**Supporting Information**

A trinuclear Cu(II) precursor for solvatochromically distinguishing CH3OH from C2H5OH

XUE-MEI GAO, WEN MA, GANG JIN, JING-ZHE LI, XUE-WEN WEI and KUAN-GUAN LIU\*

**S1. Synthesis**

Other experimental conditions have been done for getting compound **1**. The detailed description of the attempted synthesis in those reaction conditions and the resulting products are attached as follows. For reaction 1, the process is same to the synthesis of compound **1**. PhC≡CCOOH (abbreviated as PPA, 3.0×10-4 mol) was dissolved in CH3OH (3.0 mL) of Cu(CH3CN)4BF4 (3.0×10-4 mol) under ultrasonication, giving a clear yellow solution, then bpy (6.0×10-4 mol) was added and the solution change to red-brown. Then the solution was sealed and heated to 70 °C for 20 h. After cooling to room temperature, the black-brown solution was filtered. Slow evaporation of the filtrate at 5 °C afforded the product of compound **1** as blue crystals after one day. For reaction 2, the process is same to reaction 1, except that before ultrasonication treatment N2 was pumped to the methanol mixture for 30 min. For reactions 3-7, the process is same to reaction 1, except that 0.3 mmol of other carbonate sources like NaHCO3 (3), Na2CO3 (4), NH4HCO3 (5) and (NH4)2CO3 (6) were used instead of PPA and without PPA (7) for comparison. For reaction 8, Cu2(OH)2CO3 (3.0×10-4 mol) was added CH3OH (3.0 mL); after 15 min ultrasonication treatment, bpy (6.0×10-4 mol) was added under 30 min ultrasonication treatment. Then the mushy mixture was sealed and heated to 70 °C for 20 h. After cooling to room temperature, many pale green precipitate were obtained.

Table S1. Serial experiment results for preparing compound **1**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Reactions** | **Copper salts** | **Carbonate source** | **Controlled atmosphere** | **Results** |
| 1 | Cu(CH3CN)4BF4 | PPA | air | Compound **1** |
| 2 | Cu(CH3CN)4BF4 | PPA | N2 | Compound **1** |
| 3 | Cu(CH3CN)4BF4 | NaHCO3 | air | Precipitate |
| 4 | Cu(CH3CN)4BF4 | Na2CO3 | air | Precipitate |
| 5 | Cu(CH3CN)4BF4 | NH4HCO3 | air | Precipitate |
| 6 | Cu(CH3CN)4BF4 | (NH4)2CO3 | air | Precipitate |
| 7 | Cu(CH3CN)4BF4 | --- | air | Blue powder |
| 8 | Cu2(OH)2CO3 | --- | air | Precipitate |

**S2. Characterization**

new

Figure S1. The XRD pattern of result blue powder compared with the simulated data of compound **1**.

GXM2IR.tif

Figure S2. The IR spectrum of compound **1**.

GXM2 紫外吸收图.tif

Figure S3. The UV-visible spectrum for compound **1** in CH3CN with different concentrations.

WR1EPR.tifWR1EPR2.tif

**(b)**

**(a)**

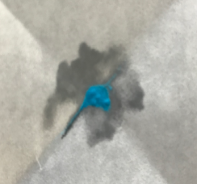
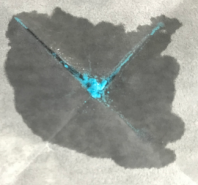
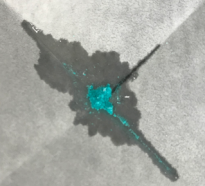
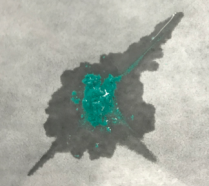
Figure S4. The solid powder (a) and the solution (b) EPR spectra of compound **1**.

**(b)**

**(a)**

GXM2TGA.tif

Figure S5. The TGA curve (a) of compound **1** and the XRD (b) of compound **1** and after 250 °C burning.



(f)

(c)

(b)

(a)

(a)

(b)

(c)

(d)

(e)

(f)

(e)

(d)

Figure S6. Thesensitivity tests with various ratios of methanol/ethanol mixtures. (a) CH3OH:C2H5OH = 1:10000, (b) CH3OH:C2H5OH = 1:5000, (c) CH3OH:C2H5OH = 1:1000, (d) CH3OH:C2H5OH = 1:100, (e) CH3OH:C2H5OH = 1:50, (f) CH3OH:C2H5OH = 1:1.

FIGS5.tif

Figure S7. The PXRD pattern of compound **1** during solvatochromism behavior.

WR1SUV1.tif WR1SUV2.tif

**(b)**

**(a)**

Figure S8. The diffuse reflectance spectra of the blue powder sample before (a) and after (b) its solvatochromism behaviors.

Table S2. Crystal data and structure refinement for **1**.

|  |  |
| --- | --- |
| Chemical formula | C64H56B4Cu3F16N12O8 |
| Formula weight | 1659.06 |
| Crystal system | Triclinic |
| Space group | P-1 |
| *a*, Ǻ | 11.4543(6) |
| *b*, Ǻ | 13.2135(6) |
| *c*, Ǻ | 25.1120(12) |
| *α*, deg | 76.0660(10) |
| *β*, deg | 88.807(2) |
| *γ*, deg | 76.3350(10) |
| *V*, Ǻ3 | 3581.9(3) |
| *Z* | 2 |
| *ρ*calc, g/cm3 | 1.538 |
| *µ*, mm-1 | 0.986 |
| Reflections collected | 47460 |
| Independent reflections | 13691 |
| Rint | 0.0347 |
| Reflections I > 2σ(I) | 13691 |
| Parameters | 996 |
| GOF on F2 | 1.041 |
| *R*1a /*wR*2b (I > 2σ(I)) | 0.0533 / 0.1351 |
| *R*1a /*wR*2b (*all*) | 0.0737 / 0.1471 |

a R1 = [Σ abs(abs(Fo) - abs(Fc))]/ [Σ abs(Fo)]. b *w*R2 = [Σ(*w*(Fo2 - Fc2)2)/ Σ[*w*(Fo2)2]0.5.