New heterocyclic metallomesogens: Synthesis, mesomorphic and thermal behaviours of Cu(II) complexes with 1,2,3-triazole-based Schiff bases ligands.

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Content:

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

1b16: light yellow, yield 41%. Elemental analysis/% : Found C 75.26, H 10.05, N 7.99; calculated (C₄₄H₇₀N₄O₃), C 75.14, H 10.04, N 7.97. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1259 (C-O ether), 1291 (C-O phenolic), 1600 (C=C), 1627 (C=N), 2919-2849 (C-H alkyl), 3426 (O-H). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.89 (t, 6H, CH₃), 1.30-1.92 (m, 48H, CH₂), 4.01 (t, 2H, OCH₂), 4.37 (t, 2H, OCH₂), 5.26 (s, 2H, OCH₂), 6.48-6.50 (m, 2H, Ar-H), 7.05 (d, 2H, Ar-H), 7.23-7.25 (m, 3H, Ar-H), 7.62 (s, 1H, N-CH), 8.52 (s, 1H, N=CH), 13.8 (s, 1H, Ar-OH).

1c16: yellow, yield 51%. Elemental analysis/% : Found C 75.79, H 10.25, N 7.69; calculated (C₄₆H₇₄N₄O₃), C 75.57, H 10.20, N 7.66. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1260 (C-O ether), 1291 (C-O phenolic), 1600 (C=C), 1627 (C=N), 2919-2849 (C-H alkyl), 3426 (O-H). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.88 (t, 6H, CH₃), 1.30-1.92 (m, 52H, CH₂), 4.01 (t, 2H, OCH₂), 4.37 (t, 2H, OCH₂), 5.26 (s, 2H, OCH₂), 6.48-6.51 (m, 2H, Ar-H), 7.05 (d, 2H, Ar-H), 7.23-7.25 (m, 3H, Ar-H), 7.62 (s, 1H, N-CH), 8.52 (s, 1H, N=CH), 13.8 (s, 1H, Ar-OH).

1d16: yellow, yield 40%. Elemental analysis/% : Found C 76.30, H 10.41, N 7.40; calculated (C₄₈H₇₈N₄O₃), C 75.94, H 10.36, N 7.38. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1259 (C-O ether), 1290 (C-O phenolic), 1599 (C=C), 1628 (C=N), 2919-2849 (C-H alkyl), 3425 (O-H). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.89 (t, 6H, CH₃), 1.31-1.92 (m, 56H, CH₂), 4.01 (t, 2H, OCH₂), 4.37 (t, 2H, OCH₂), 5.26 (s, 2H, OCH₂), 6.48-6.50 (m, 2H, Ar-H), 7.04 (d, 2H, Ar-H), 7.23-7.25 (m, 3H, Ar-H), 7.62 (s, 1H, N-CH), 8.53 (s, 1H, N=CH), 13.8 (s, 1H, Ar-OH).

1e16: yellow, yield 53%. Elemental analysis/% : Found C 76.47, H 10.48, N 7.13; calculated ($C_{50}H_{82}N_4O_3$), C 76.29, H 10.50, N 7.12. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1259 (C-O ether), 1290 (C-O phenolic), 1599 (C=C), 1627 (C=N), 2919-2849 (C-H alkyl), 3425 (O-H). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 0.89 (t, 6H, CH_3), 1.30-1.91 (m, 60H, CH_2), 4.01 (t, 2H, OCH_2), 4.37 (t, 2H, OCH_2), 5.25 (s, 2H, OCH_2), 6.48-6.50 (m, 2H, Ar-H), 7.04 (d, 2H, Ar-H), 7.23-7.25 (m, 3H, Ar-H), 7.63 (s, 1H, N-CH), 8.53 (s, 1H, N=CH), 13.8 (s, 1H, Ar-OH).

1aBr: yellow, yield 61%. Elemental analysis/% : Found C 61.20, H 6.50, N 10.94; calculated ($C_{26}H_{33}\text{BrN}_4\text{O}_2$), C 60.82, H 6.48, N 10.91. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1247 (C-O ether), 1290 (C-O phenolic), 1601 (C=C), 1622 (C=N), 2918-2847 (C-H alkyl), 3424 (O-H). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 0.89 (t, 3H, CH_3), 1.30-1.96 (m, 16H, CH_2), 4.38 (t, 2H, OCH_2), 5.26 (s, 2H, OCH_2), 7.04-7.09 (m, 3H, Ar-H), 7.21-7.30 (m, 3H, Ar-H), 7.63 (s, 1H, N-CH), 8.58 (s, 1H, N=CH), 13.7 (s, 1H, Ar-OH).

1bBr: yellow, yield 64%. Elemental analysis/% : Found C 61.17, H 6.90, N 10.34; calculated ($C_{28}H_{37}\text{BrN}_4\text{O}_2$), C 62.10, H 6.89, N 10.35. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1248 (C-O ether), 1290 (C-O phenolic), 1601 (C=C), 1623 (C=N), 2918-2847 (C-H alkyl), 3424 (O-H). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 0.89 (t, 3H, CH_3), 1.31-1.96 (m, 20H, CH_2), 4.38 (t, 2H, OCH_2), 5.26 (s, 2H, OCH_2), 7.04-7.09 (m, 3H, Ar-H), 7.20-7.30 (m, 3H, Ar-H), 7.63 (s, 1H, N-CH), 8.59 (s, 1H, N=CH), 13.7 (s, 1H, Ar-OH).

1cBr: yellow, yield 41%. Elemental analysis/% : Found C 63.41, H 7.33, N 9.89; calculated ($C_{30}H_{41}\text{BrN}_4\text{O}_2$), C 63.26, H 7.26, N 9.84. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1247 (C-O ether), 1290 (C-O phenolic), 1601 (C=C), 1622 (C=N), 2918-2847 (C-H alkyl), 3424 (O-H). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 0.89 (t, 3H, CH_3), 1.30-1.96 (m, 24H, CH_2), 4.38 (t, 2H, OCH_2), 5.26 (s, 2H, OCH_2), 7.04-7.09 (m, 3H, Ar-H), 7.20-7.30 (m, 3H, Ar-H), 7.62 (s, 1H, N-CH), 8.58 (s, 1H, N=CH), 13.7 (s, 1H, Ar-OH).

1dBr: yellow, yield 47%. Elemental analysis/% : Found C 64.64, H 7.57, N 9.98; calculated ($C_{32}H_{45}\text{BrN}_4\text{O}_2$), C 64.31, H 7.59, N 9.37. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1247 (C-O ether), 1291 (C-O phenolic), 1601 (C=C), 1622 (C=N), 2917-2847 (C-H alkyl), 3425 (O-H). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 0.88 (t, 3H, CH_3), 1.30-1.96 (m, 28H, CH_2), 4.38 (t, 2H, OCH_2), 5.26 (s, 2H, OCH_2), 7.04-7.09 (m, 3H, Ar-H), 7.20-7.30 (m, 3H, Ar-H), 7.63 (s, 1H, N-CH), 8.59 (s, 1H, N=CH), 13.8 (s, 1H, Ar-OH).

1eBr: yellow, yield 49%. Elemental analysis/% : Found C 65.54, H 7.92, N 8.94; calculated ($C_{34}H_{49}BrN_4O_2$), C 65.27, H 7.89, N 8.95. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1247 (C-O ether), 1290 (C-O phenolic), 1601 (C=C), 1622 (C=N), 2918-2847 (C-H alkyl), 3424 (O-H). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 0.89 (t, 3H, CH_3), 1.30-1.96 (m, 16H, CH_2), 4.38 (t, 2H, OCH_2), 5.26 (s, 2H, OCH_2), 7.04-7.09 (m, 3H, Ar-H), 7.21-7.30 (m, 3H, Ar-H), 7.63 (s, 1H, N-CH), 8.57 (s, 1H, N=CH), 13.8 (s, 1H, Ar-OH).

2. *The percentage yields and analytical datas for Cu(II) complexes 2 are summarized as below:*

2b16: brown, yield 81%. Elemental analysis/% : Found C 72.95, H 9.959, N 7.74; calculated ($C_{88}H_{138}CuN_8O_5$), C 72.81, H 9.58, N 7.72. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1241 (C-O ether), 1314 (C-O phenolic), 1597 (C=C), 1615 (C=N), 2922-2851 (C-H alkyl).

2c16: brown, yield 86%. Elemental analysis/% : Found C 73.51, H 9.79, N 7.44; calculated ($C_{92}H_{146}CuN_8O_5$), C 73.29, H 9.76, N 7.43. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1241 (C-O ether), 1315 (C-O phenolic), 1598 (C=C), 1616 (C=N), 2922-2851 (C-H alkyl).

2d16: brown, yield 73%. Elemental analysis/% : Found C 73.90, H 9.91, N 7.19; calculated ($C_{96}H_{154}CuN_8O_5$), C 73.73, H 9.93, N 7.17. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1241 (C-O ether), 1315 (C-O phenolic), 1597 (C=C), 1616 (C=N), 2921-2851 (C-H alkyl).

2e16: brown, yield 86%. Elemental analysis/% : Found C 73.67, H 10.04, N 6.87; calculated ($C_{100}H_{162}CuN_8O_6$), C 73.42, H 9.98, N 6.85. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1242 (C-O ether), 1315 (C-O phenolic), 1597 (C=C), 1615 (C=N), 2922-2851 (C-H alkyl).

2aBr: brown, yield 90%. Elemental analysis/% : Found C 57.66, H 5.94, N 10.28; calculated ($C_{52}H_{64}Br_2CuN_8O_4$), C 57.38, H 5.93, N 10.29. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1245 (C-O ether), 1297 (C-O phenolic), 1593 (C=C), 1613 (C=N), 2922-2850 (C-H alkyl).

2bBr: brown, yield 93%. Elemental analysis/% : Found C 59.07, H 6.37, N 9.80; calculated ($C_{56}H_{72}Br_2CuN_8O_4$), C 58.76, H 6.34, N 9.79. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1245 (C-O ether), 1298 (C-O phenolic), 1594 (C=C), 1613 (C=N), 2922-2850 (C-H alkyl).

2cBr: brown, yield 90%. Elemental analysis/% : Found C 60.36, H 6.79, N 9.35; calculated ($C_{60}H_{80}Br_2CuN_8O_4$), C 60.02, H 6.72, N 9.33. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1245 (C-O ether), 1298 (C-O phenolic), 1593 (C=C), 1613 (C=N), 2921-2850 (C-H alkyl).

2dBr: brown, yield 83%. Elemental analysis/% : Found C 61.27, H 7.04, N 8.95; calculated ($C_{64}H_{88}Br_2CuN_8O_4$), C 61.16, H 7.06, N 8.92. IR (KBr) ν_{max}/cm^{-1} : 1245 (C-O ether), 1297 (C-O phenolic), 1593 (C=C), 1612 (C=N), 2922-2850 (C-H alkyl).

2eBr: brown, yield 87%. Elemental analysis/% : Found C 62.44, H 7.42, N 8.57; calculated ($C_{68}H_{96}Br_2CuN_8O_4$), C 62.21, H 7.37, N 8.53. IR (KBr) ν_{max}/cm^{-1} : 1245 (C-O ether), 1297 (C-O phenolic), 1593 (C=C), 1613 (C=N), 2921-2850 (C-H alkyl).

3. *The percentage yields and analytical datas for ligands 3 are summarized as below:*

3bCl: yellow, yield 45%. Elemental analysis/% : Found C 66.95, H 7.57, N 11.30; calculated ($C_{28}H_{37}ClN_4O_2$), C 67.66, H 7.50, N 11.27. IR (KBr) ν_{max}/cm^{-1} : 1247 (C-O ether), 1282 (C-O phenolic), 1571 (C=C), 1625 (C=N), 2915-2847 (C-H alkyl), 3443 (O-H). 1H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.86 (t, 3H, CH_3), 1.33-1.93 (m, 20H, CH_2), 4.39 (t, 2H, OCH_2), 5.26 (s, 2H, OCH_2), 6.59-6.62 (m, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 7.31 (d, 1H, Ar-H), 7.35 (d, 2H, Ar-H), 7.69 (s, 1H, N-CH), 8.52 (s, 1H, N=CH), 13.51 (s, 1H, Ar-OH).

3cCl: yellow, yield 39%. Elemental analysis/% : Found C 66.73, H 7.85, N 10.66; calculated ($C_{30}H_{41}ClN_4O_2$), C 68.62, H 7.87, N 10.67. IR (KBr) ν_{max}/cm^{-1} : 1246 (C-O ether), 1283 (C-O phenolic), 1571 (C=C), 1625 (C=N), 2916-2848 (C-H alkyl), 3441 (O-H). 1H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.87 (t, 3H, CH_3), 1.34-1.94 (m, 24H, CH_2), 4.39 (t, 2H, OCH_2), 5.26 (s, 2H, OCH_2), 6.59-6.62 (m, 2H, Ar-H), 7.22 (d, 2H, Ar-H), 7.30 (d, 1H, Ar-H), 7.35 (d, 2H, Ar-H), 7.69 (s, 1H, N-CH), 8.52 (s, 1H, N=CH), 13.50 (s, 1H, Ar-OH).

3dCl: yellow, yield 47%. Elemental analysis/% : Found C 69.82, H 8.27, N 10.15; calculated ($C_{32}H_{45}ClN_4O_2$), C 69.48, H 8.20, N 10.13. IR (KBr) ν_{max}/cm^{-1} : 1246 (C-O ether), 1283 (C-O phenolic), 1571 (C=C), 1625 (C=N), 2915-2847 (C-H alkyl), 3441 (O-H). 1H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.86 (t, 3H, CH_3), 1.34-1.94 (m, 28H, CH_2), 4.39 (t, 2H, OCH_2), 5.26 (s, 2H, OCH_2), 6.58-6.61 (m, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 7.29 (d, 1H, Ar-H), 7.35 (d, 2H, Ar-H), 7.69 (s, 1H, N-CH), 8.52 (s, 1H, N=CH), 13.50 (s, 1H, Ar-OH).

3eCl: yellow, yield 41%. Elemental analysis/% : Found C 70.44, H 8.51, N 9.67; calculated ($C_{34}H_{49}ClN_4O_2$), C 70.26, H 8.50, N 9.64. IR (KBr) ν_{max}/cm^{-1} : 1247 (C-O ether), 1283 (C-O phenolic), 1571 (C=C), 1626 (C=N), 2916-2848 (C-H alkyl), 3442 (O-H). 1H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.87 (t, 3H, CH_3), 1.34-1.94 (m, 32H, CH_2), 4.39 (t, 2H, OCH_2), 5.26 (s, 2H,

OCH₂), 6.59-6.62 (m, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 7.30 (d, 1H, Ar-H), 7.35 (d, 2H, Ar-H), 7.70 (s, 1H, N-CH), 8.53 (s, 1H, N=CH), 13.51 (s, 1H, Ar-OH).

3aBr: yellow, yield 44%. Elemental analysis/% : Found C 61.15, H 6.52, N 10.93; calculated (C₂₆H₃₃BrN₄O₂), C 60.82, H 6.48, N 10.91. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1571 (C=C), 1626 (C=N), 2916-2848 (C-H alkyl), 3442 (O-H). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.88 (t, 3H, CH₃), 1.32-1.93 (m, 16H, CH₂), 4.39 (t, 2H, OCH₂), 5.24 (s, 2H, OCH₂), 6.69-6.62 (m, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 7.30 (d, 1H, Ar-H), 7.54 (d, 2H, Ar-H), 7.67 (s, 1H, N-CH), 8.53 (s, 1H, N=CH), 13.49 (s, 1H, Ar-OH).

3bBr: yellow, yield 49%. Elemental analysis/% : Found C 62.19, H 6.91, N 10.37; calculated (C₂₈H₃₇BrN₄O₂), C 62.10, H 6.89, N 10.35. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1571 (C=C), 1626 (C=N), 2915-2847 (C-H alkyl), 3441 (O-H). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.87 (t, 3H, CH₃), 1.31-1.93 (m, 20H, CH₂), 4.39 (t, 2H, OCH₂), 5.25 (s, 2H, OCH₂), 6.69-6.62 (m, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 7.30 (d, 1H, Ar-H), 7.54 (d, 2H, Ar-H), 7.67 (s, 1H, N-CH), 8.53 (s, 1H, N=CH), 13.50 (s, 1H, Ar-OH).

3cBr: yellow, yield 44%. Elemental analysis/% : Found C 63.61, H 7.29, N 9.85; calculated (C₃₀H₄₁BrN₄O₂), C 63.26, H 7.26, N 9.84. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1571 (C=C), 1627 (C=N), 2916-2848 (C-H alkyl), 3442 (O-H). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.88 (t, 3H, CH₃), 1.32-1.93 (m, 24H, CH₂), 4.39 (t, 2H, OCH₂), 5.25 (s, 2H, OCH₂), 6.69-6.62 (m, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 7.31 (d, 1H, Ar-H), 7.54 (d, 2H, Ar-H), 7.67 (s, 1H, N-CH), 8.53 (s, 1H, N=CH), 13.49 (s, 1H, Ar-OH).

3dBr: yellow, yield 50%. Elemental analysis/% : Found C 64.66, H 7.60, N 9.36; calculated (C₃₂H₄₅BrN₄O₂), C 64.31, H 7.59, N 9.37. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1571 (C=C), 1626 (C=N), 2916-2848 (C-H alkyl), 3441 (O-H). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.88 (t, 3H, CH₃), 1.32-1.93 (m, 28H, CH₂), 4.38 (t, 2H, OCH₂), 5.24 (s, 2H, OCH₂), 6.69-6.62 (m, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 7.30 (d, 1H, Ar-H), 7.54 (d, 2H, Ar-H), 7.67 (s, 1H, N-CH), 8.54 (s, 1H, N=CH), 13.49 (s, 1H, Ar-OH).

3eBr: yellow, yield 52%. Elemental analysis/% : Found C 65.36, H 7.93, N 8.93; calculated (C₃₄H₄₉BrN₄O₂), C 65.27, H 7.89, N 8.95. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1246 (C-O ether), 1282 (C-O phenolic), 1571 (C=C), 1627 (C=N), 2916-2848 (C-H alkyl), 3442 (O-H). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.88 (t, 3H, CH₃), 1.32-1.93 (m, 32H, CH₂), 4.38 (t, 2H, OCH₂), 5.23 (s, 2H,

OCH₂), 6.69-6.62 (m, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 7.30 (d, 1H, Ar-H), 7.54 (d, 2H, Ar-H), 7.67 (s, 1H, N-CH), 8.54 (s, 1H, N=CH), 13.50 (s, 1H, Ar-OH).

3aI: yellow, yield 46%. Elemental analysis/% : Found C 55.86, H 5.92, N 10.03; calculated (C₂₆H₃₃IN₄O₂), C 55.72, H 5.93, N 10.00. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1570 (C=C), 1626 (C=N), 2916-2848 (C-H alkyl), 3442 (O-H). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.80 (t, 3H, CH₃), 1.21-1.86 (m, 16H, CH₂), 4.29 (t, 2H, OCH₂), 5.18 (s, 2H, OCH₂), 6.50-6.59 (m, 2H, Ar-H), 6.95 (d, 2H, Ar-H), 7.23 (d, 1H, Ar-H), 7.60 (s, 1H, N-CH), 7.65 (d, 2H, Ar-H), 8.43 (s, 1H, N=CH), 13.38 (s, 1H, Ar-OH).

3bI: yellow, yield 48%. Elemental analysis/% : Found C 57.16, H 6.36, N 9.53; calculated (C₂₈H₃₇IN₄O₂), C 57.14, H 6.34, N 9.52. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1570 (C=C), 1626 (C=N), 2917-2848 (C-H alkyl), 3441 (O-H). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.80 (t, 3H, CH₃), 1.21-1.86 (m, 20H, CH₂), 4.28 (t, 2H, OCH₂), 5.18 (s, 2H, OCH₂), 6.51-6.60 (m, 2H, Ar-H), 6.95 (d, 2H, Ar-H), 7.23 (d, 1H, Ar-H), 7.60 (s, 1H, N-CH), 7.65 (d, 2H, Ar-H), 8.42 (s, 1H, N=CH), 13.38 (s, 1H, Ar-OH).

3cI: yellow, yield 53%. Elemental analysis/% : Found C 55.61, H 6.68, N 9.10; calculated (C₃₀H₄₁IN₄O₂), C 58.44, H 6.70, N 9.09. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1570 (C=C), 1627 (C=N), 2916-2848 (C-H alkyl), 3441 (O-H). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.80 (t, 3H, CH₃), 1.21-1.86 (m, 24H, CH₂), 4.28 (t, 2H, OCH₂), 5.18 (s, 2H, OCH₂), 6.50-6.59 (m, 2H, Ar-H), 6.95 (d, 2H, Ar-H), 7.23 (d, 1H, Ar-H), 7.61 (s, 1H, N-CH), 7.65 (d, 2H, Ar-H), 8.43 (s, 1H, N=CH), 13.38 (s, 1H, Ar-OH).

3dI: yellow, yield 51%. Elemental analysis/% : Found C 60.01, H 7.11, N 8.67; calculated (C₃₂H₄₅IN₄O₂), C 59.62, H 7.04, N 8.69. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1570 (C=C), 1626 (C=N), 2916-2848 (C-H alkyl), 3441 (O-H). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.80 (t, 3H, CH₃), 1.21-1.86 (m, 28H, CH₂), 4.29 (t, 2H, OCH₂), 5.18 (s, 2H, OCH₂), 6.50-6.59 (m, 2H, Ar-H), 6.95 (d, 2H, Ar-H), 7.22 (d, 1H, Ar-H), 7.60 (s, 1H, N-CH), 7.65 (d, 2H, Ar-H), 8.44 (s, 1H, N=CH), 13.39 (s, 1H, Ar-OH).

3eI: yellow, yield 46%. Elemental analysis/% : Found C 61.15, H 7.39, N 8.34; calculated (C₃₄H₄₉IN₄O₂), C 60.71, H 7.34, N 8.33. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1247 (C-O ether), 1283 (C-O phenolic), 1570 (C=C), 1625 (C=N), 2917-2849 (C-H alkyl), 3442 (O-H). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.81 (t, 3H, CH₃), 1.22-1.87 (m, 32H, CH₂), 4.29 (t, 2H, OCH₂), 5.18 (s, 2H,

OCH₂), 6.50-6.59 (m, 2H, Ar-H), 6.96 (d, 2H, Ar-H), 7.23 (d, 1H, Ar-H), 7.61 (s, 1H, N-CH), 7.65 (d, 2H, Ar-H), 8.43 (s, 1H, N=CH), 13.38 (s, 1H, Ar-OH).

4. *The percentage yields and analytical datas for Cu(II) complexes 4 are summarized as below:*

4bCl: brown, yield 81%. Elemental analysis/% : Found C 64.00, H 6.89, N 10.62; calculated (C₅₆H₇₂Cl₂CuN₈O₄), C 63.71, H 6.87, N 10.61. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1251 (C-O ether), 1324 (C-O phenolic), 1590 (C=C), 1601 (C=N), 2917-2850 (C-H alkyl).

4cCl: brown, yield 87%. Elemental analysis/% : Found C 64.99, H 7.31, N 10.10; calculated (C₆₀H₈₀Cl₂CuN₈O₄), C 64.82, H 7.25, N 10.08. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1250 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1600 (C=N), 2917-2850 (C-H alkyl).

4dCl: brown, yield 89%. Elemental analysis/% : Found C 69.13, H 7.61, N 9.60; calculated (C₆₄H₈₈Cl₂CuN₈O₄), C 65.82, H 7.59, N 9.59. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1250 (C-O ether), 1324 (C-O phenolic), 1589 (C=C), 1601 (C=N), 2917-2850 (C-H alkyl).

4eCl: brown, yield 73%. Elemental analysis/% : Found C 66.92, H 7.90, N 9.17; calculated (C₆₈H₉₆Cl₂CuN₈O₄), C 66.73, H 7.91, N 9.15. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1250 (C-O ether), 1324 (C-O phenolic), 1589 (C=C), 1600 (C=N), 2917-2850 (C-H alkyl).

4aBr: brown, yield 89%. Elemental analysis/% : Found C 57.62, H 5.94, N 10.31; calculated (C₅₂H₆₄Br₂CuN₈O₄), C 57.38, H 5.93, N 10.29. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1251 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1601 (C=N), 2917-2850 (C-H alkyl).

4bBr: brown, yield 89%. Elemental analysis/% : Found C 58.88, H 6.36, N 9.81; calculated (C₅₆H₇₂Br₂CuN₈O₄), C 58.76, H 6.34, N 9.79. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1250 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1601 (C=N), 2917-2850 (C-H alkyl).

4cBr: brown, yield 78%. Elemental analysis/% : Found C 60.12, H 6.79, N 9.35; calculated (C₆₀H₈₀Br₂CuN₈O₄), C 60.02, H 6.72, N 9.33. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1251 (C-O ether), 1322 (C-O phenolic), 1589 (C=C), 1601 (C=N), 2916-2849 (C-H alkyl).

4dBr: brown, yield 84%. Elemental analysis/% : Found C 61.49, H 7.04, N 8.93; calculated (C₆₄H₈₈Br₂CuN₈O₄), C 61.16, H 7.06, N 8.92. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1251 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1600 (C=N), 2917-2850 (C-H alkyl).

4eBr: brown, yield 89%. Elemental analysis/% : Found C 62.29, H 7.38, N 8.54; calculated (C₆₈H₉₆Br₂CuN₈O₄), C 62.21, H 7.37, N 8.53. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1251 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1601 (C=N), 2917-2850 (C-H alkyl).

4aI: brown, yield 83%. Elemental analysis/% : Found C 53.20, H 5.44, N 9.49; calculated ($C_{52}H_{64}I_2CuN_8O_4$), C 52.82, H 5.46, N 9.48. IR (KBr) ν_{max}/cm^{-1} : 1250 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1601 (C=N), 2917-2850 (C-H alkyl).

4bI: brown, yield 91%. Elemental analysis/% : Found C 54.55, H 5.91, N 9.09; calculated ($C_{56}H_{72}I_2CuN_8O_4$), C 54.30, H 5.86, N 9.05. IR (KBr) ν_{max}/cm^{-1} : 1250 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1600 (C=N), 2918-2850 (C-H alkyl).

4cI: brown, yield 73%. Elemental analysis/% : Found C 55.94, H 6.24, N 8.67; calculated ($C_{60}H_{80}I_2CuN_8O_4$), C 55.66, H 6.23, N 8.65. IR (KBr) ν_{max}/cm^{-1} : 1251 (C-O ether), 1323 (C-O phenolic), 1590 (C=C), 1601 (C=N), 2917-2850 (C-H alkyl).

4dI: brown, yield 86%. Elemental analysis/% : Found C 57.61, H 6.64, N 8.33; calculated ($C_{64}H_{88}I_2CuN_8O_4$), C 56.91, H 6.57, N 8.30. IR (KBr) ν_{max}/cm^{-1} : 1250 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1601 (C=N), 2917-2850 (C-H alkyl).

4eI: brown, yield 77%. Elemental analysis/% : Found C 58.25, H 6.86, N 7.95; calculated ($C_{68}H_{96}I_2CuN_8O_4$), C 58.05, H 6.88, N 7.96. IR (KBr) ν_{max}/cm^{-1} : 1250 (C-O ether), 1323 (C-O phenolic), 1589 (C=C), 1600 (C=N), 2916-2849 (C-H alkyl).

5. Synthesis and characterization

The nonlinear liquid crystalline bidentate Schiff bases **1** and their corresponding Cu(II) complexes **2** were synthesized by conventional method (Scheme 1). The intermediate compound with terminal alkyne group was prepared by the alkylation of 4-acetamidophenol and propargyl bromide in the presence of potassium carbonate as the base. This compound subsequently underwent Cu(I) catalyzed “click reaction” with 1-azidoalkane ($C_nH_{2n+1}N_3$; $n=10,12,14,16$ and 18) to yield the 1,2,3-triazole ring intermediate. The amide functional group of this intermediate was hydrolyzed to amine group by concentrated hydrochloric acid and followed by the condensation reaction with 4-(hexadecanoyloxy)-2-hydroxybenzaldehyde or 4-bromosalicylaldehyde to give the desired Schiff bases. The Cu(II) complexes were synthesized through the reaction between the 1,2,3-triazole-based Schiff bases and Cu(II) acetate dihydrate in ethanol. The preparation of Cu(II) complexes **4** and their ligands **3** (Scheme 2) were carried out using the same reagent and method as described in Scheme 1, but only with the use of different reagent for the synthesis of intermediate with terminal alkynes group. In order to avoid the alkylation of *ortho*-hydroxyl group in 2,4-dihydroxybenzaldehyde, a weaker base potassium

bicarbonate was used instead of potassium carbonate. The chemical structure of the targeted ligands and their corresponding Cu(II) complexes were confirmed by FT-IR, ^1H -NMR, UV-visible spectroscopic techniques and elemental analysis.

The comparison between the IR spectra of the uncoordinated ligands and their corresponding complexes showed that the C=N stretching frequency for Cu(II) complexes **2a16-2e16** and **2aBr-2eBr** is shifted to lower region by 11-13 cm^{-1} and 9-11 cm^{-1} as compared to their respective ligands. Besides, a larger shift was observed in Cu(II) complexes **4**, where the values are shifted by 24-25 cm^{-1} as compared to ligands **3**. This observation can be due to the coordination of N atom to the Cu(II) leading to the formation of new Cu-N bond [1,2,3-8]. The stretching frequency of phenolic C-O is shifted to higher frequency upon complexation. The values changed from 1290-1291 cm^{-1} (**1a16-1e16**) to 1314-1315 cm^{-1} (**2a16-2e16**), 1290-1291 cm^{-1} (**1aBr-1eBr**) to 1297-1298 cm^{-1} (**2aBr-2eBr**) and 1282-1283 cm^{-1} for ligands **3** to 1322-1324 cm^{-1} for their corresponding complexes **4**. These observations indicate the formation of new Cu-O bond through the deprotonation of OH group and the coordination of O^- ion to the Cu(II) ion [4,5,9,10]. Furthermore, the absence of the O-H band of free ligands in the Cu(II) metal complexes also supported the formation of new Cu-O bond [1,2,3-8]. The representative IR spectra are shown in Figure 1.

In order to further substantiate the structures of these Cu(II) complexes, the percentage of carbon, hydrogen and nitrogen composition for all the complexes were determined via the CHN microanalysis. The results show that the percentages of C, H and N in the respective complexes are in agreement with its empirical formula in which the ratio of ligand to Cu is 2:1. The ^1H NMR spectra for all the Cu(II) complexes displayed only the broad signals from the alkyl and alkoxy flexible chain. All the proton signals close to the paramagnetic Cu(II) ion center are not detectable [3,6].

The electronic spectra for all the ligands and Cu(II) complexes exhibit almost the same characteristics. As such, the spectra for ligand **1d16** and Cu(II) complex **2d16** (Figure 2) have been chosen as representative for detailed discussion. The UV-visible absorption spectra of the ligands and their complexes are represented by two main groups of absorption bands. The electronic spectra for ligand **1d16** consist of an intense band at 338 nm which can be related to $n-\pi^*$ transition of the azomethine chromophore and non-bonding valence shell electron pairs from the ligands. Another intra-ligand transition band at 288 nm in the higher energy region is

assignable to the $\pi-\pi^*$ transition of benzene rings. Upon complexation with Cu(II) ion, these bands are red shifted to the longer wavelength at 383 nm and 308 nm (Figure 2). The expected characteristic of the d-d transitions in the visible region at 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.

6. Figures

Figure 1: Representative IR spectra of (i) ligand **1cBr** and (ii) Cu(II) complex **2cBr**

Figure 2: UV-visible spectra for ligand **1c16** and Cu(II) complex **2d16**.

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Scheme 2: Synthetic routes toward formation of **3aCl-3eCl**, **3aBr-3eBr**, **3aI-3eI** and their corresponding Cu(II) complexes **4aCl-4eCl**, **4aBr-4eBr** and **4aI-4eI**.