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Twin effects of induction and stabilization of SmA* phase by Cu(II) upon 4,4'-disubstituted salicylideneimine containing [1,2,3]-triazole and cholesterol arms

Boon-Teck Heng[a], Guan-Yeow Yeap[a*], Wan Ahmad Kamil Mahmood[a], Kiyoshi Miyashita[b] and Masato M.Ito[b]

[a]*Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia.*
[b]*Department of Environmental Engineering for Symbiosis, Faculty of Engineering, Soka University, Hachioji, Tokyo 192-8577, Japan*

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1. The CHN microanalyses, ^{1}H NMR and ^{13}C NMR for intermediates **1-6.**

1.1 Intermediate **1**

Elemental analysis/%: Found C 43.89, H 2.47, N 34.12; calculated ($C_6H_4N_4O_2$), C 43.91, H 2.46, N 34.14. ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 7.73 (d, 2H, Ar-H), δ 8.47 (d, 2H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: δ 123.9, δ 129.6, δ 147.7, δ 150.0 ($C_{aromatic}$).

1.2 Intermediate **2**

Elemental analysis/%: Found C 49.13, H 3.67, N 25.46; calculated ($C_9H_8N_4O_3$), C 49.09, H 3.66, N 25.45. ^{1}H NMR (500 MHz, DMSO), δ/ppm: δ 5.40 (d, 2H, OCH_2), δ 8.22 (d, 2H, Ar-H), δ 8.44 (d, 2H, Ar-H), δ 8.90 (s, 1H, N-CH). ^{13}C NMR (75 MHz, DMSO) δ/ppm: δ 55.4 ($O\underline{C}H_2$), δ 121.1, δ 123.9, δ 140.9, δ 147.7 ($C_{aromatic}$), δ 119.8, δ 144.8 ($C_{triazole}$).

1.2 Intermediate **3**

All intermediates **3a-3e** with even alkanoate chain ranging from $C_{14}H_{29}$ to $C_{20}H_{41}$ show similar characteristics of ^{1}H and ^{13}C NMR spectral. Thus, a representative of **3a** is shown below.

3a: Elemental analysis/%: Found C 62.72, H 7.54, N 13.92; calculated ($C_{21}H_{30}N_4O_4$), C 62.67, H 7.51, N 13.92. ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.83 (t, 3H, CH_3), δ 1.25-1.55 (m, 18H, aliphatic protons), δ 2.35 (t, 2H, CH_2), δ 5.32 (s, OCH_2), δ 8.00 (d, 2H, Ar-H), δ 8.18 (s, 1H, N-CH), δ 8.45 (d, 2H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm: δ 14.13 ($\underline{C}H_3$), δ 22.7-34.17 ($C_{\text{aliphatic}}$), δ 173.8 ($\underline{C}$=O), δ 57.4 ($O\underline{C}H_2$), δ 120.5, δ 124.3, δ 139.8, δ 145.3 (C_{aromatic}), δ 121.9, δ 143.8 (C_{triazole}).

1.3 Intermediate **4**

All intermediates **4a-4e** with even alkanoate chain ranging from $C_{14}H_{29}$ to $C_{20}H_{41}$ show similar characteristics of ^{1}H and ^{13}C NMR spectral. Thus, a representative of **4a** is shown below:

4a: Elemental analysis/%: Found C 67.76, H 8.64, N 15.03; calculated ($C_{21}H_{32}N_4O_2$), C 67.71, H 8.66, N 15.04. ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.83 (t, 3H, CH_3), δ 1.25-1.55 (m, 18H, aliphatic protons), δ 2.35 (t, 2H, CH_2), δ 5.32 (s, OCH_2), δ 6.80 (s, 2H, Ar-NH_2), δ 8.00 (d, 2H, Ar-H), δ 8.18 (s, 1H, N-CH), δ 8.45 (d, 2H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm: δ 14.13 ($\underline{C}H_3$), δ 22.7-34.17 ($C_{\text{aliphatic}}$), δ 173.8 ($\underline{C}$=O), δ 57.4 ($O\underline{C}H_2$), δ 120.5, δ 124.3, δ 139.8, δ 145.3 (C_{aromatic}), δ 121.9, δ 143.8 (C_{triazole}).

1.4 Intermediate **5**

All intermediates **5a-5e** with even alkanoate chain ranging from $C_{14}H_{29}$ to $C_{20}H_{41}$ show similar characteristics of ^{1}H and ^{13}C NMR spectral. Thus, a representative of **5a** is shown below:

5a: Elemental analysis/%: Found C 69.08, H 7.20, N 11.13; calculated ($C_{29}H_{36}N_4O_4$), C 69.02, H 7.19, N 11.10. ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.83 (t, 3H, CH_3), δ 1.25-1.55 (m, 18H, aliphatic protons), δ 2.35 (t, 2H, CH_2), δ 5.23 (s, OCH_2), δ 6.30 (s, 1H, Ar-H), δ 6.42 (d, 1H, Ar-H), δ 7.46 (d, 1H, Ar-H), δ 7.57 (d, 2H, Ar-H), δ 7.98 (d, 2H, Ar-H), δ 8.87 (d, 2H, N-CH and N=CH), δ 10.35 (s, 1H, Ar-OH), δ 13.30 (s, 1H, Ar-OH). ^{13}C

NMR (75 MHz, $CDCl_3$), δ/ppm: δ 14.13 ($\underline{C}H_3$), δ 22.7-34.17 ($C_{aliphatic}$), δ 173.8 ($\underline{C}$=O), δ 57.4 (O$\underline{C}H_2$), δ 107.8, δ 100.5, δ 113.7, δ 121.6, δ 122.9, δ 132.7, δ 137.9, δ 149.7, δ δ 162.9, δ 163.7 ($C_{aromatic}$), δ 121.9, δ 143.8 ($C_{triazole}$), δ 160.10 (H$\underline{C}$=N).

1.5 Intermediate **6**

Elemental analysis/%: Found C 70.88, H 10.37; calculated ($C_{35}H_{61}BrO_2$), C 70.80, H 10.36. ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.60 (s, 3H, CH_3), δ 0.78-1.92 (m, 50H, aliphatic and cholesteric protons), δ 2.22-2.28 (m, 4H, CH_2), δ 3.32 (t, 2H, $BrCH_2$), δ 4.53 (m, 1H, O-CH), δ 5.30 (t, 1H, C=CH). ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm: δ 12.2-57.1 ($C_{aliphatic}$ and $C_{cholesteric}$), δ 74.1 ($\underline{C}$-O), δ 122.9 (C=$\underline{C}H_{cholesteric}$), δ 140.1 ($\underline{C}$=$CH_{cholesteric}$), δ 173.5 ($\underline{C}$=O).

2. Characterization

The comparison IR spectrum in Figure 1 shows that the C=N stretching frequency for Cu(II) complexes **8a-8e** is shifted to lower region by 15-17 cm^{-1} as compared to their respective ligands**.** This observation confirmed the formation of new Cu-N bond, where the non-bonding electron on N atom is coordinated to the Cu(II) metal ion and led to the reduce in C=N bond order [1-8]. Besides, the disappearance of the O-H band of free ligands in the Cu(II) complexes indicates that the OH group is deprotonated and then it is coordinated to Cu(II) metal ion to form Cu-O bond [1-8]. This observation is further supported by the stretching frequency of phenolic C-O in ligands **7a-7e** are shifted from 1296-1297 cm^{-1} to 1314-1315 cm^{-1} upon complexation [4,5,9].

The structures of these Cu(II) complexes were further substantiated by electronic spectra and CHN microanalysis. The CHN microanalysis results show that the percentages of C, H and N in the respective complexes are compatible with its empirical formula in which the ratio of ligand to Cu is 2:1. The electronic spectra of the ligands **7a-7e** and their Cu(II) complexes **8a-8e** were recorded in chloroform and the representative spectra are despite in Figure 2. The UV-visible absorption spectrum of the ligand exhibits a strong absorption band at 349 nm, which is due to the overlapping of π–π* and n–π* transition of the ligand chromophor. Upon formation of Cu(II) complex, this band is red shifted to lower energy region at 390 nm. This shift could be contributed by the donation of lone pair electrons from the nitrogen atoms of the azomethine group to the Cu(II) ion [10]. Another transition band at 311 nm in the higher energy region can be assignable to the *π*–*π** transition of aromatic rings. The expected characteristic of the d–d transitions in the visible region at about 600 nm for the complexes were not detectable even in the concentrated solutions. This observation is due to the forbidden transition of the highly symmetrical Cu(II) complexes.

3. Figures

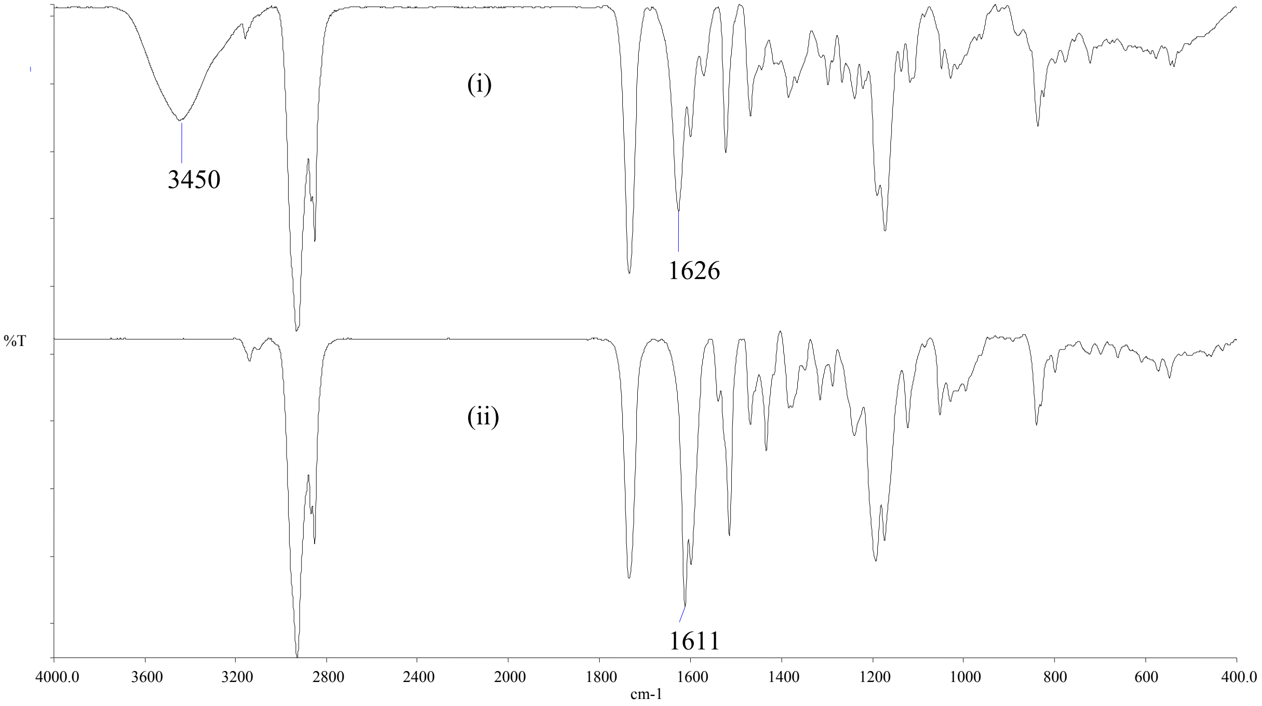

Figure 1: Representative IR spectra of (i) ligand **7c** and (ii) Cu(II) complex **8c.**

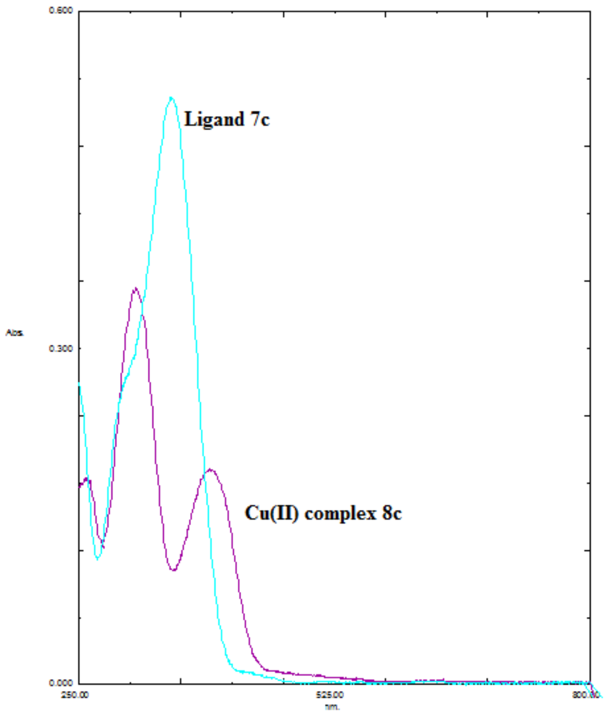

Figure 2: UV-visible spectra for ligand **7c** and Cu(II) complex **8c.**

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