Ar-H), δ 7.12 (m, 4H, Ar-H), δ 7.30 (d, 2H, Ar-H), δ 7.44 (d, 1H, Ar-H), δ 7.63 (s, 1H, N-CH), δ 8.17 (d, 2H, Ar-H), 8.62 (s, 1H, N=CH), 13.45 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.25 (CH_3), δ 22.91-32.20 ($C_{\text{aliphatic}}$), δ 50.88, δ 62.83 (OCH_2), δ 110.95, δ 113.39, δ 115.32, δ 116.69, 117.45, δ 122.70, δ

122.94, δ 132.80, δ 132.91, δ 133.41, δ 145.00, δ 155.46, δ 162.91, δ 163.17, δ 164.38 (C_{aromatic}), δ 122.81, δ 143.87 (C_{triazole}), δ 161.95 ($\text{HC}=\text{N}$).

4aCl: light yellow, yield 49%. Elemental analysis/% : Found C 67.48, H 6.31, N 9.53; calculated ($\text{C}_{33}\text{H}_{37}\text{ClN}_4\text{O}_4$), C 67.28, H 6.33, N 9.51;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1260 (C-O ether), 1320 (C-O phenolic), 1608 (C=C), 1618 (C=N), 1723 (C=O ester), 2920-2850 (C-H alkyl), 3438 (O-H). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3H, CH_3), δ 1.28-1.93 (m, 16H, CH_2), δ 4.37 (t, 2H, OCH_2), δ 5.30 (s, 2H, OCH_2), δ 6.83 (d, 1H, Ar-H), δ 6.89 (s, 1H, Ar-H), δ 7.10 (d, 2H, Ar-H), δ 7.22 (d, 2H, Ar-H), δ 7.38 (d, 2H, Ar-H), δ 7.42 (d, 1H, Ar-H), δ 7.64 (s, 1H, N-CH), δ 8.14 (d, 2H, Ar-H), 8.60 (s, 1H, N=CH), 13.36 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.12 (CH_3), δ 22.68-31.89 ($C_{\text{aliphatic}}$), δ 50.55, δ 62.25 (OCH_2), δ 110.65, δ 113.23, δ 114.70, δ 116.98, δ 121.96, δ 122.68, δ 129.56, δ 132.44, δ 132.67, δ 133.31, δ 146.78, δ 155.00, δ 162.51, δ 162.68, δ 164.16 (C_{aromatic}), δ 122.45, δ 143.45 (C_{triazole}), δ 162.12 ($\text{HC}=\text{N}$).

4bCl: light yellow, yield 43%. Elemental analysis/% : Found C 68.32, H 6.76, N 9.05; calculated ($\text{C}_{35}\text{H}_{41}\text{ClN}_4\text{O}_4$), C 68.11, H 6.70, N 9.08;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1262 (C-O ether), 1320 (C-O phenolic), 1608 (C=C), 1618 (C=N), 1724 (C=O ester), 2919-2850 (C-H alkyl), 3438 (O-H). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3H, CH_3), δ 1.27-1.94 (m, 20H, CH_2), δ 4.37 (t, 2H, OCH_2), δ 5.30 (s, 2H, OCH_2), δ 6.82 (d, 1H, Ar-H), δ 6.89 (s, 1H, Ar-H), δ 7.10 (d, 2H, Ar-H), δ 7.21 (d, 2H, Ar-H), δ 7.38 (d, 2H, Ar-H), δ 7.42 (d, 1H, Ar-H), δ 7.64 (s, 1H, N-CH), δ 8.14 (d, 2H, Ar-H), 8.60 (s, 1H, N=CH), 13.36 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.12 (CH_3), δ 22.68-31.89 ($C_{\text{aliphatic}}$), δ 50.55, δ 62.25 (OCH_2), δ 110.64, δ 113.24, δ 114.68, δ 116.98, δ 121.98, δ 122.68, δ 129.59, δ 132.44, δ 132.67, δ 133.31, δ 146.78, δ 155.00, δ 162.51, δ 162.68, δ 164.16 (C_{aromatic}), δ 122.46, δ 143.45 (C_{triazole}), δ 162.11 ($\text{HC}=\text{N}$).

4cCl: light yellow, yield 47%. Elemental analysis/% : Found C 69.05, H 7.01, N 8.69; calculated ($\text{C}_{37}\text{H}_{45}\text{ClN}_4\text{O}_4$), C 68.87, H 7.03, N 8.68;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1260 (C-O ether), 1320 (C-O phenolic), 1607 (C=C), 1619 (C=N), 1724 (C=O ester), 2919-2850 (C-H alkyl), 3438 (O-H). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3H, CH_3), δ 1.28-1.93 (m, 24H, CH_2), δ 4.38 (t, 2H, OCH_2), δ 5.30 (s, 2H, OCH_2), δ 6.82 (d, 1H, Ar-H), δ 6.89 (s, 1H, Ar-H), δ 7.10 (d, 2H, Ar-H), δ 7.21 (d, 2H, Ar-H), δ 7.38 (d, 2H, Ar-H), δ 7.42 (d, 1H, Ar-H), δ 7.64 (s, 1H, N-CH), δ 8.14 (d, 2H, Ar-H), 8.60 (s, 1H, N=CH), 13.36 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.10 (CH_3), δ 22.67-31.87 ($C_{\text{aliphatic}}$), δ 50.56, δ 62.25 (OCH_2), δ 110.66, δ 113.22, δ 114.70, δ 116.98, δ 121.96,

δ 122.67, δ 129.54, δ 132.44, δ 132.69, δ 133.31, δ 146.78, δ 155.00, δ 162.51, δ 162.68, δ 164.16 (C_{aromatic}), δ 122.43, δ 143.48 (C_{triazole}), δ 162.12 ($\text{HC}=\text{N}$).

4dCl: light yellow, yield 49%. Elemental analysis/% : Found C 69.66, H 7.38, N 8.35; calculated ($\text{C}_{39}\text{H}_{49}\text{ClN}_4\text{O}_4$), C 69.57, H 7.34, N 8.32;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1260 (C-O ether), 1320 (C-O phenolic), 1608 (C=C), 1619 (C=N), 1724 (C=O ester), 2919-2850 (C-H alkyl), 3439 (O-H). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3H, CH_3), δ 1.28-1.93 (m, 28H, CH_2), δ 4.38 (t, 2H, OCH_2), δ 5.31 (s, 2H, OCH_2), δ 6.82 (d, 1H, Ar-H), δ 6.88 (s, 1H, Ar-H), δ 7.10 (d, 2H, Ar-H), δ 7.21 (d, 2H, Ar-H), δ 7.38 (d, 2H, Ar-H), δ 7.42 (d, 1H, Ar-H), δ 7.64 (s, 1H, N-CH), δ 8.14 (d, 2H, Ar-H), 8.61 (s, 1H, N=CH), 13.36 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.12 (CH_3), δ 22.68-31.89 ($C_{\text{aliphatic}}$), δ 50.55, δ 62.25 (OCH_2), δ 110.65, δ 113.23, δ 114.70, δ 116.98, δ 121.96, δ 122.66, δ 129.56, δ 132.43, δ 132.67, δ 133.31, δ 146.78, δ 155.07, δ 162.51, δ 162.69, δ 164.16 (C_{aromatic}), δ 122.45, δ 143.45 (C_{triazole}), δ 162.14 ($\text{HC}=\text{N}$).

4eCl: light yellow, yield 51%. Elemental analysis/% : Found C 70.51, H 7.68, N 8.04; calculated ($\text{C}_{41}\text{H}_{53}\text{ClN}_4\text{O}_4$), C 70.21, H 7.62, N 7.99;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1260 (C-O ether), 1320 (C-O phenolic), 1607 (C=C), 1618 (C=N), 1723 (C=O ester), 2919-2850 (C-H alkyl), 3439 (O-H). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3H, CH_3), δ 1.28-1.93 (m, 28H, CH_2), δ 4.37 (t, 2H, OCH_2), δ 5.30 (s, 2H, OCH_2), δ 6.82 (d, 1H, Ar-H), δ 6.88 (s, 1H, Ar-H), δ 7.11 (d, 2H, Ar-H), δ 7.21 (d, 2H, Ar-H), δ 7.37 (d, 2H, Ar-H), δ 7.42 (d, 1H, Ar-H), δ 7.64 (s, 1H, N-CH), δ 8.14 (d, 2H, Ar-H), 8.60 (s, 1H, N=CH), 13.35 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.13 (CH_3), δ 22.69-31.90 ($C_{\text{aliphatic}}$), δ 50.54, δ 62.25 (OCH_2), δ 110.65, δ 113.23, δ 114.70, δ 116.98, δ 121.96, δ 122.68, δ 129.56, δ 132.43, δ 132.67, δ 133.32, δ 146.78, δ 155.04, δ 162.53, δ 162.68, δ 164.17 (C_{aromatic}), δ 122.44, δ 143.45 (C_{triazole}), δ 162.13 ($\text{HC}=\text{N}$).

4dBr: yellow, yield 38 %. Elemental analysis/% : Found C 65.51, H 6.91, N 7.82; calculated ($\text{C}_{39}\text{H}_{49}\text{BrN}_4\text{O}_4$), C 65.26, H 6.88, N 7.81;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1260 (C-O ether), 1320 (C-O phenolic), 1608 (C=C), 1620 (C=N), 1723 (C=O ester), 2920-2849 (C-H alkyl), 3424 (O-H). ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, 3H, CH_3), δ 1.23-1.96 (m, 28H, CH_2), δ 4.39 (t, 2H, OCH_2), δ 5.32 (s, 2H, OCH_2), δ 6.85 (d, 1H, Ar-H), δ 6.90 (s, 1H, Ar-H), δ 7.11 (d, 2H, Ar-H), δ 7.18 (d, 2H, Ar-H), δ 7.45 (d, 1H, Ar-H), δ 7.50 (d, 2H, Ar-H), δ 7.65 (s, 1H, N-CH), δ 8.17 (d, 2H, Ar-H), 8.63 (s, 1H, N=CH), 13.35 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.25 (CH_3), δ 22.93-32.21 ($C_{\text{aliphatic}}$), δ 50.88, δ 62.84 (OCH_2), δ 110.99, δ 113.50, δ 115.33, δ 117.38, δ 120.78,

δ 122.98, δ 132.80, δ 132.90, δ 133.57, δ 135.08, δ 147.91, δ 155.70, δ 163.04, δ 163.19, δ 164.33 (C_{aromatic}), δ 122.68, δ 143.68 (C_{triazole}), δ 162.51 ($HC=N$)

4dI: yellow, yield 30 %. Elemental analysis/% : Found C 61.33, H 6.52, N 7.31; calculate ($C_{39}H_{49}IN_4O_4$), C 61.25, H 6.46, N 7.33;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1250 (C-O ether), 1291 (C-O phenolic), 1609 (C=C), 1619 (C=N), 1736 (C=O ester), 2917-2847 (C-H alkyl), 3444 (O-H). ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, 3H, CH_3), δ 1.23-1.93 (m, 28H, CH_2), δ 4.38 (t, 2H, OCH_2), δ 5.33 (s, 2H, OCH_2), δ 6.86 (d, 1H, Ar-H), δ 6.91 (s, 1H, Ar-H), δ 7.05 (d, 2H, Ar-H), δ 7.11 (d, 2H, Ar-H), δ 7.44 (d, 1H, Ar-H), δ 7.64 (s, 1H, N-CH), δ 7.76 (d, 2H, Ar-H), δ 8.17 (d, 2H, Ar-H), 8.63 (s, 1H, N=CH), 13.35 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.12 (CH_3), δ 22.69-31.92 ($C_{\text{aliphatic}}$), δ 50.59, δ 62.25 (OCH_2), δ 110.87, δ 113.27, δ 114.80, δ 118.64, δ 121.59, δ 123.14, δ 132.46, δ 132.53, δ 133.34, δ 138.52, δ 148.10, δ 155.08, δ 162.68, δ 162.86, δ 164.15 (C_{aromatic}), δ 121.99, δ 143.21 (C_{triazole}), δ 162.19 ($HC=N$)

4dH: yellow, yield 46 %. Elemental analysis/% : Found C 73.38, H 7.86, N 8.76; calculate ($C_{39}H_{50}N_4O_4$), C 73.32, H 7.89, N 8.77;. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1256 (C-O ether), 1291 (C-O phenolic), 1607 (C=C), 1629 (C=N), 1734 (C=O ester), 2917-2848 (C-H alkyl), 3446 (O-H). ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, 3H, CH_3), δ 1.26-1.96 (m, 28H, CH_2), δ 4.38 (t, 2H, OCH_2), δ 5.33 (s, 2H, OCH_2), δ 6.83 (d, 1H, Ar-H), δ 6.90 (s, 1H, Ar-H), δ 7.12 (d, 2H, Ar-H), δ 7.32 (d, 2H, Ar-H), δ 7.42-7.48 (m, 3H, Ar-H), δ 7.65 (s, 1H, N-CH), δ 8.18 (d, 2H, Ar-H), 8.65 (s, 1H, N=CH), 13.65 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.42 (CH_3), δ 22.94-32.23 ($C_{\text{aliphatic}}$), δ 50.86, δ 62.85 (OCH_2), δ 110.96, δ 113.31, δ 115.23, δ 117.58, δ 121.46, δ 122.75, δ 127.23, δ 129.75, δ 132.74, δ 132.81, δ 133.41, δ 135.11, δ 155.42, δ 163.16, δ 163.37, δ 164.40 (C_{aromatic}), δ 121.56, δ 143.87 (C_{triazole}), δ 162.12 ($HC=N$).

2. Characterization

The elemental analysis results show that the percentages for carbon, hydrogen and nitrogen in the respective Cu(II) complexes are consistent with its empirical formula.

The coordination of the ligands **4** to Cu(II) ion involves the salicylaldimines fragments. The corresponding changes can be inferred from the relevant IR frequency associated with the complexation of metal (Figure 1). The IR spectra showed that the C=N stretching frequency is

shifted to a lower region by 14-15 cm^{-1} in Cu(II) complexes **5** as compared to uncoordinated ligand **4**. The observation can be due to the coordination of N atom to the Cu(II) metal ion leading to the reduction in the C=N bond order [1-8]. Besides, the stretching frequency of phenolic C-O is shifted upon complexation in which the values change from 1291-1292 cm^{-1} to 1266-1267 cm^{-1} for fluoro substituent, 1320 cm^{-1} to 1307-1308 cm^{-1} for chloro and bromo substituents, 1291 cm^{-1} to 1267 cm^{-1} for iodo and unsubstituted ligands. These observations indicate the deprotonation of OH which occurred prior to coordination with Cu(II) ion [9,10]. Furthermore, the absence of the O-H band of free ligands in the Cu(II) metal complexes also confirmed the formation of new Cu-O bond [1-8].

In order to further substantiate the structures of these ligands and their Cu(II) complexes, the UV-Vis spectra were measured by using chloroform as solvent. Figure 2 shows the electronic spectra for ligand **4eF** and Cu(II) complex **5eF**. The electronic spectra of free ligand consist of an intense band and a weak band at 275 nm and 315 nm, respectively. These two bands can be attributed to $\pi \rightarrow \pi^*$ electronic transitions of the ligand chromophore. Another band in longer wavelength region of the spectra at 339 nm is related to $n \rightarrow \pi^*$ electronic transitions of the azomethine chromophore. The spectra of Cu(II) complexes exhibit 3 groups of absorption bands at 262 nm, 282 nm and 383 nm. The first and second bands are attributed to the $\pi \rightarrow \pi^*$ electronic transitions. The third band is red shifted to longer wavelength in comparison with that in free ligands (339 nm). This shift could be attributed to the ligand metal charge transfer (LMCT) which is due to the transition of non-bonding electron pairs from nitrogen atom of azomethine to Cu(II) metal ion [10]. These observation suggested the formation of Cu(II) complexes. The other ligands and Cu(II) complexes exhibit similar pattern of UV-Vis spectra as shown by **4eF** and complex **5eF**. It is also worth to mention that the ^1H NMR spectra for Cu(II) complexes displayed only broad alkyl signals as all proton signals in close proximity with the paramagnetic Cu(II) centers are not observed.

3. Figures

Figure 1: Representative IR spectra of (i) ligand **4eF** and (ii) Cu(II) complex **5eF**

Figure 2: UV-visible spectra for ligand **3c** and Cu(II) complex **4c**.

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