Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Colorimetric and fluorescent pH and Cu^{2+} probes induced by photoisomerization of a maleonitrile-based Salen ligand

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Materials and instrumentation: All reagents were purchased from commercial suppliers and used without further purification. Both *cis*-SL and *trans*-SL were prepared and characterized according to our previous report.[9b] ^{1}HNMR (400MHz) spectra were recorded in DMSO-d_6. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. UV/vis absorption spectra were recorded using a UV 765 spectrophotometer with quartz cuvettes of 1 cm pathlength. Fluorescence spectra were obtained using F-7000 Fluorescence spectrophotometer (Hitachi) at room temperature. The slit width was 5.0 nm for both excitation and emission. The photon multiplier voltage was 400 V. Samples in solution were contained in 10.0 mm path length quartz cuvettes (3.5 mL volume).

Measurement of fluorescence quantum yield (Φ): Φ was measured by the optical dilute method with a standard of quinine sulfate (Φ_r = 0.55, quinine in 0.05 mol dm^{-3} sulfuric acid) calculated by: $\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r)$, where the subscripts s and r refer to the sample and reference standard solution respectively; n is the refractive index of the solvents; D is the integrated intensity. The excitation intensity B is calculated by: $B = 1 - 10^{-A\,L}$, where A is the absorbance at the excitation wavelength and L is the optical path length (L = 1 cm in all cases). The refractive indices of the solvents at room temperature are taken from standard source. Errors for Φ values (± 10%) are estimated.

Measurement of Sensing: Each metal ion or pH titration experiment was started with *cis*-SL or *trans*-SL (6 mL) of known concentration (1.0×10^{-5} and 1.0×10^{-6} mol dm^{-3} in MeCN for absorption and florescence measurement, respectively). For the titration, various metal ions (nitrate, 2.0×10^{-2} mol dm^{-3} in H_2O) or H^+/OH^- were added by a microsyringe. All absorption and florescence measurements were monitored 30 and 120 minutes after adding metal ions and H^+/OH^-, respectively, to the ligand solutions at room temperature.

The experiments involving ***cis*-SL** must be carried out in the present of dim red light and in the absence of room light or heating. When doing experiments about ***trans*-SL**, however, not only ***trans*-SL** was used directly, but also ***cis*-SL** could be adopted after fully changing into ***trans*-SL** by the irradiation. No such isomer tautomerism was found in solid samples. Solid-state samples as well as their solutions were not found to decompose in air and room light within several months.

Synthesis of *cis*-SL: Diaminomaleonitrile (108mg, 1mmol) and 4-(diethylamino)salicylaldehyde (405mg, 2.1mmol) were stirred for 2 days at room temperature in 100 mL of absolute ethanol containing one drop of sulfuric acid as a catalyst. A dark green precipitate was filtered and washed with ethanol and 3 h later, washed with diethyl ether. An impurity was removed by chromatography on silica, using CH_2Cl_2 as eluent. All procedures were carried out in absence of room light (32% yield). ^{1}H-NMR: ($CDCl_3$) 1.21 (t, 12H), 3.39–3.45 (q, 8H), 6.16 (d, 2H), 6.3 (dd, 2H), 7.19 (d, 2H), 8.34 (s, 2H), 12.29 (s, 2H); Anal.Calcd (found): C, 68.10 (67.91); H, 6.59 (6.87); N, 18.34 (18.17); EI-MS, m/z 458.

Synthesis of *trans*-SL: Diaminomaleonitrile (108 mg, 1mmol) and 4-(diethylamino)salicylaldehyde (386 mg, 2mmol) were refluxed for 19h at 78ºC in 100 mL of absolute ethanol containing one drop of sulfuric acid as a catalyst. A dark violet precipitate was filtered and washed with ethanol. An impurity was removed by chromatography on silica, using CH_2Cl_2: EtOAc=3:1 as eluent. All procedures were carried out under room light (12% yield). ^{1}H-NMR: ($CDCl_3$) 1.21 (t, 12H), 3.39–3.45 (q, 8H), 6.16 (d, 2H), 6.3 (dd, 2H), 7.19 (d, 2H), 8.34 (s, 2H), 11.7 5 (s, 2H); EI-MS, m/z 458.

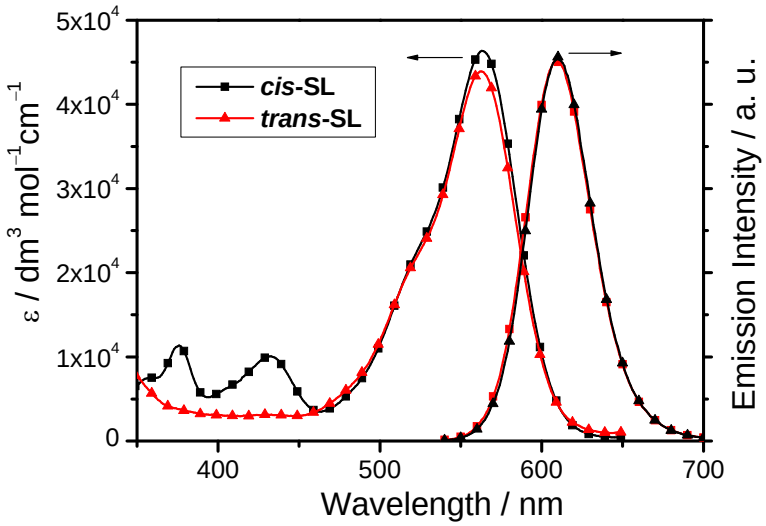

Fig. S1 Absorption and emission spectra (excited at 540 nm) of ***cis*-SL** and ***trans*-SL** in MeCN at room temperature.

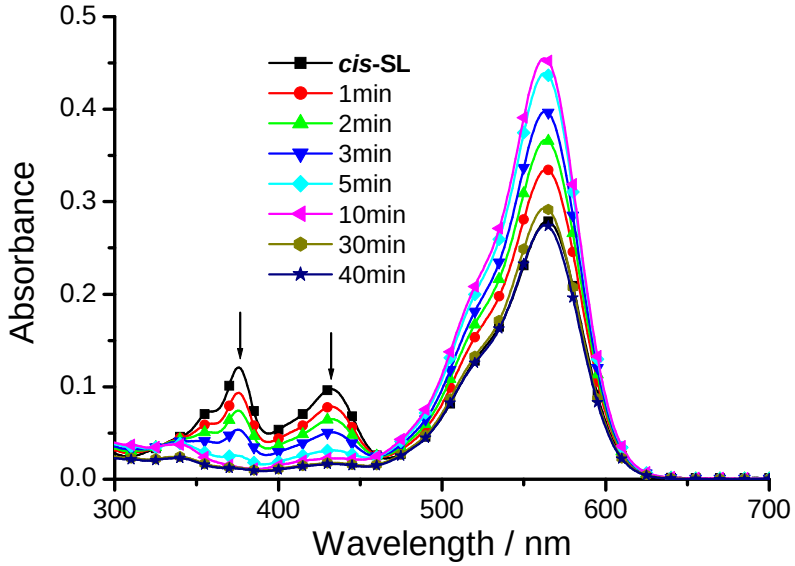

Fig. S2 Absorption spectra of ***cis*-SL** in MeCN under the irradiation of UV lamp (30 W) (the absorption first goes up (10 min) and then drops again (30–40 min). This might be caused by the decomposition of **SL** under UV irradiation). ***Cis*-SL** was almost totally and irreversibly tautomerized into ***trans*-SL**, which was confirmed by ^{1}H NMR and thin-layer chromatography.[9b]

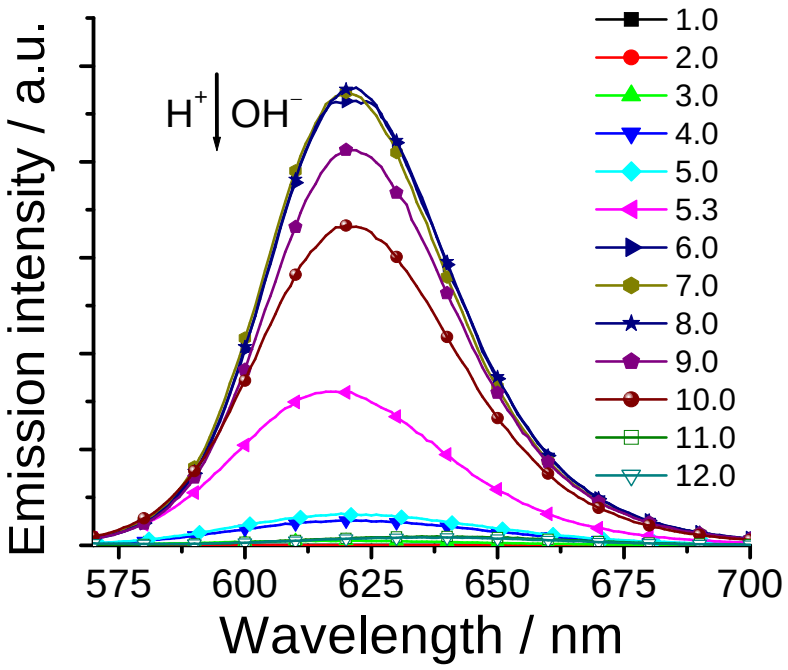

Fig. S3 Emission spectra of ***trans*-SL** (1.0×0^{-6} mol dm^{-3}, excited at 540 nm) at different pH values in MeCN.

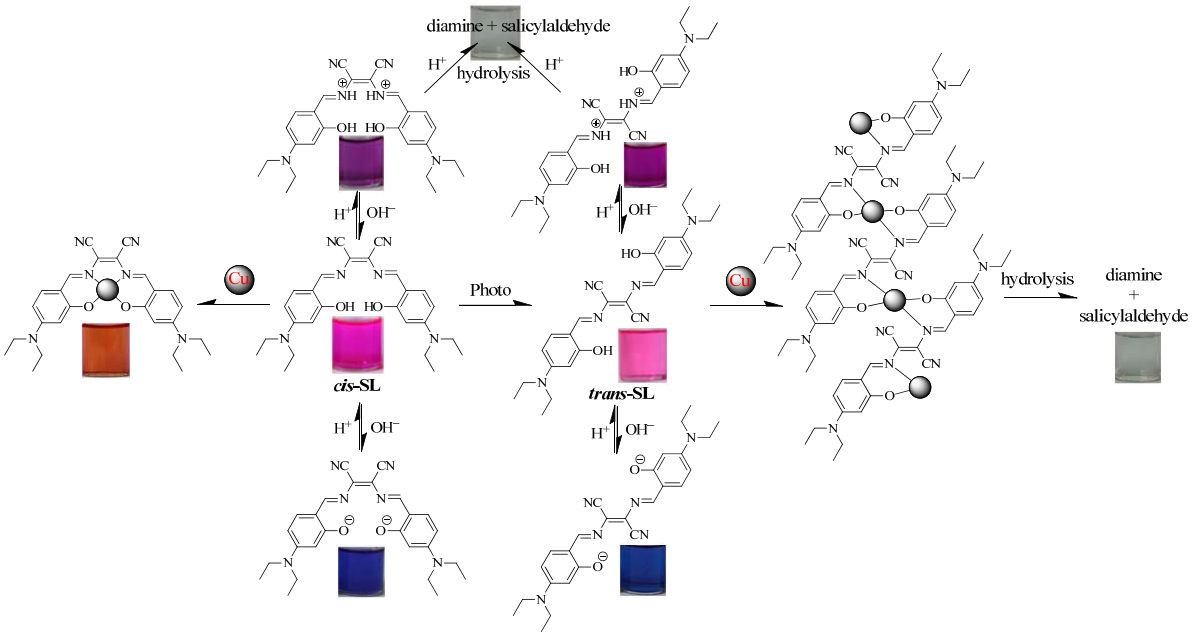

Fig. S4 Chemical structures of ***cis*-SL** and ***trans*-SL** and their proposed mechanisms for Cu^{2+} and pH probes.

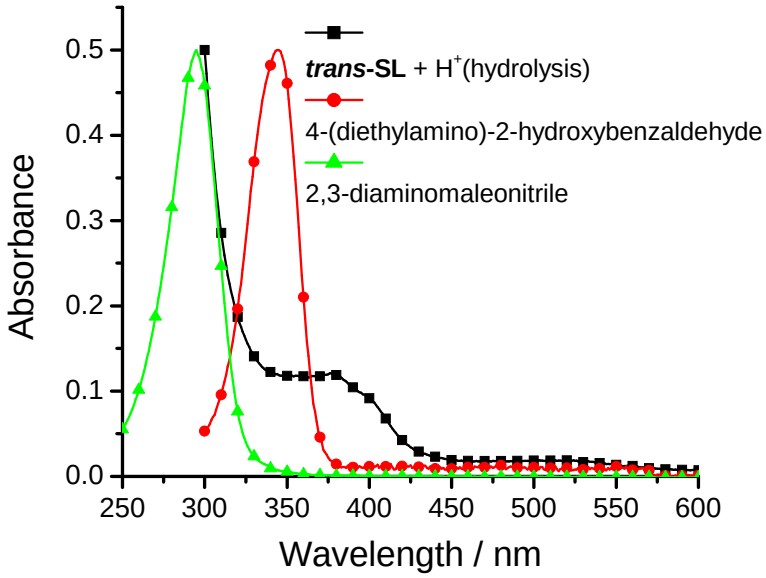

Fig. S5 Absorption spectra in MeCN at room temperature.

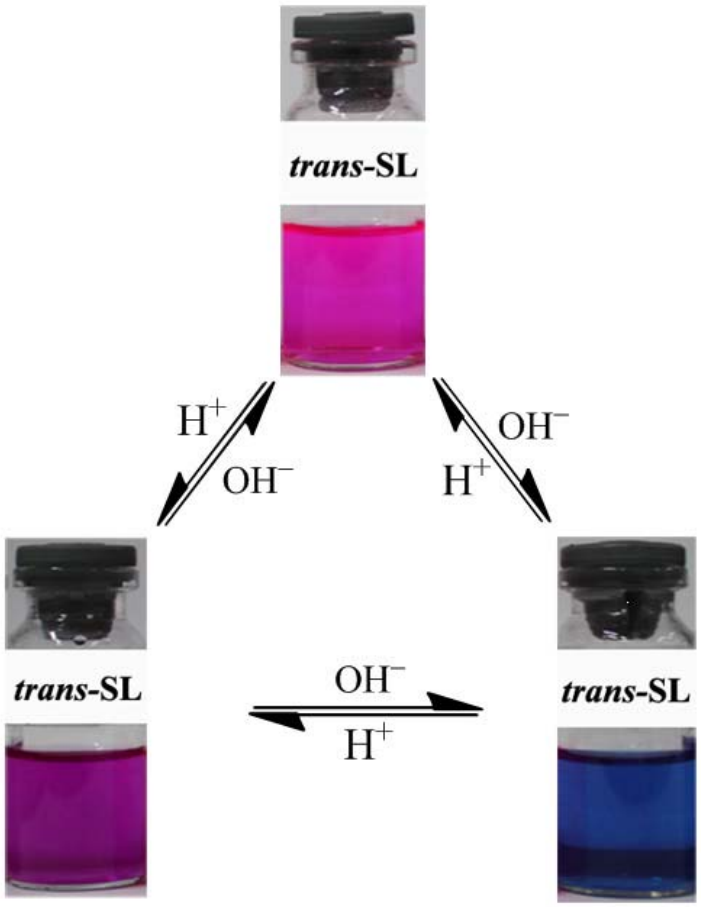

Fig. S6 Photographs of reversible color changes for ***trans*-SL** in MeCN (1.0×10^{-5} mol dm^{-3}).

Fig. S7. Photographs (top: under room light; bottom: under 360 nm UV light; L = ***trans*-SL**; 1.0×10^{-5} mol dm^{-3}; M+L = all the 18 metal ions+***trans*-SL**,).

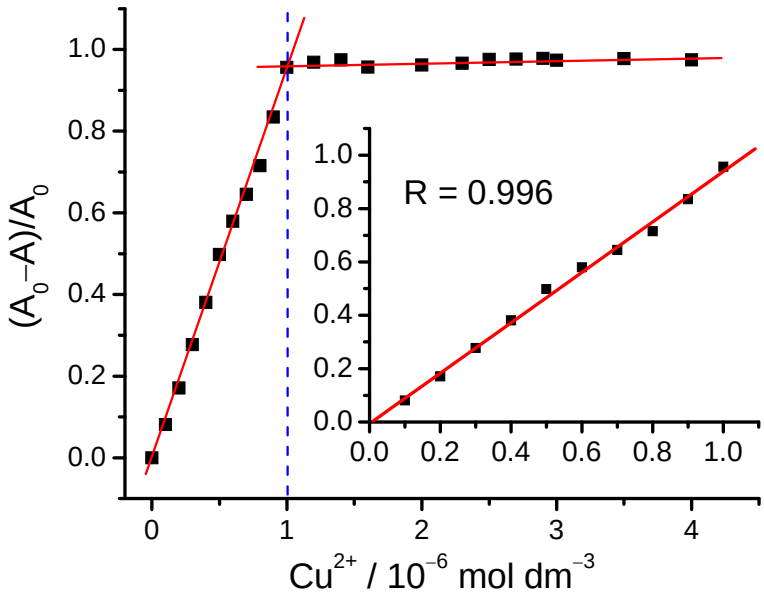

Fig. S8 Plots of $(A_0-A)/A_0$ (λ = 564 nm) as a function of Cu^{2+} concentration for ***trans*-SL** in MeCN (1.0×10^{-5} mol dm^{-3}).

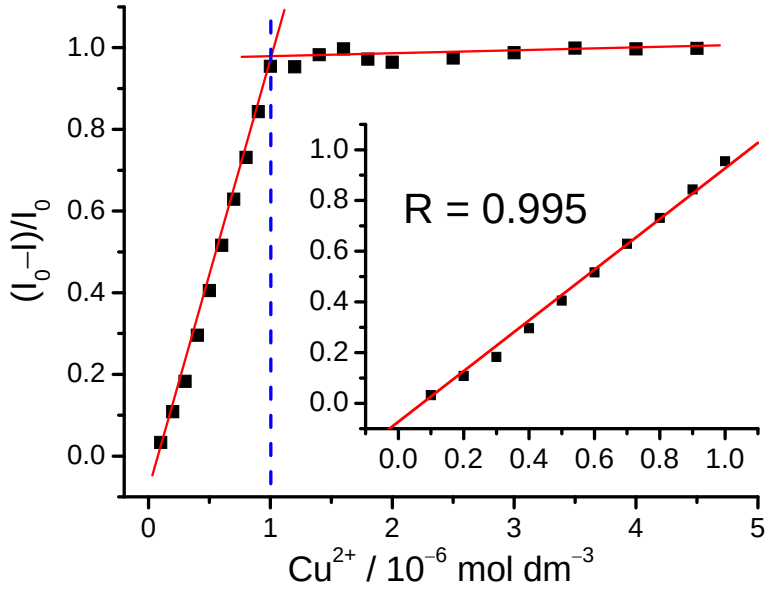

Fig. S9 Plots of $(I_0-I)/I_0$ (λ = 610 nm) as a function of Cu^{2+} concentration for ***trans*-SL** in MeCN (1.0×10^{-6} mol dm^{-3}).

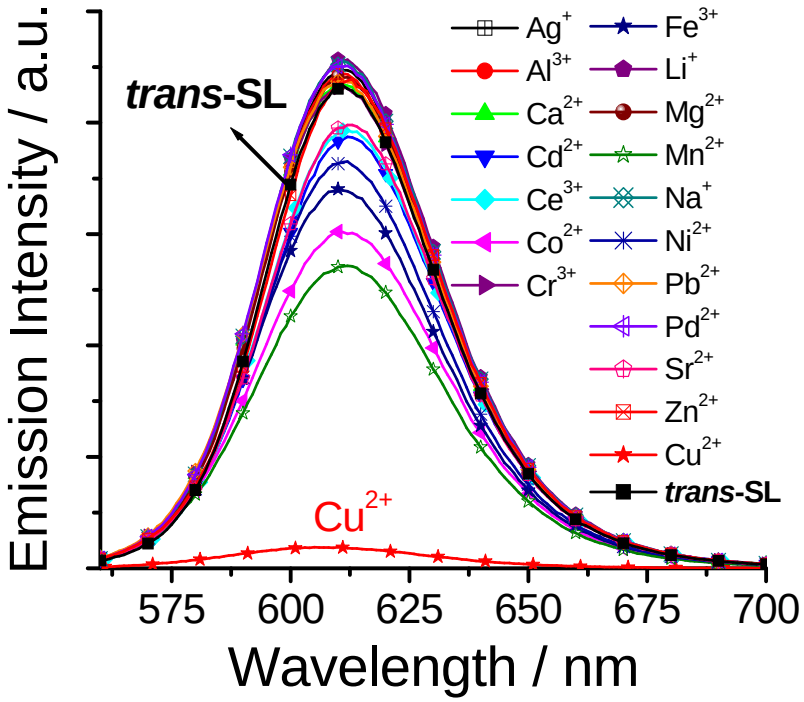

Fig. S10 Emission spectra (excited at 540 nm) of ***trans*-SL** in MeCN (1.0×10^{-6} mol dm^{-3}) upon addition of 2 equiv. of different metal ions.

Fig. S11. Photographs of ***cis*-SL** and ***trans*-SL** (from left to right: **SL**; **SL** + 1.0 equiv. of Cu^{2+}; **SL** + 1.0 equiv. of 4-(diethylamino)-2-hydroxybenzaldehyde + 1.0 equiv. of Cu^{2+}; **SL** + 1.0 equiv. of 2,3-diaminomaleonitrile + 1.0 equiv. of Cu^{2+}).

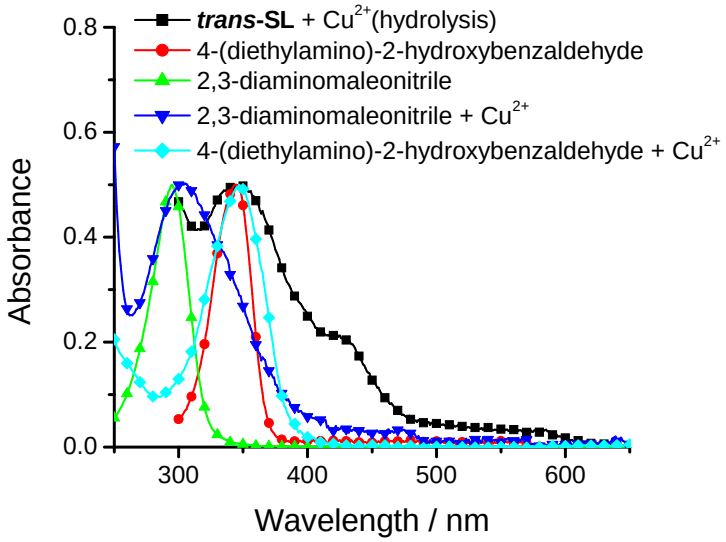

Fig. S12. Absorption spectra in MeCN at room temperature.

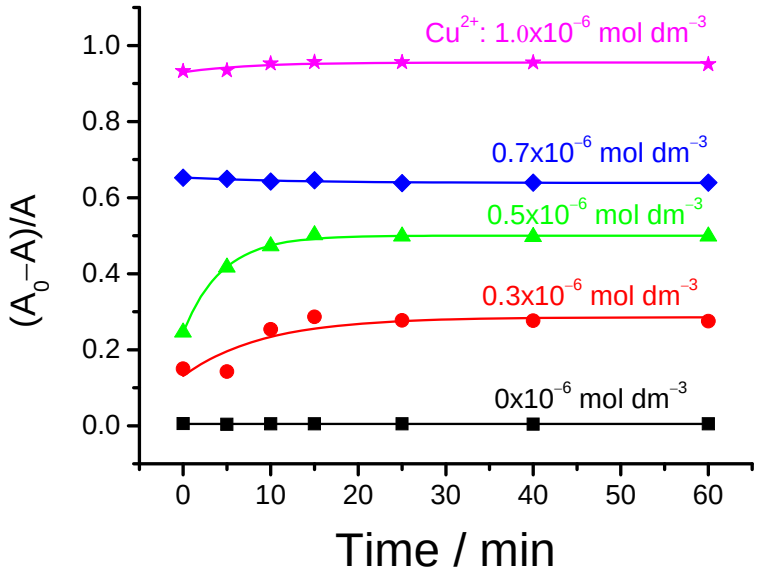

Fig. S13. Kinetics of absorption response (λ = 564 nm) rate of ***trans*-SL** in MeCN (1.0×10^{-5} mol dm^{-3}) upon addition of Cu^{2+} with different concentrations.

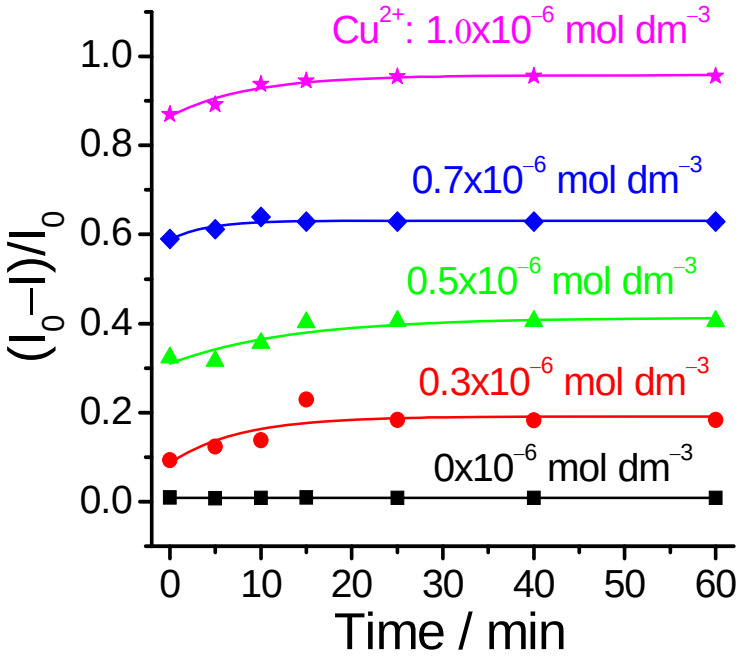

Fig. S14. Kinetics of emission response (λ = 610 nm, excited at 540 nm) rate of ***trans*-SL** in MeCN (1.0×10^{-6} mol dm^{-3}) upon addition of Cu^{2+} with different concentrations.

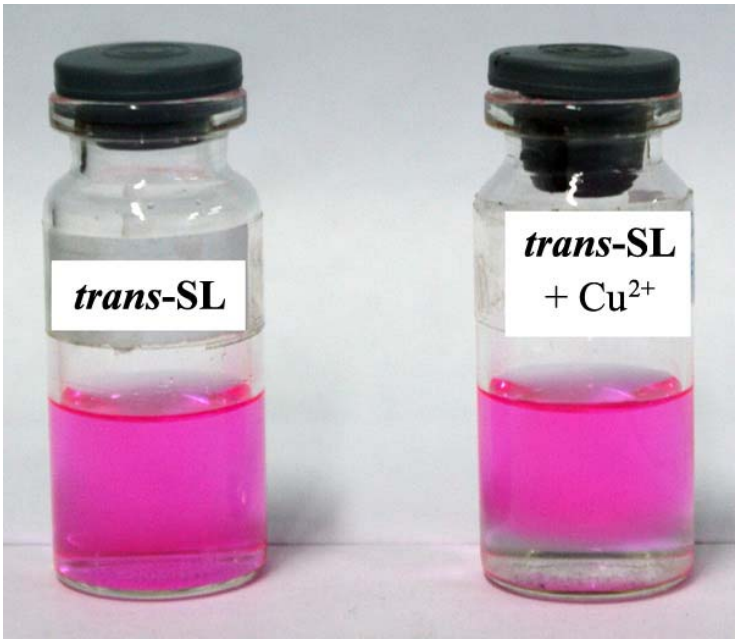

Fig. S15. Photographs of ***trans*-SL** (1.0×10^{-5} mol dm^{-3} in MeCN) without and with adding one drop (5×10^{-6} dm^{-3}) of Cu^{2+} (2.0×10^{-2} mol dm^{-3} in H_2O) immediately.

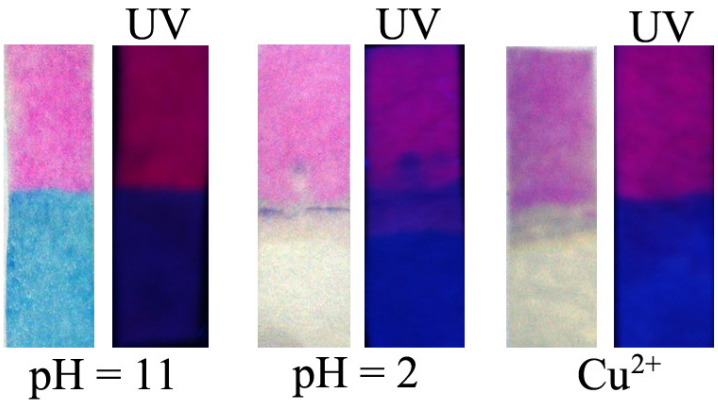

Fig. S16. Colour changes (left: under room light; right: under 360 nm UV light) of homemade test paper based on ***trans*-SL** after dipping half way into an aqueous medium containing H^+ (pH = 2), OH^- (pH = 11), or Cu^{2+} (1.0×10^{-5} mol dm^{-3}).

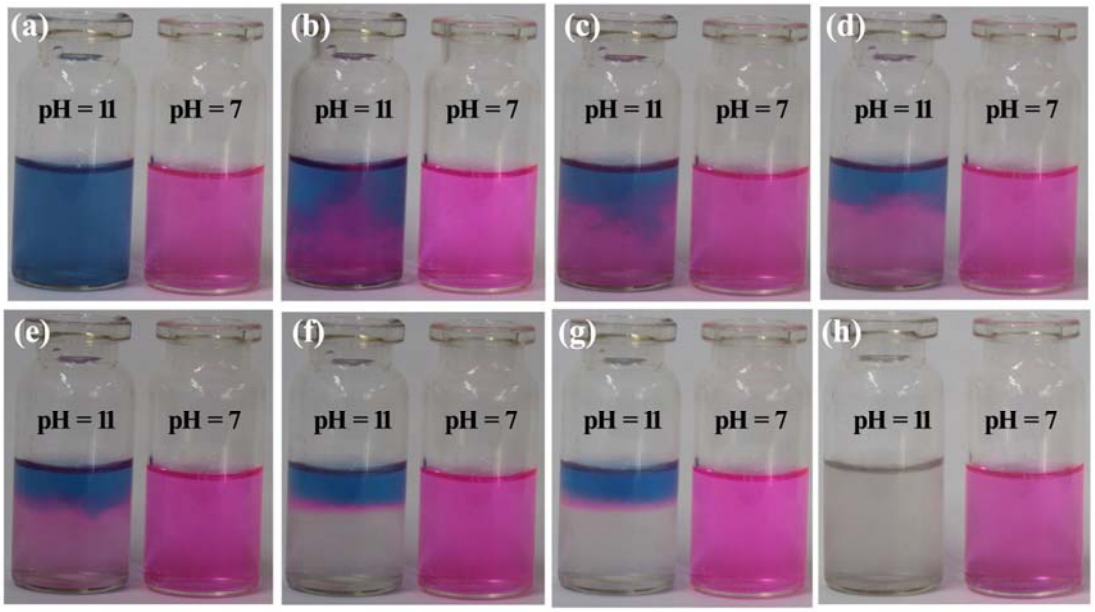

Fig. S17 Photographs of ***trans*-SL** (1.0×0^{-5} mol dm^{-3}) in MeCN with (left: pH = 11) and without (right: pH = 7) adding Cu^{2+} (a: before adding; b: adding immediately; c: 2 seconds after adding; d: 5 seconds after adding; e: 10 seconds after adding; f: 30 seconds after adding; g: 120 seconds after adding; h: shaking after step g). At pH value of 2, ***trans*-SL** would be decomposed through hydrolysis and thus formed colorless diamine and aldehyde precursors. If further adding Cu^{2+} to the above colorless solution, there is no obvious change. At pH value of 7, adding Cu^{2+} to ***trans*-SL** solution would undergo Cu^{2+}-promoted hydrolysis, as shown in Fig. S7. At pH value of 11, ***trans*-SL** would deprotonated, resulting in a color change from pink into blue (a). If further adding Cu^{2+} to the above blue solution, the color would reverse back into pink at first and would subsequently change into colorless (a–h). This is caused by the fact that, at first, adding Cu^{2+} would lead to the decrease of pH value and then the deprotonated ***trans*-SL** (blue color) would reverse back (pink color). However, the solution color would change into colorless over time by undergoing Cu^{2+}-promoted hydrolysis.