

Supporting Information

for

**Proton-Controllable Fluorescent Switch Based on Interconversion of Polynuclear
and Dinuclear Copper(II) Complexes**

Contents

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General information All solvents and reagents were obtained from commercial sources and used as received without further purification. IR data were obtained as Nujol mulls on a Perkin-Elmer Paragon 500 IR 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. Ultraviolet-Visible spectra were recorded on a Hitachi Model U-3501 Spectrophotometer and a Hewlett Packard 8453 Ultraviolet/Visible Absorption Spectrometer. NMR spectra were obtained on a Bruker Avance 500 NMR spectrometer. Fluorescence emission spectra were recorded at 25 °C on a Aminco-Bowman Series2 fluorescent spectrophotometer.

1. Synthesis of *N,N'*-bis[(2-pyridyl)methyl]isophthalamide (**L1**):

An ice-cold CHCl_3 solution (20 mL) of isophthaloyl chloride (4.0602g, 20 mmol) was added dropwise to a rigorously stirred CHCl_3 solution (20 mL) of 2-(aminomethyl)pyridine (4.3256g, 40 mmol) and triethylamine (5mL) in an ice bath. The reaction solution was stirred for 2 h and allowed to warm up to room temperature and then rotary evaporated. The resulting white residues were collected and washed twice with H_2O and dried to yield 6.2248 g (89.8%) of **L1**. mp: 156 ~157°C. δ_{H} (500 MHz; d_6 -DMSO) 4.60 (4 H, d, $^3J_{\text{H,H}} = 5.8$ Hz, CH_2), 7.265 (2 H, t, $^3J_{\text{H,H}} = 6$ Hz, pyridineH), 7.347 (2H, d, $^3J_{\text{H,H}} = 7.7$ Hz, pyridineH), 7.610 (1 H, t, $^3J_{\text{H,H}} = 7.7$ Hz, ArH), 7.759 (2 H, td, $^3J_{\text{H,H}} = 7.7$ Hz, $^4J_{\text{H,H}} = 1.6$ Hz, pyridineH), 8.073 (2 H, dd, $^3J_{\text{H,H}} = 7.7$ Hz, $^4J_{\text{H,H}} = 1.6$ Hz, ArH), 8.461 (1 H, s, ArH), 8.515(2 H, d $^3J_{\text{H,H}} = 4.35$ Hz, pyridineH), 9,211 (2 H, t $^3J_{\text{H,H}} = 5.8$ Hz, CONH). IR (Nujol): ν_{CO} 1648 cm^{-1} ; ν_{NH} 3257 cm^{-1} ; ν_{OH} 3431 cm^{-1} . Elemental Analysis for **L1**, $\text{C}_{20}\text{H}_{19}\text{O}_2.5\text{N}_4$, Calcd. (Found): C, 67.59 (67.45); H, 5.24 (5.59); N, 16.17 (15.93).

2. Synthesis of $\{[\text{Cu}_2(\text{L1})_2(\text{ClO}_4)_2](\text{ClO}_4)_2\}_n$ (Complex 1):

A solution of $[\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ (1.2146g, 3.28 mmol) in 10 mL methanol was added slowly to a 10 mL CH_3OH solution of **L1** (1.1355g, 3.28 mmol). The reaction mixture was stirred at room temperature for 30 min. The blue precipitates were filtered and

washed with methanol (5 mL) and then dried to yield 1.896 g (95%) of complex **1**. The blue crystals suitable for X-ray crystallography analysis were obtained by slow diffusion of Et₂O to a MeCN solution. Absorption spectrum (MeOH-MeCN (1:1) co-solvent) [λ_{max} , nm (ϵ , M⁻¹cm⁻¹): 708 (46.36). IR (Nujol): ν_{CO} 1617 cm⁻¹; ν_{NH} 3343 cm⁻¹; ν_{ClO_4} 1104 cm⁻¹. Elemental Analysis for complex **1**: C₄₀H₃₆Cl₄Cu₂N₈O₂₀: Anal. Calcd. (found) for C₂₀H₁₈N₄O₁₀Cl₂Cu: C, 39.46 (39.63); H, 2.98 (2.66); N, 9.20 (9.17).

3. Synthesis of [Cu₂(L1-2H)₂] (Complex 2):

To a 25 mL methanol-acetonitrile (1:1) solution of complex **1** (0.1222g, 0.2 mmol) was added slowly a 10 mL methanol solution of potassium hydroxide (0.022g, 0.4 mmol). The solution was stirred at room temperature for 30 min and then filtered to remove the white residues. The filtrate was rotary evaporated to dryness to yield the green products, which were recrystallized twice from methanol and diethyl ether, and then dried in vacuo to yield 0.0705 g (86%) of the green products. The green crystals suitable for X-ray structure determination were obtained from slow diffusion of diethyl ether into a methanol solution of complex **2**. Absorption spectrum (MeOH-MeCN (1:1) co-solvent) [λ_{max} , nm (ϵ , M⁻¹cm⁻¹): 387 (3483), 608 (487), 847(103,sh). IR (Nujol): ν_{CO} 1552 cm⁻¹; $\nu_{\text{H}_2\text{O}}$ 3380 cm⁻¹. Elemental Analysis for complex **2**: C₄₀H₃₆Cu₂N₈O₆ Calcd. (Found): C, 56.40 (56.14); H, 4.26 (3.85); N, 13.15 (13.37).

4. Experiment on the coumarin 343 fluorescence quenching process by {[Cu₂(L1)₂(ClO₄)₂](ClO₄)₂}_n.

Fluorescence quenching experiments on coumarine 343 by complex **1** were carried out in MeOH-MeCN(1:1) co-solvent. The experimental samples (entry 1~9) of 10ml each were prepared according to the 9 entries shown in the Table. The fluorophore was excited at 420 nm, and the emission spectra were collected between 430nm and 600nm.

Exp. No.	equiv. of complex 1	equiv. of coumarine 343
1	0	1
2	1	1
3	2	1
4	4	1
5	10	1
6	50	1
7	100	1
8	150	1
9	250	1

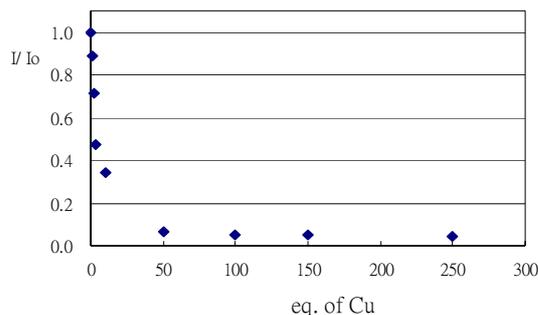


Fig. S1 Titration of coumarine 343 with complex **1**. (I_0 was defined as the fluorescence intensity of exp. No. 1.)

5. Emission spectrum of coumarine 343 anion and [Cu-R₃₄₃COO] adduct

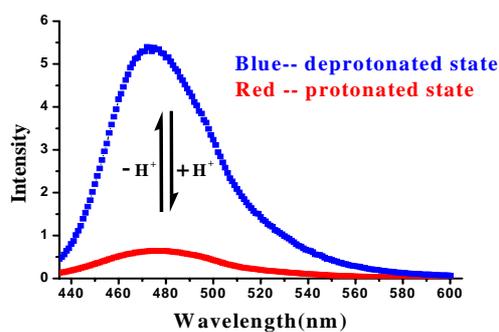


Fig. S2 Typical emission spectrum of coumarine 343 anion (blue, λ_{\max} 471nm) and [Cu-R₃₄₃COO] adduct (red, λ_{\max} 480nm)