Supporting Information

A facile iodide-controlled fluorescent switch based on the interconversion between two- and three-coordinate copper(I) complexes

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Contents

General information All manipulations were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. Acetonitrile and dichloromethane were distilled from CaH_2 before use. Diethyl ether was dried by distillation from sodium benzophenone prior to use. All reagents were obtained from commercial sources and used as received without further purification. ^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature using Bruker Avance 400 and 500 MHz spectrometers. IR data were obtained as Nujol mulls on a Bruker Alpha-T FTIR spectrometer. Mass spectra were acquired on a Finnigan TSQ 700 spectrometer. Elemental analyses were performed on a HERAEUS CHN-O-S-Rapid elemental analyzer by Instruments Center, National Chung Hsin University, and a HERAEUS VarioEL-Ⅲ Analyzer by Advanced Instrument Center, National Taiwan University. Fluorescence emission spectra were recorded at ambient on a Hitachi F-7000 fluorescence spectrophotometer. Ultraviolet-Visible spectra were recorded on a Hewlett Packard 8453 Ultraviolet/Visible Absorption Spectrometer.

1. **Synthesis of** 1,3-bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-2-phenyl-2,3-dihydro-1*H*-perimidine**,** L^{ph}**:**

A 30 ml diethylether solution of 1,8-diaminonaphthalene 1.36g (8.6 mmole) and benzaldehyde1.01g (9.5mmole) was vigorously stirred at room temperature for 13 hours. This solution was filtrated and the solvent was removed under vacuum. A mixture of the residue and 3,5-dimethylpyrazolemethanol 2.17g (17mmole) in acetonitrile (30ml) was stirred at room temperature for 24 hours. The brown precipitates formed was filtered off and extracted with n-hexane to give 2.50g (63%) of L^{ph}. ^{1}H NMR (CD_2Cl_2, 500.13 MHz): δ 7.38- 7.35 (m, 2H), 7.29- 7.27 (m, 4H), 7.06- 6.99 (m, 4H), 5.83 (s, 2H, pyrazole-CH), 5.74 (s, 1H, CH), 5.74 (d, 2H, $^{2}J_{HH}$ = 14.2 Hz), 5.42 (d, 2H, $^{2}J_{HH}$ = 14.2 Hz), 2.24 (s, 6H, CH_3), 2.17 (s, 6H, CH_3) ppm. ^{13}C

NMR (CD_2Cl_2, 125.77 MHz): δ 148.39, 140.62, 140.34, 140.18, 135.13, 128.59, 128.08, 127.54, 127.51, 120.17, 118.26, 110.13, 106.69, 72.36, 65.53, 13.88, 11.46 ppm. Positive ESI-MS: 485.4 ($M+Na^+$, 100%). Anal. Calcd for $C_{29}H_{30}N_6$ (L^{Ph}): C, 75.30; H, 6.54; N, 18.17. Found: C, 75.37; H, 6.60; N, 18.16.

2. **Synthesis of Complex** $[Cu(L^{ph})](ClO_4)$ **1**·(ClO_4):

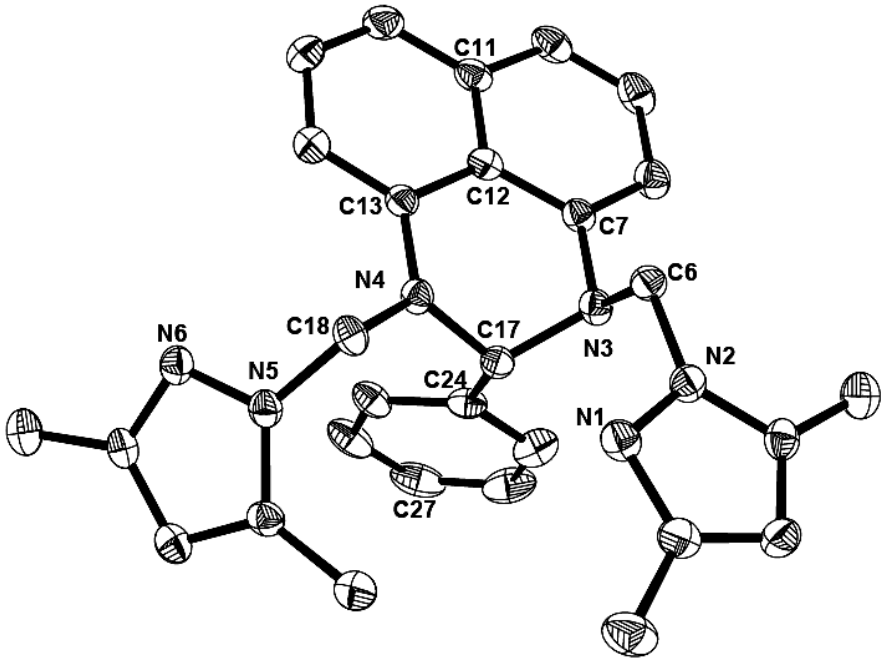
Method 1: A 7ml CH_2Cl_2 solution of $[Cu(MeCN)_4]ClO_4$ (0.15 g, 0.46mmol) and L^{Ph} (0.21g, 0.46mmol) was stirred at room temperature for 2 hr under N_2. After the addition of 10ml Et_2O, the white precipitates formed was filtered off and washed by 5ml CH_2Cl_2 and 10ml Et_2O for two times. The resulting white solid was dried under vacuum to yield 0.21g (74 %) of **1**·(ClO_4). Single crystals of **1**·(ClO_4) were obtained after cooling the saturated, hot CH_3CN solution to room temperature. IR(Nujol): ν_{ClO_4}- 1093, 622 cm^{-1}. ^1H NMR (CD_2Cl_2, 500.13 MHz): δ 7.31- 7.16 (m, 9H, naphthalene and phenyl CH), 6.94 (s, 1H, CH), 6.47- 6.45 (m,2H, phenyl CH), 6.07 (s, 2H, pyrazole-CH), 5.96 (s, 4H, CH_2), 2.56 (s, 6H, CH_3), 2.35 (s, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 125.77 MHz): δ 151.83, 143.32, 140.03, 137.26, 135.48, 129.40, 129.07, 127.60, 126.89, 120.60, 116.97, 108.04, 106.21, 79.01, 63.80, 15.61, 12.05 ppm. Positive ESI-MS: 525.3 (M^+, 100%). Anal. Calcd for $C_{29}H_{30}ClCuN_6O_4$ (**1**·(ClO_4) ·CH_2Cl_2): C, 55.68; H, 4.83; N, 13.43. Found: C, 55.59; H, 4.63; N, 13.89.

Method 2: $AgClO_4$ (10.9mg, 0.05mmol) was added to an acetonitrile solution (10 mL) of complex **2** (34.6 mg, 0.05mmol). The mixture was stirred for at room temperature for 5 min and the yellow precipitate was formed immediately. The resulting solution was filtered by celite and the filtrate was dried under vacuum. The isolated complex **1**·(ClO_4) was determined and confirmed by IR and H NMR and gave a yield higher than 96%.

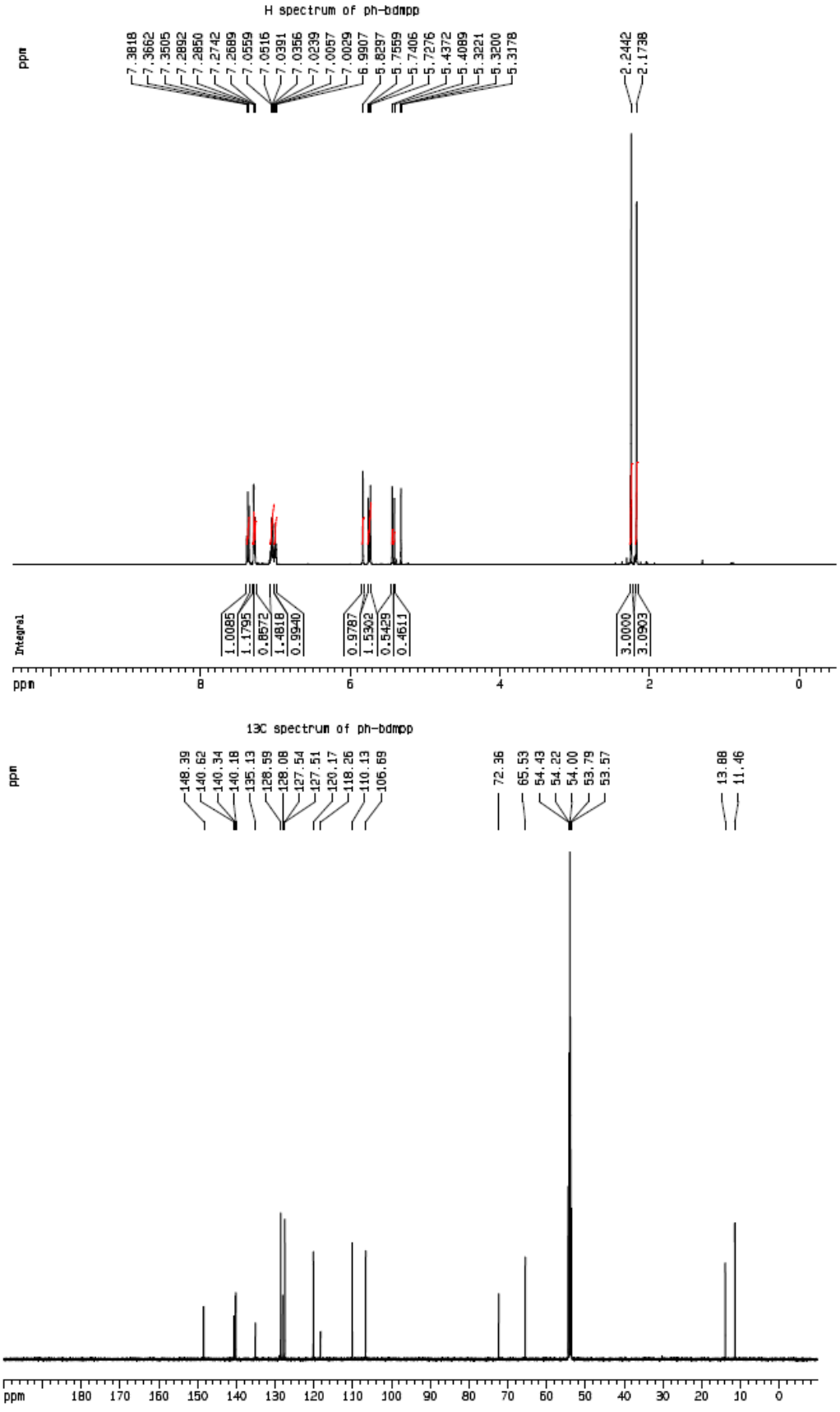
3. **Synthesis of Complex** [Cu(L^{ph})I] **2**:

Method 1: The reaction of CuI (60mg, 0.314 mmol) and L^{Ph} (146.3 mg, 0.316 mmol) was carried out following a procedure similar to that described for the synthesis of complex **1**·(ClO_4) in a 85% yield (173.6 mg). Single crystals were grown from CH_2Cl_2/Et_2O. ^{1}H NMR (CD_2Cl_2, 500.13 MHz): δ 7.31- 6.64 (m, 9H, naphthalene and phenyl CH), 6.65 (d,2H, phenyl CH), 5.98 (s, 2H, pyrazole-CH), 5.93 (d, 2H, $^2J_{HH}$ = 13.7 Hz, CH_2), 5.78 (d, 2H, $^2J_{HH}$ = 13.6 Hz, CH_2), 2.49 (s, 3H, CH_3), 2.34 (s, 3H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 125.77 MHz): δ 149.64, 141.77, 140.49, 138.72, 135.18, 129.17, 128.72, 127.38, 127.07, 120.53, 117.89, 107.99, 107.33, 76.29, 63.98, 14.99, 12.12 ppm. Positive ESI-MS: 525.2 ([M-I]$^+$, 100%). Anal. Calcd for $C_{30}H_{32}Cl_2CuN_6I$ (**2**): C, 48.83; H, 4.37; N, 11.39. Found: C, 49.10; H, 4.58; N, 11.72.

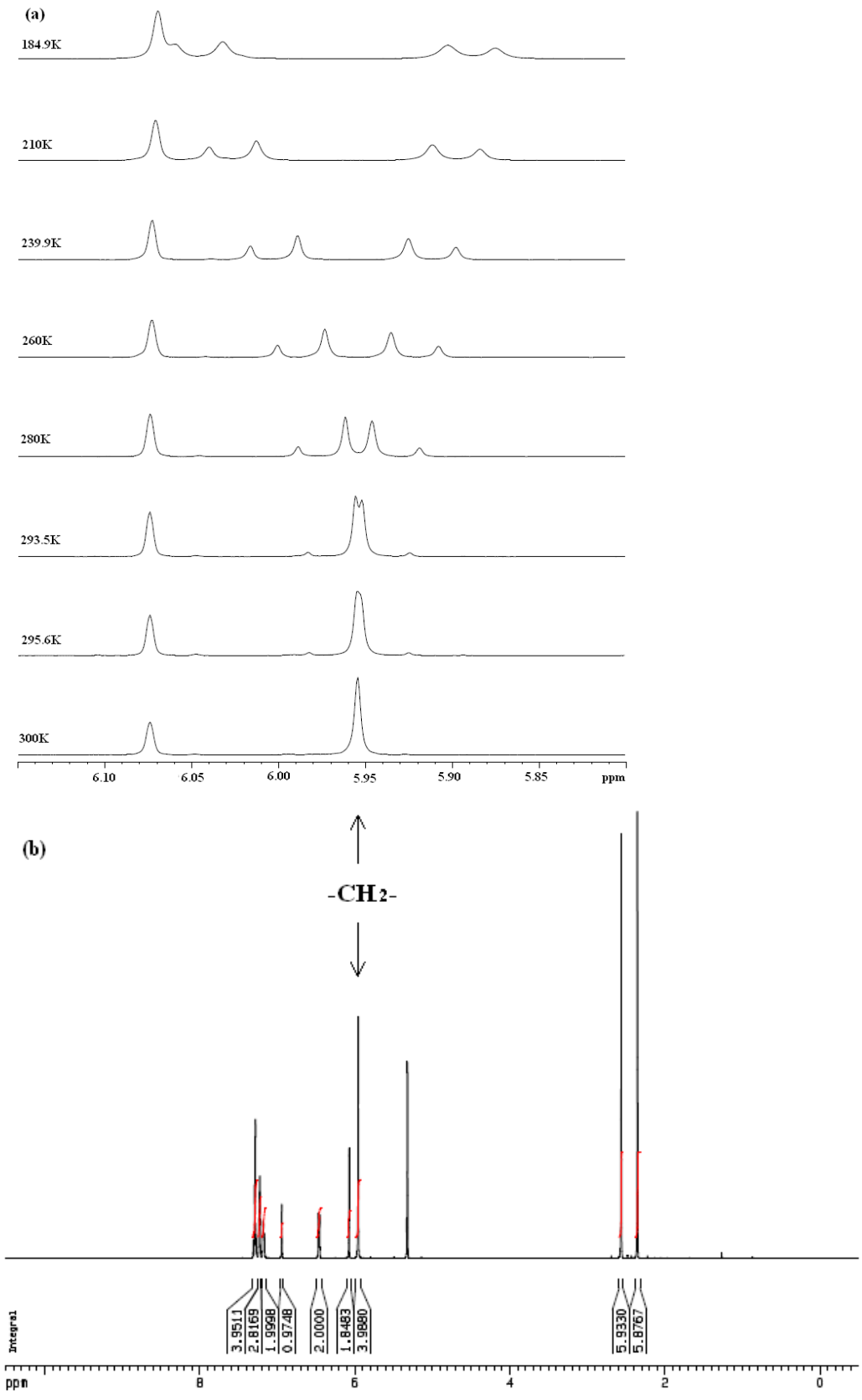
Method 2: To a stirred solution of complex **1**·(ClO_4) (17.3 mg, 0.028mmol) in 10 CH_2Cl_2 was added a solution of n-Bu_4NI (10.2mg, 0.028mmol) in 5ml CH_2Cl_2. After reaction for 30 min at room temperature, the resulting solution was dried under vacuum. The solid was analyzed by ^{1}H NMR in CD_2Cl_2 and the yield of **2** is nearly quantitative. The ^{1}H NMR spectrum of the solid is almost identical with that of complex **2** in addition to the signals of butyl groups. ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ 7.31- 6.66 (m, 9H, naphthalene and phenyl CH), 6.67 (d,2H, phenyl CH), 5.98 (s, 2H, pyrazole-CH), 5.93 (d, 2H, $^2J_{HH}$ = 13.7 Hz), 5.78 (d, 2H, $^2J_{HH}$ = 13.6 Hz), 3.16 (t, 8H, n-Bu CH_2), 2.49 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 1.67- 1.60 (m, 8H, n-Bu CH_2), 1.48- 1.39 (m, 8H, n-Bu CH_2), 1.02 (t, 12H, n-Bu CH_3) ppm.



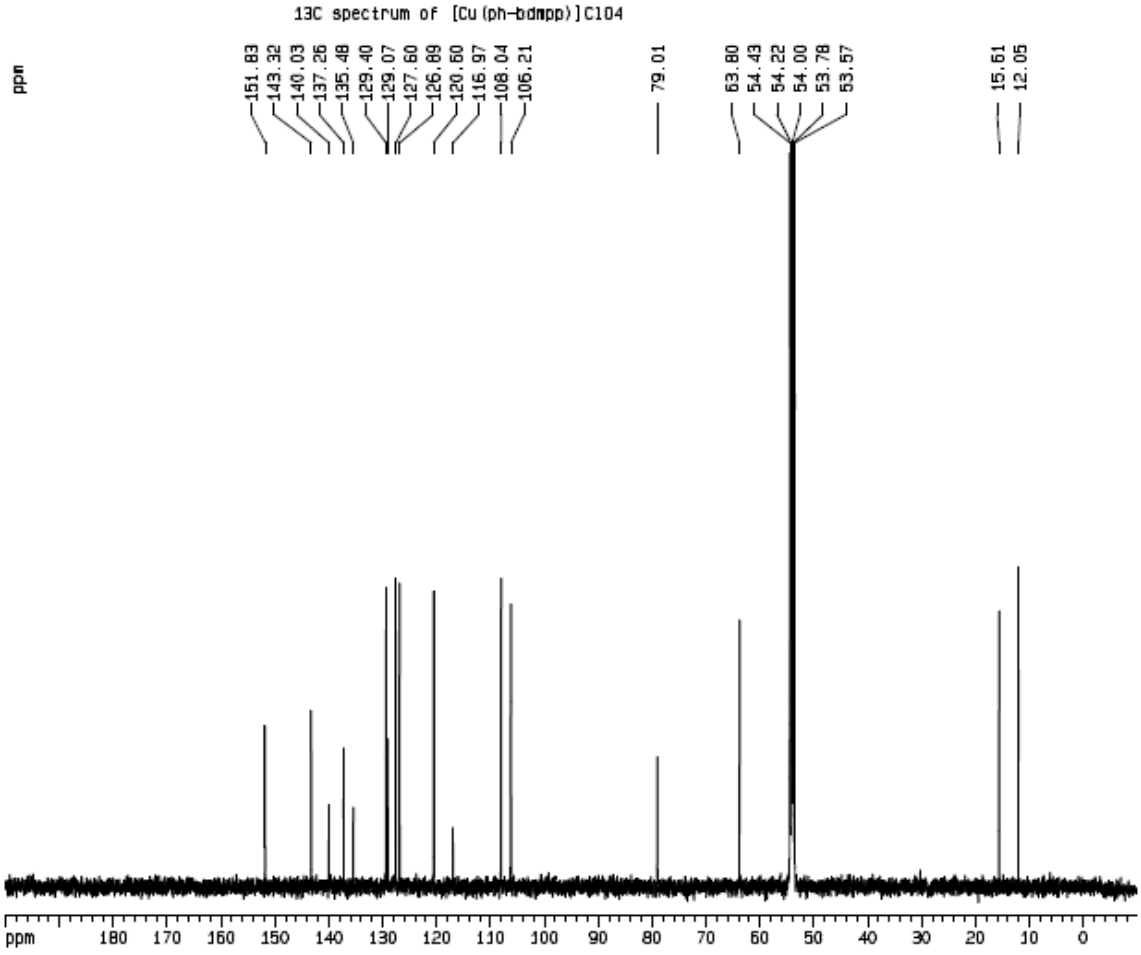
4. Figure S1 Molecular structure of ligand L^{Ph} (hydrogen atoms have been omitted for clarity). Selected bond distances (Å) and bond angles (°): C7–N3 1.445 (4), C7–C12 1.420 (5), C12–C13 1.440 (5), C13–N4 1.393 (4), C17–N3 1.467 (4), C17–N4 1.456 (4), C6–N3 1.479 (4), C18–N4 1.435 (4); C6–N3–C7 110.7 (3), C7–N3–C17 109.8 (3), C6–N3–C17 112.1 (3), C13–N4–C17 116.5 (3), C13–N4–C18 123.3 (3), C17–N4–C18 120.1 (3), N3–C17–N4 111.0 (3).



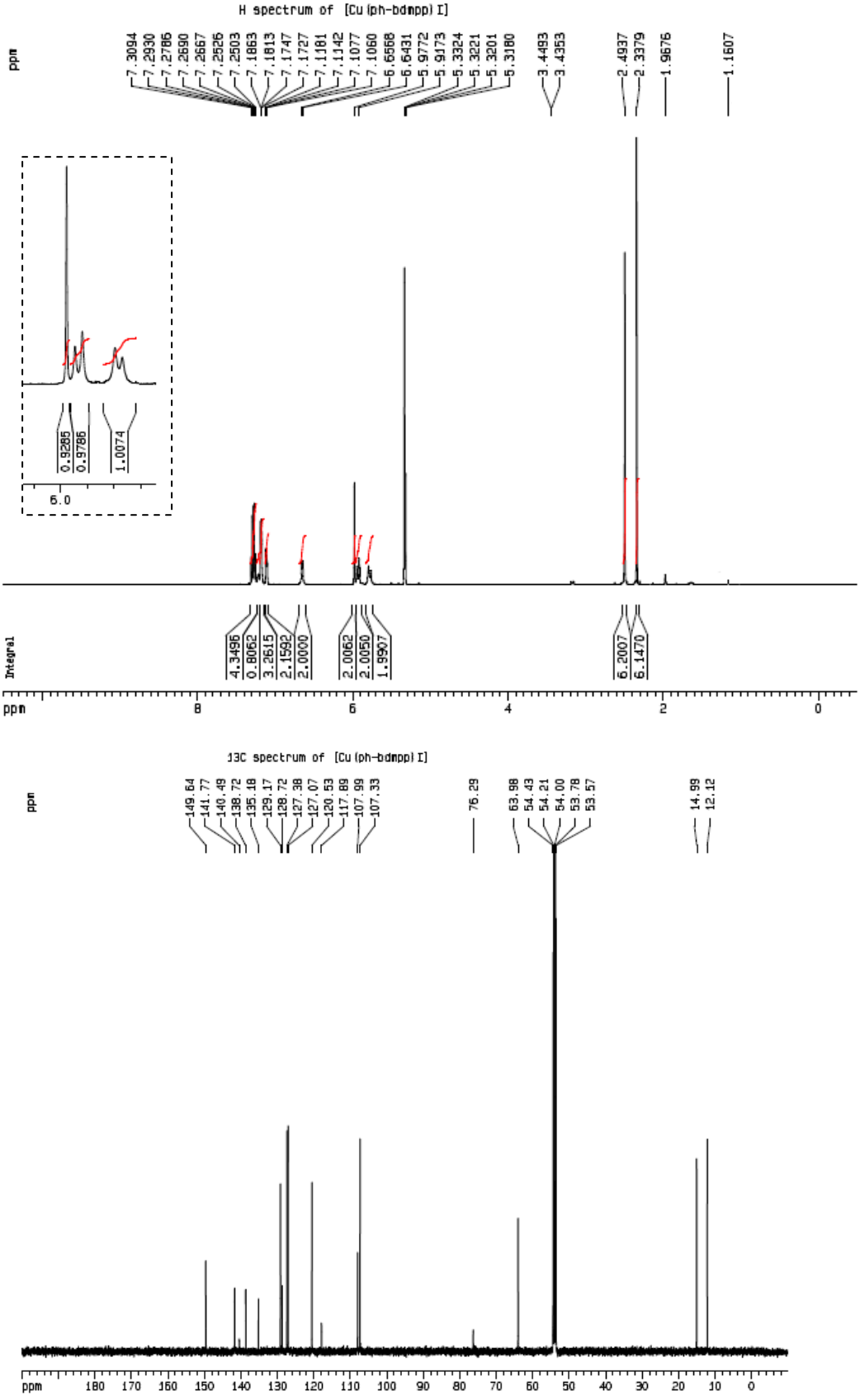
5. Figure S2 ^{1}H & ^{13}C NMR spectra of ligand L^{ph}.



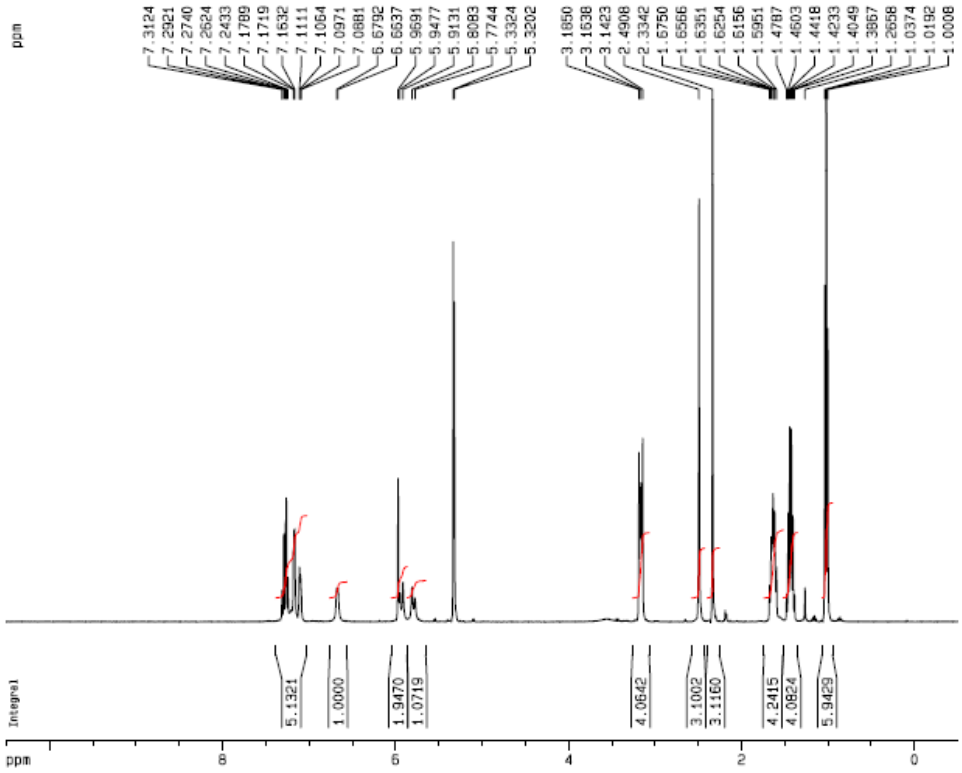
6. Figure S3 Variable temperature ^{1}H NMR spectra of the methylene portion in $\mathbf{1}^{+}$ (a), and ^{1}H NMR spectrum of $\mathbf{1}^{+}$ (b).



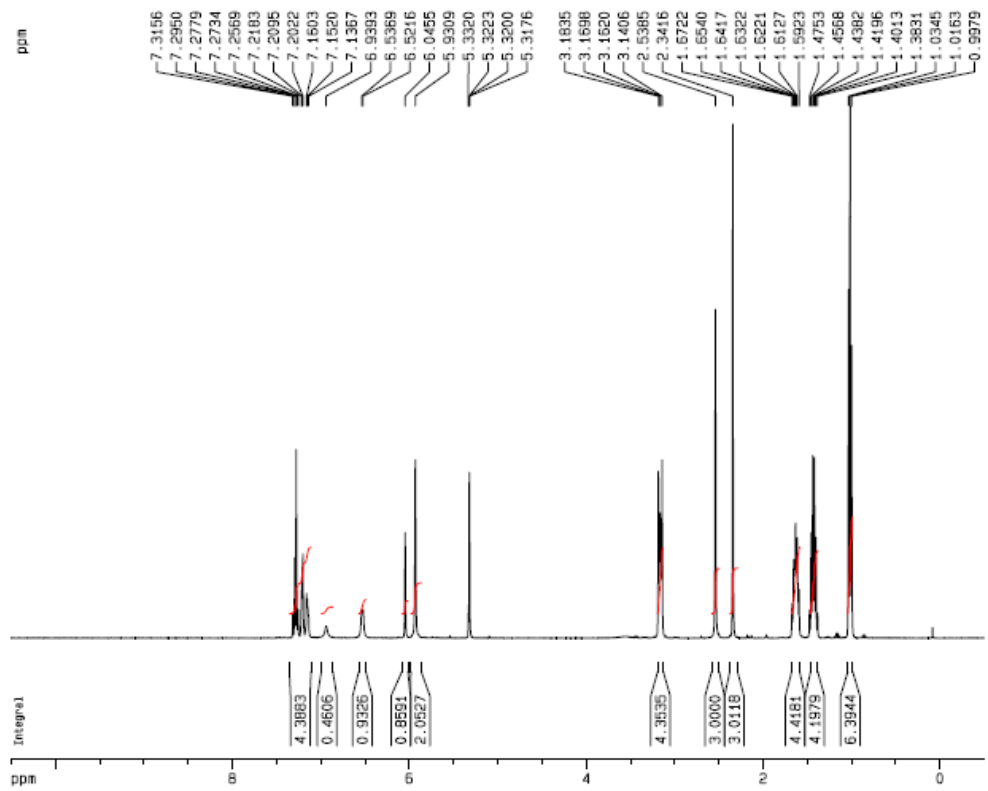
7. Figure S4 ^{13}C NMR spectra of complex **1**·(ClO_4)**.**



8. Figure S5 ^{1}H & ^{13}C NMR spectra of complex **2**.



9. Figure S6 ^{1}H NMR spectrum of the reaction of **1**·(ClO_4) with n-Bu_4I.



10. Figure S7 ^{1}H NMR spectrum of the reaction of **1**·(ClO_4) with n-Bu_4I and Ag(ClO_4).

11. Fluorescence titration experiments

Fluorescence quenching and blank experiments on L^{Ph} by $[Cu(MeCN)_4](ClO_4)$, CuI and n-Bu_4NI were carried out in CH_2Cl_2 with a concentration of $6.8*10^{-5}$ M. $[Cu(MeCN)_4](ClO_4)$, CuI were dissolved in $MeCN/CH_2Cl_2$ mix solvent to improve their solubility.)

EXP I Ligand L^{Ph} vs. $[Cu(MeCN)_4(ClO_4)]$

Exp. No.	equiv. of L^{Ph}	equiv. of $[Cu(MeCN)_4](ClO_4)$
1	1	0
2	1	0.2
3	1	0.4
4	1	0.6
5	1	0.8
6	1	1.0
7	1	1.5
8	1	2

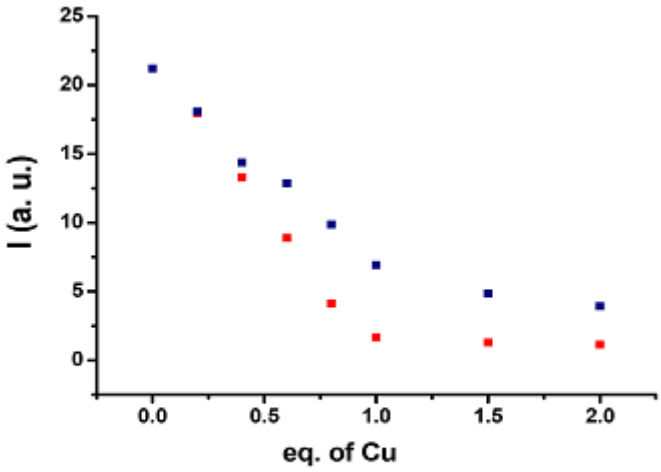


Fig. S8 Titration of L^{Ph} with $[Cu(MeCN)_4](ClO_4)$ (red dot) and CuI(blue dot).

EXP II Ligand L^{Ph} vs. CuI

Exp. No.	equiv. of L^{Ph}	equiv. of CuI
1	1	0
2	1	0.2
3	1	0.4
4	1	0.6
5	1	0.8
6	1	1.0
7	1	1.5
8	1	2

EXP III Ligand L^{Ph} vs. n-Bu_4NI

Exp. No.	equiv. of L^{Ph}	equiv. of n-Bu_4NI
1	1	0
2	1	0.2
3	1	0.4
4	1	0.6
5	1	0.8
6	1	1.0
7	1	1.5
8	1	2

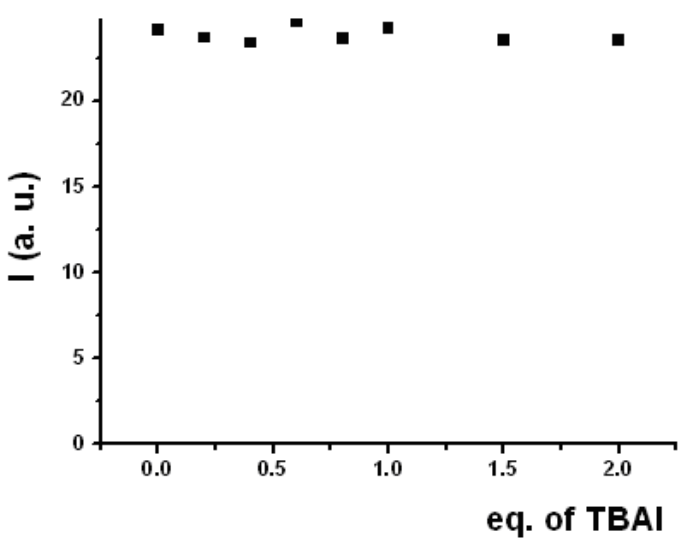


Fig S9

EXP IV Complex **1**·(ClO_4) vs. n-Bu_4NI (The spectral change of fluorescence spectra upon a gradual addition of n-BuN_4I to complex **1** with a concentration of 2.76*10-5 M.)

Exp. No.	equiv. of L^{Ph}	equiv. of n-Bu_4NI
1	1	0
2	1	0.1
3	1	0.2
4	1	0.3
5	1	0.4
6	1	0.5
7	1	0.6
8	1	0.7
9	1	0.8
10	1	0.9
11	1	1.0

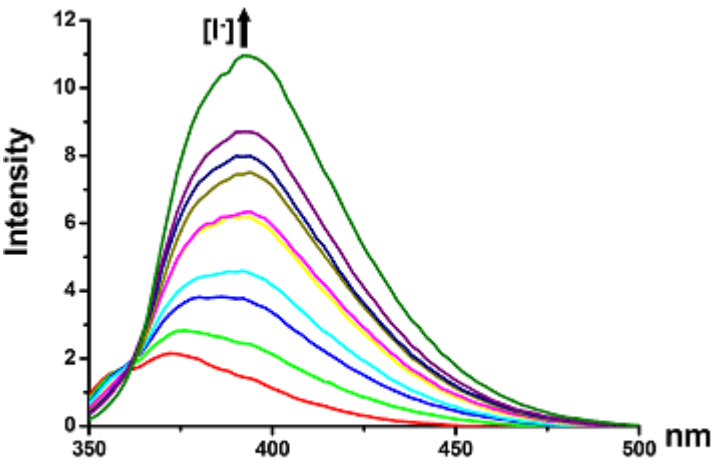


Fig S10

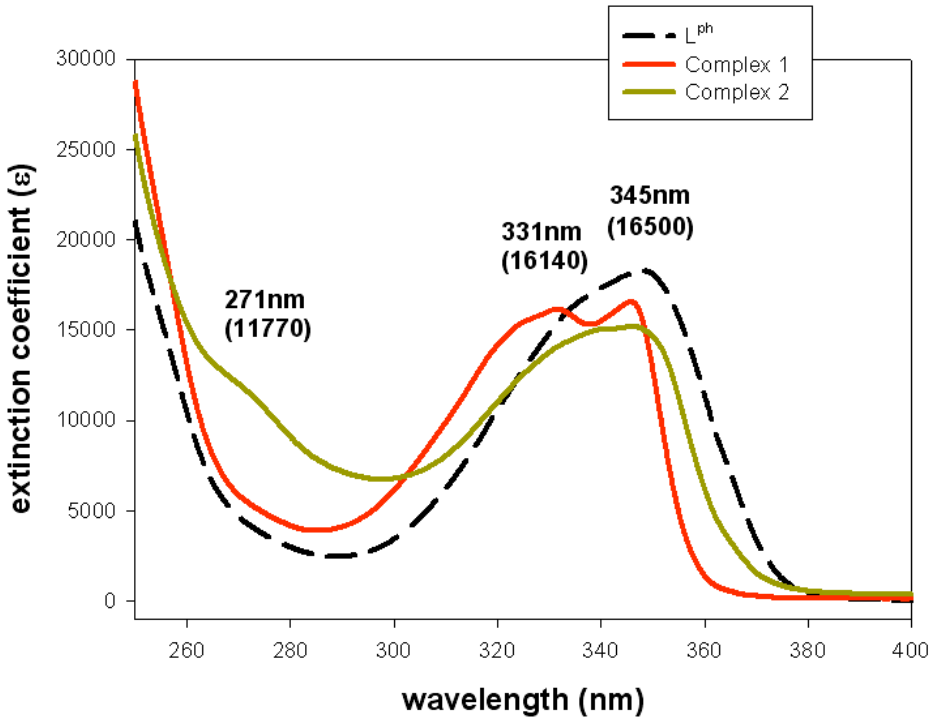


Figure S11. Absorption spectra of L^{Ph}, **1**·(ClO_4) and **2**.

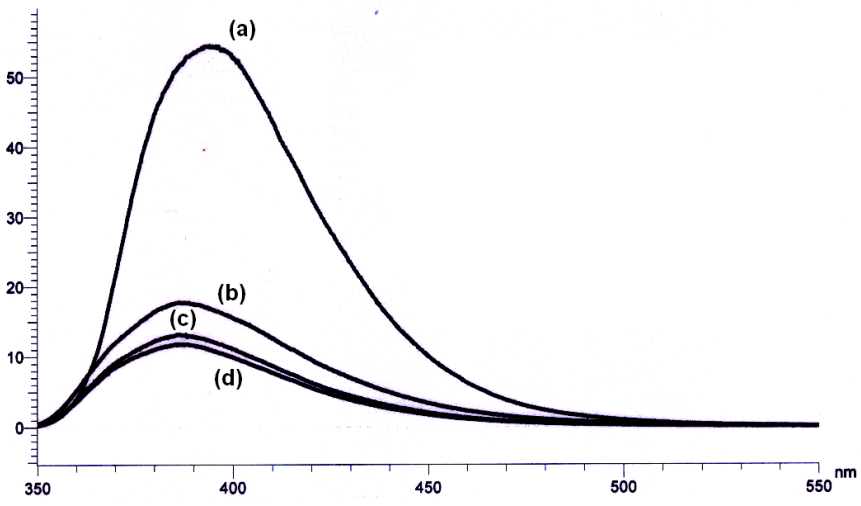


Figure S12 The change of the emission intensity for free ligand L^{Ph} (a) and its complexation with Ni^{2+} ion in a molar ratio (L^{Ph} : Ni^{2+}) of 1.0 : 0.5 (b); 1.0 : 1.0 (c) and 1.0 : 1.5 (d).

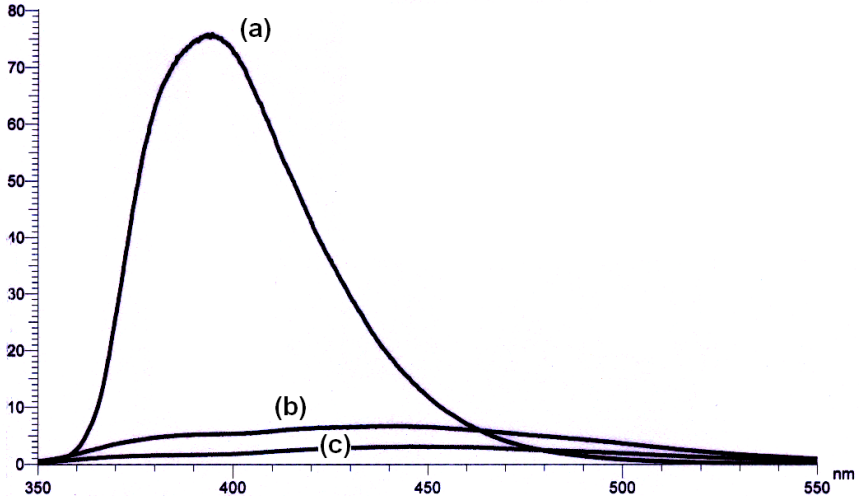


Figure S13 The change of the emission intensity for free ligand L^{Ph} (a) and its complexation with Cu^{2+} ion in a molar ratio (L^{Ph} : Cu^{2+}) of 1.0 : 0.5 (b) and 1.0 : 1.0 (c).

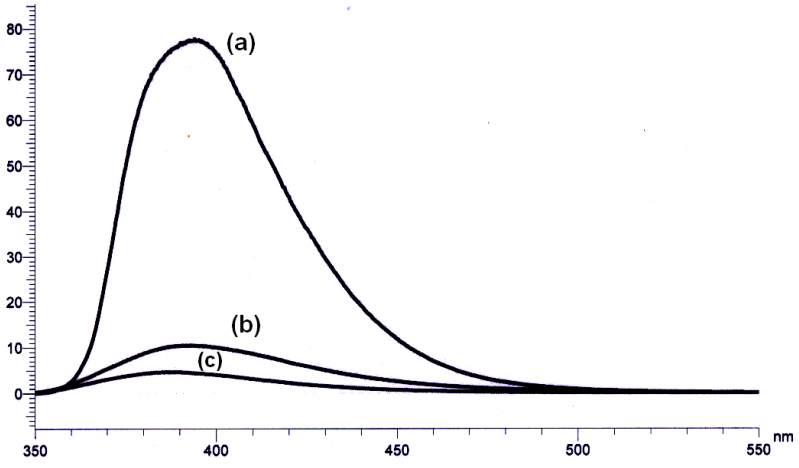


Figure S14 The change of the emission intensity for free ligand L^{Ph} (a) and its complexation with Zn^{2+} ion in a molar ratio (L^{Ph} : Zn^{2+}) of 1.0 : 0.5 (b) and 1.0 : 1.0 (c).