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1D Cu^{I} coordination polymers based on triphenylarsine and *N,N′*-ditopic co-ligands: synthesis, crystal structure and TADF properties

Yan V. Demyanov, Marianna I. Rakhmanova, Irina Yu. Bagryanskaya and Alexander V. Artem'ev

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§1. Materials and Instrumentation

CuI (≥99%, Sigma), Ph_3As (≥97%, Alfa Aesar), 4,4′-bipyridine (≥99%, Merck) and pyrazine (≥99%, Merck) were used as purchased. All the solvents prior to use were purified by common protocols. All synthetic procedures were carried out under an argon atmosphere using standard Schlenk technique.

FT-IR spectra were recorded on a Bruker Vertex 80 spectrometer at ambient temperature. The microanalyses were performed on a MICRO cube analyzer. PXRD analyses were performed on a Shimadzu XRD-7000 diffractometer (Cu-Kα radiation, Ni – filter, 3–35° 2ϑ range, 0.03° 2ϑ step, 5s per point).

Excitation and emission spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon) equipped with a cooled PC177CE-010 photon detection module and an R2658 photomultiplier. The emission decays were recorded on the same instrument. The absolute PLQYs were determined at 298 K using a Fluorolog 3 Quanta-phi integrating sphere. Temperature-dependent excitation and emission spectra as well as emission decays were recorded using an Optistat DN optical cryostat (Oxford Instruments) integrated with above spectrometer.

§2. Synthetic procedures and characterization data

General procedure for synthesis of 1 and 2·MeCN

To a mixture of CuI (8 mg, 0.042 mmol) and $AsPh_3$ (25.7 mg, 0.084 mmol) in DMF (2 mL), 4,4′-bipyridine (9.8 mg, 0.063 mmol) or pyrazine (5 mg, 0.063 mmol) was added dropwise (dissolved in several drops of MeCN) and stirred at room temperature for 30 min. The formed precipitate was centrifuged, washed by Et_2O (3 x 2 mL) and dried in vacuum.

$[\{Cu_2I_2(AsPh_3)_2\}(4,4'\text{-bipyridine})]_n$ (**1**).
Light green powder. Yield: 61 mg (90%). FT-IR (KBr, cm^{-1}): 419 (w), 465 (s), 471 (s), 569 (w), 617 (w), 629 (s), 669 (m), 694 (vs), 733 (vs), 743 (vs), 810 (s), 854 (w), 920 (w), 964 (w), 1001 (m), 1024 (m), 1042 (w), 1065 (m), 1076 (m), 1086 (w), 1155 (w), 1186 (m), 1215 (m), 1273 (w), 1308 (w), 1406 (s), 1433 (s), 1481 (s), 1530 (m), 1580 (m), 1599 (s), 1651 (w), 1771 (w), 1827 (w), 1890 (w), 1964 (w), 2995 (w), 3049 (m), 3069 (w). Calcd. for $C_{46}H_{38}As_2Cu_2I_2N_2$ (1149.55): C, 48.1; H, 3.3; N, 2.4. Found: C, 48.0; H, 3.3; N, 2.4.

$[\{Cu_2I_2(AsPh_3)_2\}(\text{pyrazine})]_n\cdot$MeCN (**2**·MeCN).
Orange powder. Yield: 57 mg (88%). FT-IR (KBr, cm^{-1}): 419 (m), 436 (m), 451 (s), 476 (m), 617 (w), 669 (w), 692 (m), 739 (m), 748 (w), 804 (m), 847 (vw), 912 (vw), 999 (w), 1024 (w), 1049 (m), 1078 (w), 1121 (m), 1157 (m), 1184 (vw), 1221 (vw), 1273 (vw), 1306 (vw), 1416 (vs), 1435 (m), 1477 (m), 1580 (vw), 1670 (w), 1769 (vw), 1846 (vw), 1892 (vw), 1965 (vw), 2251 (w), 2855 (vw), 2924 (w), 3051 (w), 3069 (vw). Calcd. for $C_{42}H_{37}As_2Cu_2I_2N_3$ (1114.51): C, 45.3; H, 3.3; N, 3.8. Found: C, 45.4; H, 3.3; N, 3.9.

§3. Powder X-ray diffraction data

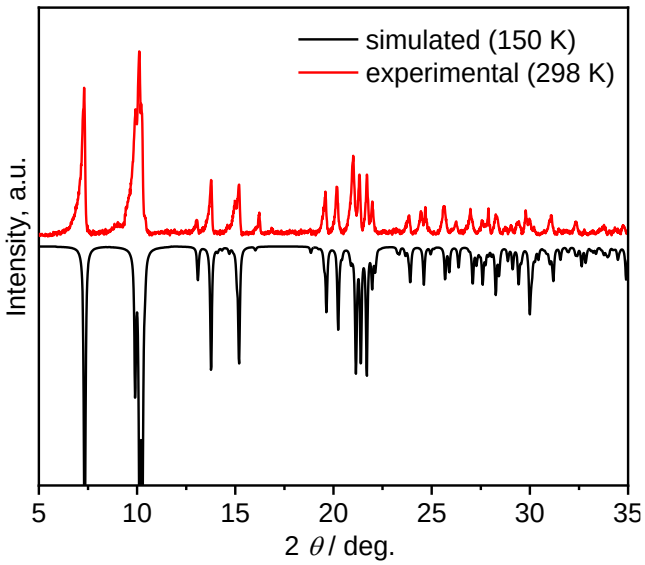

Figure S1. Experimental and simulated PXRD patterns of **1**.

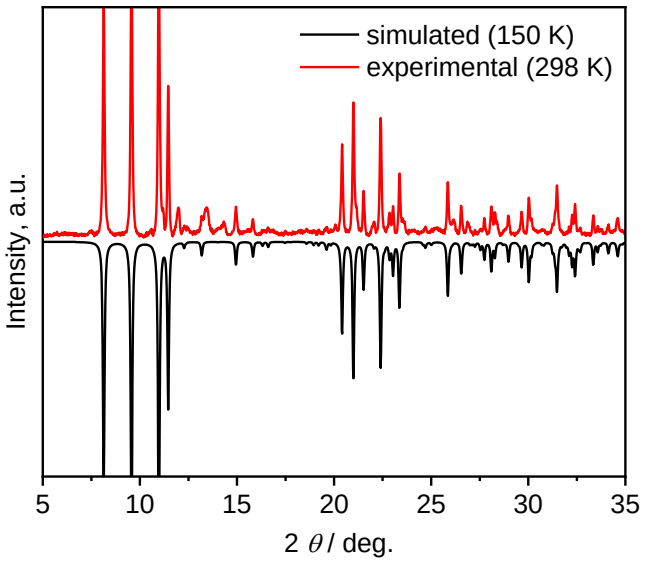

Figure S2. Experimental and simulated PXRD patterns of **2**·MeCN.

§4. FT-IR spectra

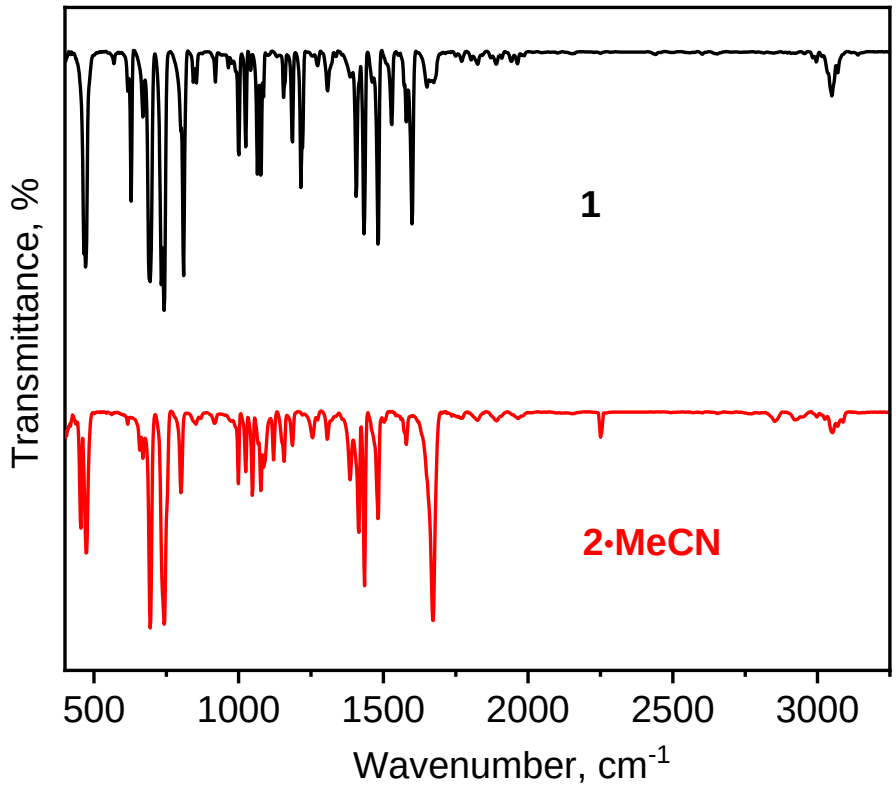

Figure S3. FT-IR spectra for the complexes **1** and **2**·MeCN in the 400–3250 cm^{-1} region.

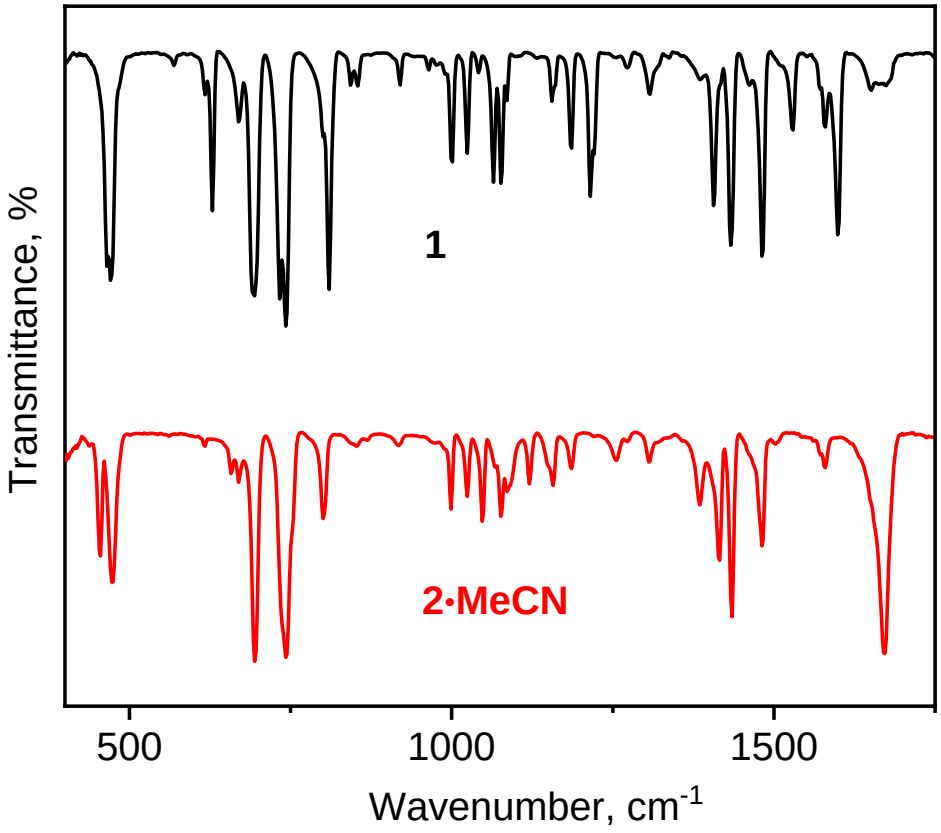

Figure S4. FT-IR spectra for the complexes **1** and **2**·MeCN in the fingerprint region.

§5. Temperature dependent excitation spectra of 1 and 2·MeCN

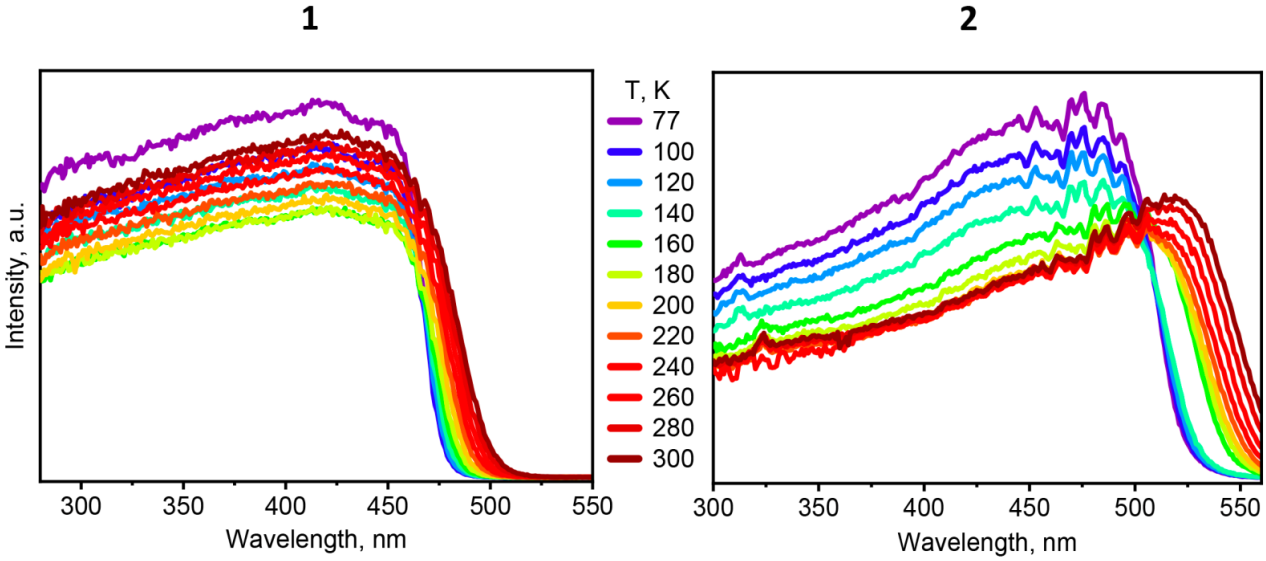

Figure S5. Temperature dependent excitation spectra of **1** (λ_{em} = 560 nm) and **2**·MeCN (λ_{em} = 625 nm).

§6. Temperature dependences of emission decay times

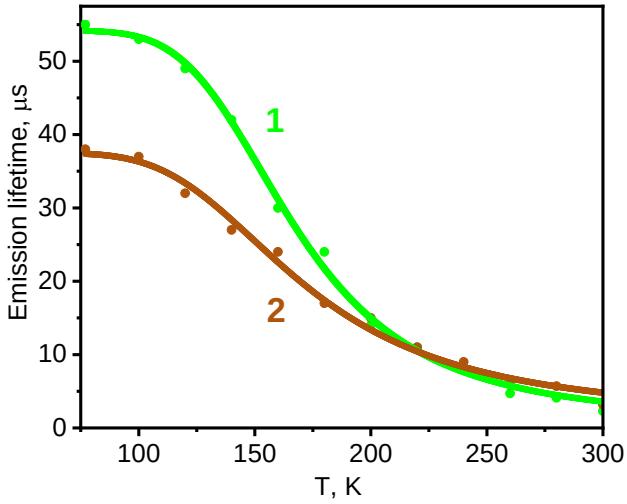

Figure S6. Emission lifetimes of **1** and **2**·MeCN against temperature (λ_{ex} = 390 nm).

To evaluate singlet-triplet splitting (ΔE_{ST}) for CPs **1** and **2**·MeCN, the experimental τ(T) dependences (Fig. S6) were fitted using Boltzmann type equation (Eq. S1) proposed for TADF model:[S1]

$$\tau_{obs}(T) = (3 + \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right))/(\frac{3}{\tau_T} + \frac{1}{\tau_S}\exp(-\frac{\Delta E_{ST}}{k_B T})) \qquad \text{(Eq. S1)}$$

where τ_S and τ_T are the lifetimes of the S_1 and T_1 excited states, respectively, and k_B is the Boltzmann constant. The resulting ΔE_{ST} values are outlined in Table 1 of the main document.

§7. References

S1 *Highly Efficient OLEDs Materials Based on Thermally Activated Delayed Fluorescence*, Ed. Yersin, H.; Wiley-VCH, Weinheim, 2019.