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# Luminescent $[Cu_8I_8L_6]$ wheel and $[Cu_2I_2L_3]$ cage assembled from CuI and 3,6-bis(diphenylphosphino)pyridazine

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## §1. Reagents and instrumentation details

CuI (99%, Sigma), $CH_3CN$ (HPLC grade, Cryochrom) were commercial products. 3,6-Bis(diphenylphosphino)pyridazine (dppz) was synthesized according to the known procedure.[S1] The microanalyses were performed on a MICRO cube analyzer. Thermogravimetric analyses were carried out in a closed $Al_2O_3$ pan under argon flow at 5 °C/min heating rate using a Netzsch STA 449 F1 Jupiter STA. FT-IR spectra were collected on a Bruker Vertex 80 spectrometer.

The solid-state reflectance spectra were recorded on a Shimadzu UV-3101 spectrophotometer. The reflectance data were converted into a spectrum applying a Kubelka–Munk function. Excitation and emission spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon) with a cooled PC177CE-010 photon detection module equipped with an R2658 photomultiplier. The emission decays were measured on the same instrument. The absolute PLQYs were measured using a Fluorolog 3 Quanta-phi integrating sphere. Temperature dependences of luminescence were carried out using Optistat DN optical cryostats (Oxford Instruments).

## §2. Synthetic procedures

**$[Cu_8I_8L_6]$** (**1**·$4CH_3CN$)

CuI (30 mg, 0.15 mmol) and dppz (53 mg, 0.12 mmol) were added to acetonitrile (5 mL) and stirred for 10 min in air until the orange precipitate was obtained (*ca.* 1 min). Then the solvent was decanted, and the product was dried in air. Orange powder. Stable in air and moisture. Yield: 67 mg (85%). FT-IR (KBr, $cm^{-1}$): 426 (m), 517 (m), 534 (s), 617 (w), 642 (w), 694 (vs), 743 (s), 839 (vw), 920 (vw), 999 (w), 1028 (w), 1070 (w), 1096 (m), 1157 (w), 1186 (w), 1281 (w), 1310 (vw), 1381 (w), 1435 (s), 1481 (m), 1508 (vw), 1541 (vw), 1572 (vw), 1585 (w), 1632 (w), 1890 (vw), 1967 (vw), 2855 (vw), 2924 (vw), 3051 (w). *Anal.* Calcd: $C_{176}H_{144}Cu_8I_8N_{16}P_{12}$ (4371.53); C, 48.3; H, 3.3; N, 5.1. Found: C, 48.1; H, 3.3; N, 5.3.

**$[Cu_2I_2L_3]$** (**2**)

CuI (20 mg, 0.10 mmol), dppz (67 mg, 0.15 mmol) and $PPh_3$ (131 mg, 0.50 mmol) were added in $CH_2Cl_2$ (10 mL) and the solution was stirred in air at ambient temperature for 10 min. The solution was then filtered and precipitated by $Et_2O$ and a greenish precipitate was obtained. Then the solvent was decanted and the solid was dried in air. Air- and moisture-stable greenish-white powder. Yield: 70 mg (88%). FT-IR (KBr, $cm^{-1}$): 461 (w), 488 (m), 515 (m), 540 (m), 617 (w), 644 (w), 694 (vs), 743 (s), 841 (vw), 922 (vw), 999 (w), 1028 (w), 1070 (w), 1094 (m), 1157 (w), 1186 (w), 1281 (w), 1310 (w), 1375 (w), 1435 (s), 1481 1512 (vw), 1539 (vw), 1572 (w), 1585 (w), 1632 (w), 1721 (w), 813 (vw), 1892 (vw), 1960 (vw), 2855 (w), 2924 (w), 3051 (w). *Anal.* Calcd: $C_{84}H_{66}Cu_2I_2N_6P_6$ (1724.05); C, 58.5; H, 3.9; N, 4.9. Found: C, 58.4; H, 3.9; N, 4.7.

## §3. Single crystal X-ray crystallography

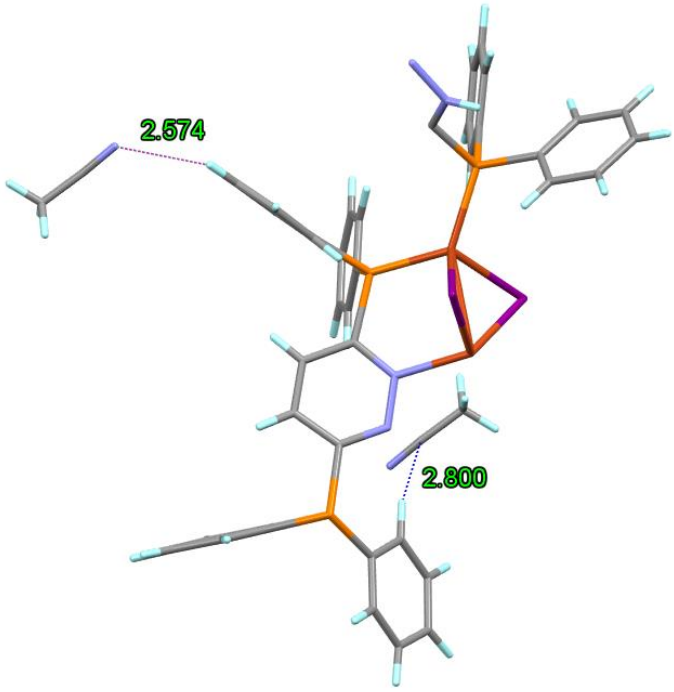


**Figure S1**. Asymmetric unit of **1**·7$CH_3CN$ with $CH_3CN$ molecules bonded via C–N···H–$C_{Ph}$ (magenta) and N–C···H–$C_{Ph}$ (blue) weak interactions.

## §4. Powder X-ray crystallography

Due to fast amorphization of **1**·7$CH_3CN$ and **2**·2$Et_2O$·$CH_3CN$·$CH_2Cl_2$ at ambient conditions, powder XRD data was carried at 150 K with a Bruker D8 Venture with a CMOS PHOTON III detector and IμS 3.0 source (CuKα radiation, mirror optics). The sample were prepared by applying a powder directly from the mother liquor onto a Mylar loop with a small amount of epoxy resin. Diffraction patterns with continuous diffraction arcs were obtained by the φ-scanning method (360°). To improve the powder orientation statistics, 5 scans were taken at different positions of the goniometer along ω from –240 to 0°. Correction for an external standard (Si) and integration were carried out using the Dioptas program.[S2]

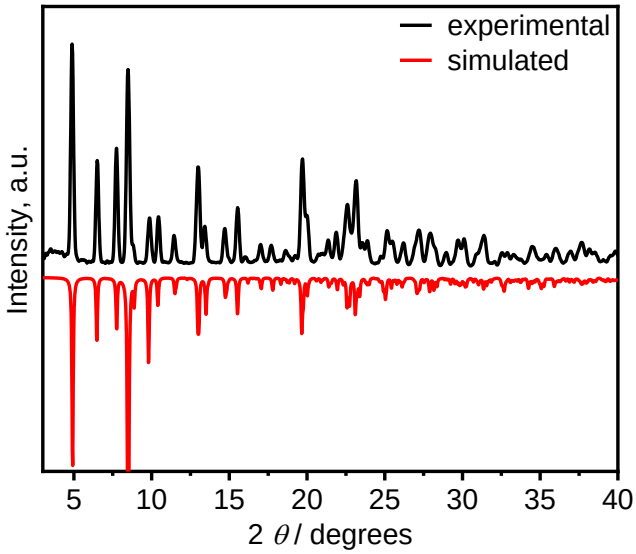


**Figure S2**. Experimental and simulated PXRD patterns for complex **1**·7$CH_3CN$ recorded at 150 K.

## §5. Miscellaneous

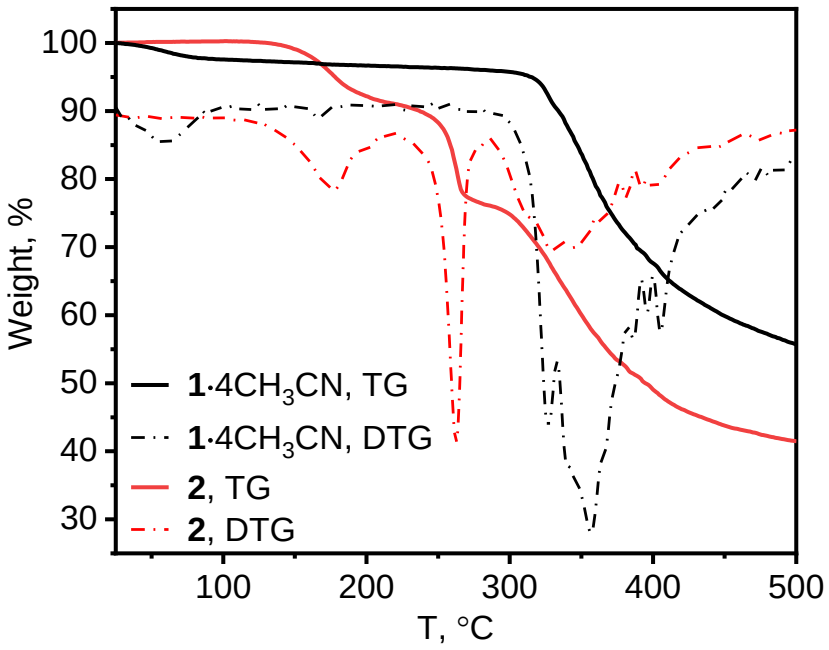


**Figure S3**. TGA and DTG curves for as-synthesized samples of **1**·4$CH_3CN$ and **2**.

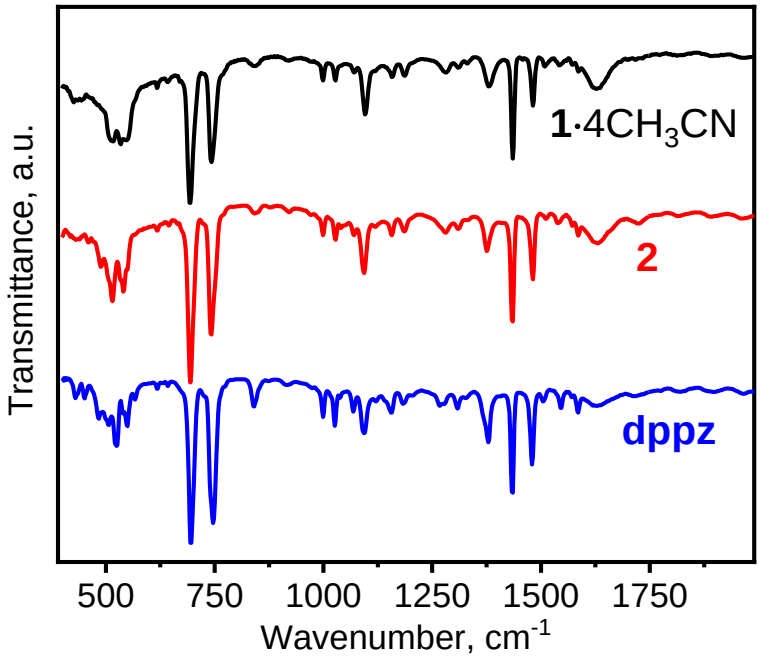


**Figure S4**. FT-IR spectra of complexes **1**·4$CH_3CN$, **2** and dppz ligand.

## §6. Photophysical data

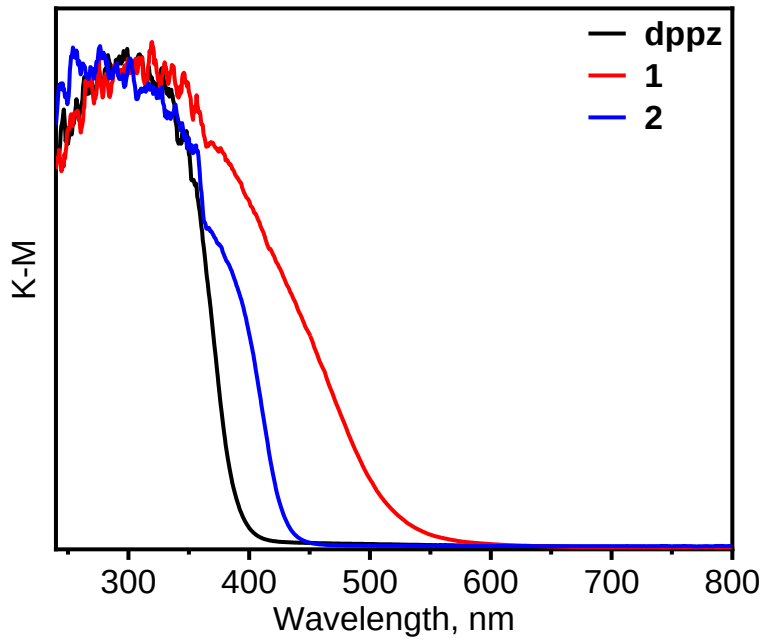


**Figure S5**. UV–Vis absorption spectra (plotted as Kubelka–Munk function) of complexes **1**·4$CH_3CN$, **2** and dppz ligand.

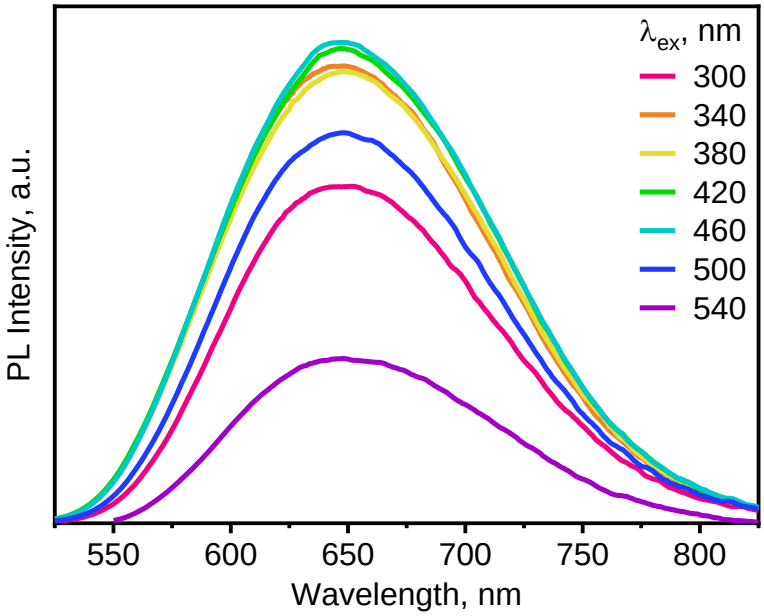


**Figure S6**. The excitation-wavelength dependent emission spectra of **1**·4$CH_3CN$ at 300 K.

## §7. References

S1 Z.-Z. Zhang, H.-K. Wang, Y.-J. Shen, H.-G. Wang and R.-J. Wang, *Journal of Organometallic Chemistry*, 1990, **381**, 45-52.

S2 C. Prescher and V. B. Prakapenka, *High Pressure Research*, 2015, **35**, 223-230.