

Mechanochromic photoluminescence in a dinuclear alkynyl copper(I) complex with in an extremely short Cu(I)⋯Cu(I) separation

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Experimental

General experimental methods: All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Diethyl ether was distilled from sodium–benzophenone, CH₃CN was distilled from CaH₂. ¹H-NMR spectra were recorded at 300.13 MHz, ¹³C NMR spectra were recorded at 75.61 MHz, ³¹P NMR spectra were recorded at 121.49 MHz in CD₂Cl₂. the *bis*-1,2-diphenylphosphinobenzene (dppb) ligand was prepared according to a procedure described in the literature.¹ Other reagents were obtained from commercial suppliers and used as received. Infra-red spectra were measured using Tensor 27 (ATR diamond) Bruker spectrometer. IR data are reported as characteristic bands (cm⁻¹).

Photophysical characterization

UV-vis absorption spectra were registered on a Perkin-Elmer Lambda 750S spectrophotometer. Emission spectra were measured using a Jobin Yvon Fluorolog 3-22 spectrofluorometer with a 450 W xenon lamp, double-grating monochromators, and a TBX-04 photomultiplier. Measurements in frozen 2-MeTHF glasses were carried out in a right angle configuration using 5 mm quartz NMR tubes and a liquid nitrogen Dewar with quartz windows. Measurements in the solid state were carried out in front face configuration using solid samples supported between quartz coverslips. An Oxford Instruments Optistat-DN cryostat was employed for low-temperature measurements in the solid state. Lifetimes were determined using the Fluorolog's FL-1040 phosphorimeter accessory ($\tau > 10 \mu\text{s}$) or a IBH FluoroHub controller in TCSPC mode using a 372 nm pulsed NanoLED source ($\tau < 10 \mu\text{s}$); the estimated uncertainty is $\pm 10\%$ or better. Emission quantum yields were determined using a Hamamatsu C11347 Absolute PL Quantum Yield Spectrometer; the estimated uncertainty is $\pm 5\%$ or better.

Crystal data for **1**. Yellow prismatic crystals: C₇₆H₅₈P₄Cu₂, triclinic, P-1, $a = 10.7851(3)$, $b = 12.7214(4)$, $c = 12.9752(4)$ Å, $\alpha = 66.4000(10)$, $\beta = 73.5420(10)$, $\gamma = 72.6740(10)^\circ$, $V = 1529.66(8)$ Å³, $Z = 1$, $T = 200(2)$ K, $m = 2.179$ mm⁻¹, 28238 reflections measured, 5556 independent ($R_{\text{int}} = 0.0162$), 371 parameters, no restraints, final R indices $R_1 [I \geq 2\sigma(I)] = 0.0250$ and wR_2 (all data) = 0.680, GOF on $F^2 = 1.044$, max/min residual electron density = 0.26/-0.27 e.Å⁻³.

A single crystal of the compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected at 200K with a BRUKER Kappa-APEXII diffractometer with micro-focused Cu-K α radiation. APEX 3 suite and SAINT program (BRUKER) were used to carry out data collection, unit-cell parameters refinement, integration and data reduction. SADABS (BRUKER) was used for scaling and multi-scan absorption corrections. In the Olex2 suite², the structure was solved with Sir92³ program and refined by full-matrix least-squares methods using SHELXL-14⁴.

CCDC 1943516 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Synthesis of complex [Cu(μ^2 - η^1 -C \equiv CPh)(dppb)]₂ (**1**): To a solution of [Cu(CH₃CN)₄]BF₄ (200 mg; 0.64 mmol) and suspended cesium carbonate (210 mg; 0.64 mmol) in acetonitrile (20 mL) was

added phenylacetylene (70 mg; 0.68 mmol) at 0°C. The mixture was stirred and allowed to warm up to room temperature during 4 hours. Then, dppb (285 mg; 0.64 mmol) solid was added at once and the mixture was stirred at room temperature overnight. Finally the mixture was filtered through a pad of celite. Slow evaporation of the solvent gave a green/yellow microcrystalline solid (310 mg; 0,52 mmol). Yield: 81%.

Anal. Calcd. (%) for $C_{38}H_{29}CuP_2 \cdot 2CH_3CN$ (692,16 g.mol⁻¹): C 72.77, H 5.09; found: C 72.07, H 4.74.

¹H-NMR (300.13 MHz, CD₂Cl₂): δ = 7.54-6.96 (m, 29 H, *dppb* + phenylalkynyl) ppm.

¹³C{¹H}-NMR (75.47 MHz, CD₂Cl₂): δ = 125.6 (s); 128.7 (s); 128.8 (t, J_{CP} = 4.2 Hz); 129.2 (s); 129.6 (t, J_{CP} = 2.6 Hz); 130.3 (s); 131.2 (s); 132.3 (s); 132.6 (s); 133.6 (t, J_{CP} = 2.6 Hz); 135.0 (t, J_{CP} = 4.3 Hz); 135.3 (s) ppm.

³¹P{¹H}-NMR (121.49 MHz, CD₂Cl₂): δ = -9.99 (broad), *dppb*) ppm.

IR (ATR): ν = 2039 cm⁻¹ (-C≡C-)

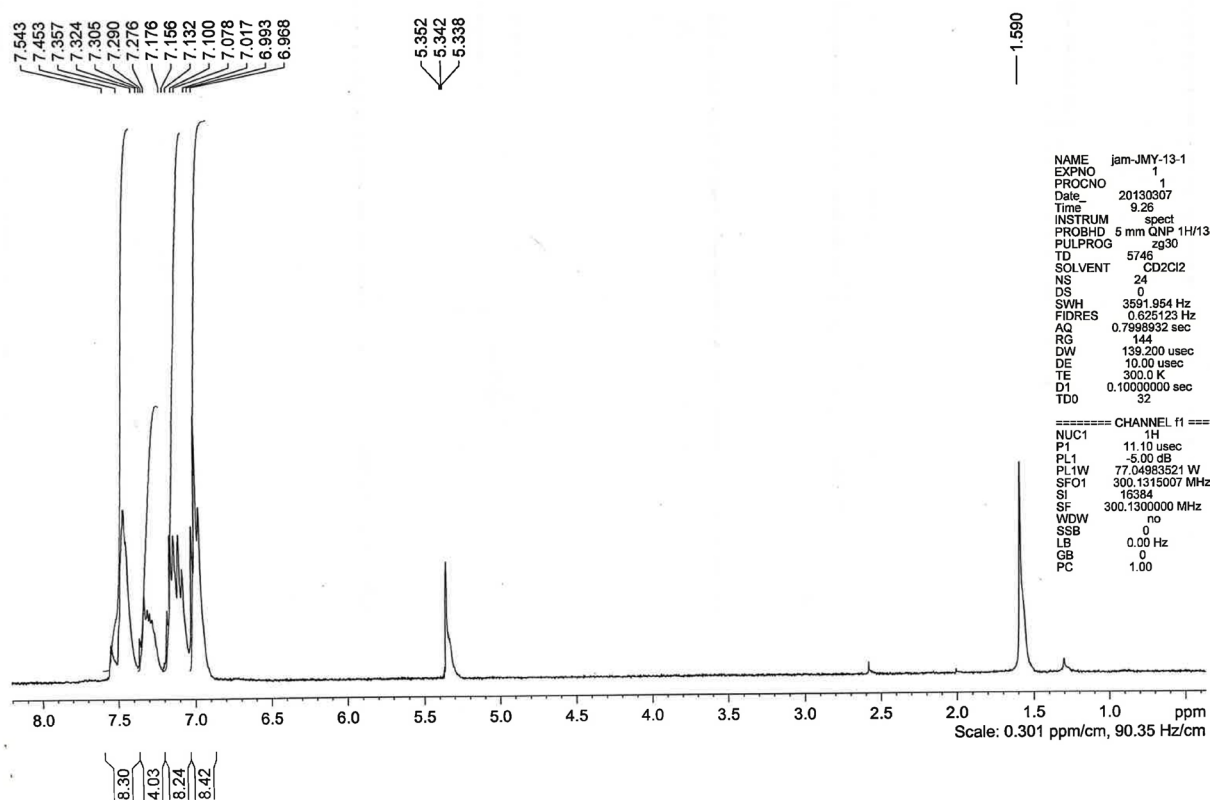


Figure S1: ¹H-NMR spectrum of complex **1** in CD₂Cl₂

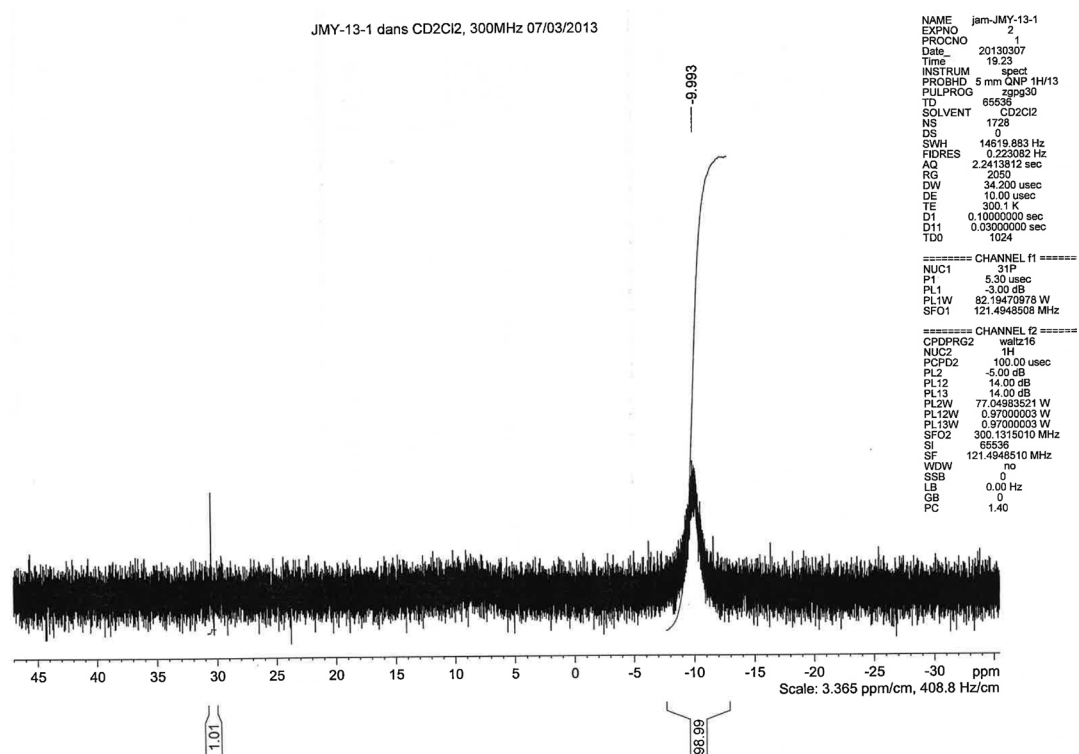


Figure S2: ³¹P-NMR spectrum of complex **1** in CD₂Cl₂

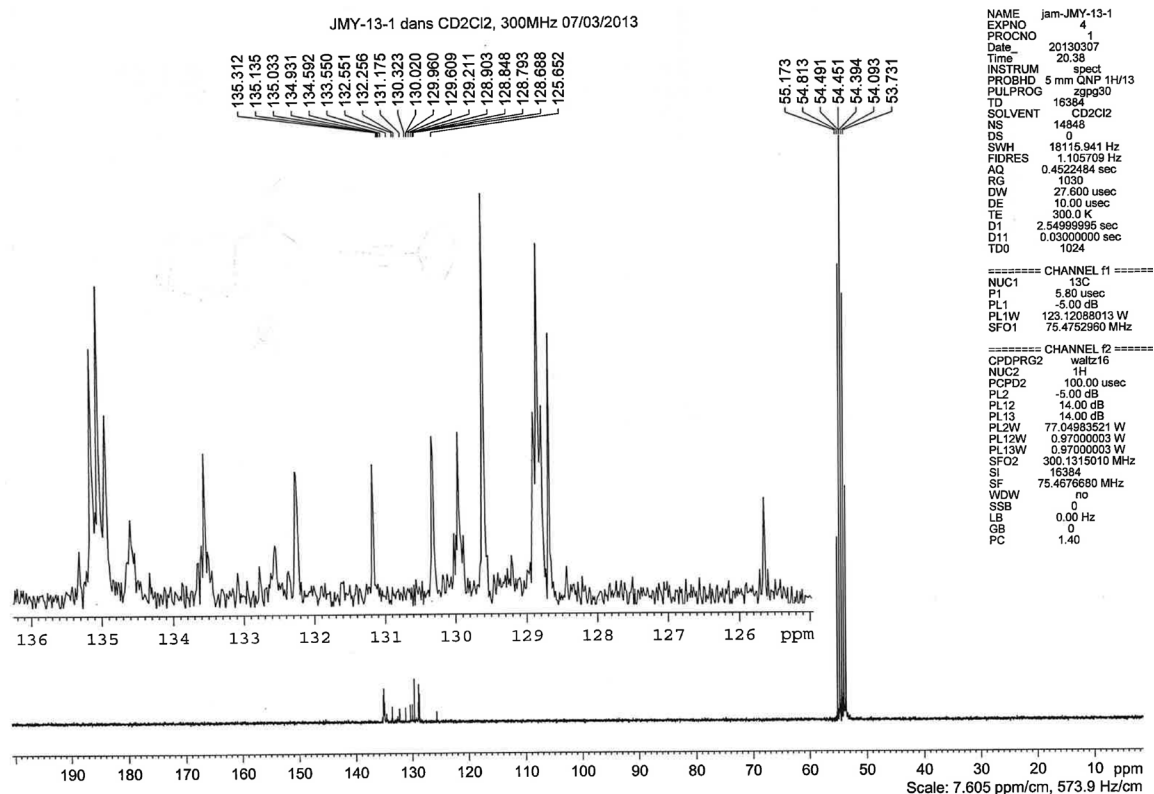


Figure S3: ¹³C-NMR spectrum of complex **1** in CD₂Cl₂

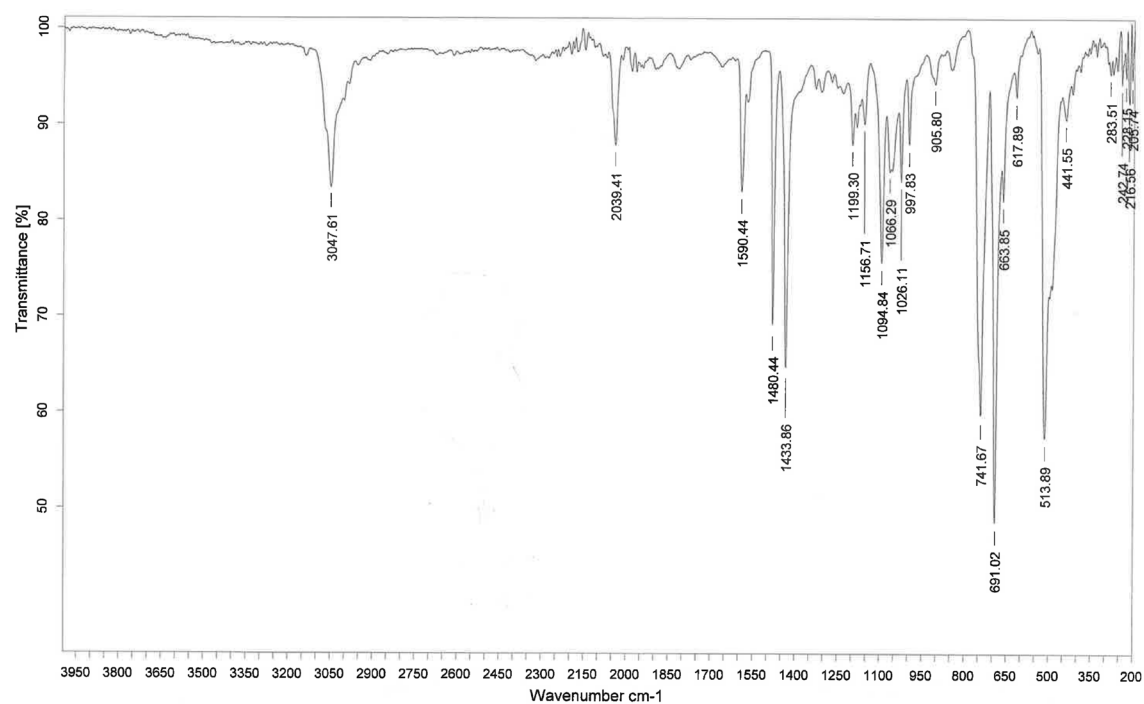


Figure S4: IR spectrum of complex **1** ATR technique

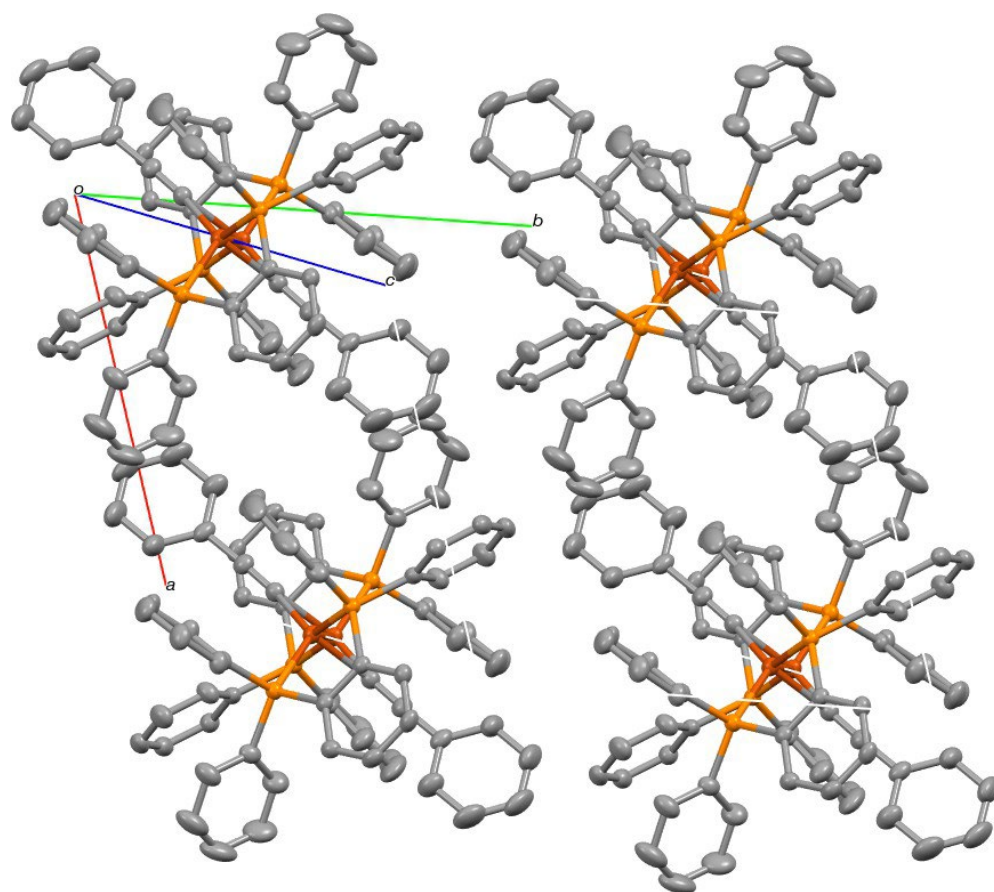


Figure S5: View of the unit cell showing the absence of π -stacking or similar interactions in the crystal structure of complex **1**

¹ Tunney, S. E.; Stille, J. K., *J. Org. Chem.* 1987, **52**, 748.

² O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339

³ A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, et M. Camalli, *J. Appl. Cryst.* 1994, **27**, 435

⁴ G. M. Sheldrick, *Acta Crystallographica Section C* 2015, **71**, 3