Azo–hydrazone tautomerism observed from UV–vis spectra by pH control and metal-ion complexation for two heterocyclic Disperse Yellow dyes

Xiao-Chun Chen, Tao Tao, Yin-Ge Wang, Yu-Xin Peng, Wei Huang, Hui-Fen Qian

Electronic Supporting Information

Fig. SI1. FT–IR spectrum of HL$_{1}$H$_{1}$.
Fig. S12. FT–IR spectrum of H\textsubscript{L}2\textsubscript{2H}.

Fig. S13. FT–IR spectrum of Cu\textsubscript{2}(L\textsubscript{2A})\textsubscript{4}.
**Fig. S14.** $^1$H NMR spectrum of HL$_{1\text{-H}}$ at the low-field range.

**Fig. S15.** $^1$H NMR spectrum of HL$_{2\text{-H}}$ at the low-field range.
Fig. S16. $^1$H NMR spectrum of HL$_{1,4}$H by adding solid NaOH in its DMSO-$d^6$ solvent.

Fig. S17. UV–vis absorption spectra of dye HL$_{1,4}$H in methanol at room temperature. pH values are adjusted by dropping excess NaOH and then different amounts of HCl.
**Fig. SI8.** The simulative (black line) and experimental (red line) powder X-ray diffraction patterns for HL₁-H₁.

**Fig. SI9.** The simulative (black line) and experimental (red line) powder X-ray diffraction patterns for HL₂-H₁.
**Fig. SI10.** The simulative (black line) and experimental (red line) powder X-ray diffraction patterns for Cu$_2$(L$_2$A)$_4$.

**Fig. SI11.** Calculated spatial representations of HOMOs and LUMOs for dyes HL$_{1\text{-H}}$ and HL$_{2\text{-H}}$ with the B3LYP/6–31(d) level.
Fig. S112. ESI–TOF–MS spectrum of Cu$_2$(L$_2$)$_3$ in the negative ion mode.

Fig. S113. $^{13}$C NMR spectrum of HL$_1$H.
Fig. SI14. $^{13}$C NMR spectrum of HL$_2$H.$^\text{I}$