## **Copper(I)** Diketiminate Phenanthroline complexes

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## **SUPPORTING INFORMATION**



**Fig. S1** Crystal structures of **3**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.



**Fig. S2** Emission spectra upon excitation at different wavelengths in the longest wavelength transition of **3b**. A Gaussian function was used to subtract the baseline, originating from stray light from the excitation beam. Intensity of **E1** diminishes between 610 and 640 nm. Emissions **E2** and **E3** are obtained as superimposed peaks in varying ratios, resulting in an apparent displacement of the obtained maximum.

## Solid state emission spectra

Obtained emission spectra displayed asymmetric peak profiles, which could not be fitted with a single Gaussian function, or even a second maximum at lower wavelength ( $\Delta v = 50$ -110 nm). The relative intensities of both peaks or the peak profiles varied in repeated experiments (different target spots chosen on the solid) or with different excitation energies using the same target spot. Lower excitation energies generally favoured the longer-wavelength emission and we ascribed this emission tentatively to a decomposition of the air-sensitive compounds on the surface. Its location of the surface and different absorption coefficient of both species could be responsible for the variations in the intensities of both peaks. The overlap of two emission (in combination with the fact that multiple luminescent states were observed in solution), would require rather intensive investigations before reliable  $\lambda_{max}$  values could be extracted from the data. We

thus refrain from reporting  $\lambda_{max}$  values for solid state emissions and limit us to the statement that all complexes are emissive in the solid state.



Fig. S3 Solid state emission spectrum of 4b with 5% beam intensity.



Fig. S4 Solid state emission spectrum of 4b with 100% beam intensity.

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**Fig. S5** Absorption spectra of  $nacnac^{Bn}Cu(styrene)$  (thick line) and  $(nacnac^{Bn})_2Zn$  (thin line) in diethyl ether solution