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Supporting Information

Crystallization-enhanced emission through hydrogen-bond interactions in blends containing hydroxyl-functionalized azine and poly(4-vinyl pyridine)

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1,2-bis(2,4-dihydroxybenzylidene)hydrazine (CN4OH)

To a solution of 2,4-dihydroxybenzaldehyde (1 g, 7.24 mmol) in ethanol (50 mL), hydrazine hydrate (0.21 g, 3.45 mmol) was added dropwise with vigorous stirring at room temperature. After the addition, the stirred mixture was allowed to react at room temperature overnight, The precipitate was then filtered and washed with ethanol three times (3 x 50 mL). After drying final product was obtained as yellow solid (0.7g,75 % yield) ^{1}H NMR (500 MHz, d_6-DMSO): δ 6.32 (d, 2H, H_f), 6.4 (dd, 2H, H_e), 7.41 (d, 2H, H_d), 8.76 (s, 2H, H_c), 10.18 (s, 2H, H_b), 11.38 (s, 2H, H_a) (Figure S1). ^{13}C NMR (500 MHz, d_6-DMSO) δ 103.0 (C_g), 108.8 (C_f), 110.8 (C_e), 133.6 (C_d), 161.5 (C_c), 162.6 (C_b), 162.9 (C_a) (Figure S2). MS m/e: calcd for $C_{14}H_{12}N_2O_4$, 272.08; found,273.086 (M^+). Anal. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; N, 10.29; O, 23.51. Found: C, 61.53; H, 4.80; N, 10.25; O, 23.42.

1,2-bis(2-hydroxybenzylidene)hydrazine (CN2OH)

To a solution of 2-hydroxybenzaldehyde (1 g, 8.2 mmol) in ethanol (50 mL), hydrazine hydrate (0.24 g, 3.9 mmol) was slowly added with vigorous stirring at room temperature. The mixtures were then stirred overnight and the resulting precipitates were filtered. The resulting yellow solid was further washed by ethanol three times (3 x 50 mL). After drying, final product (0.72 g, 77% yield) was obtained. ^{1}H NMR (500

MHz, $CDCl_3$) δ 6.96 (t, 2H, H_f), 7.04 (d, 2H, H_e), 7.36 (t, 2H, H_d), 7.41 (d, 2H, H_c), 8.71 (s, 2H, H_b), 11.37 (s, 2H, H_a) (Figure S3). ^{13}C NMR (500 MHz, $CDCl_3$) δ 117.7 (C_g), 117.9 (C_f), 120.8 (C_e), 133.2 (C_d), 133.4 (C_c), 160.6 (C_b), 165.5 (C_a) (Figure S4). MS m/e: calcd for $C_{14}H_{12}N_2O_2$,240.09; found,241.097 (M^+). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66; O, 13.32. Found: C, 69.70; H, 5.43; N, 11.61; O, 13.26.

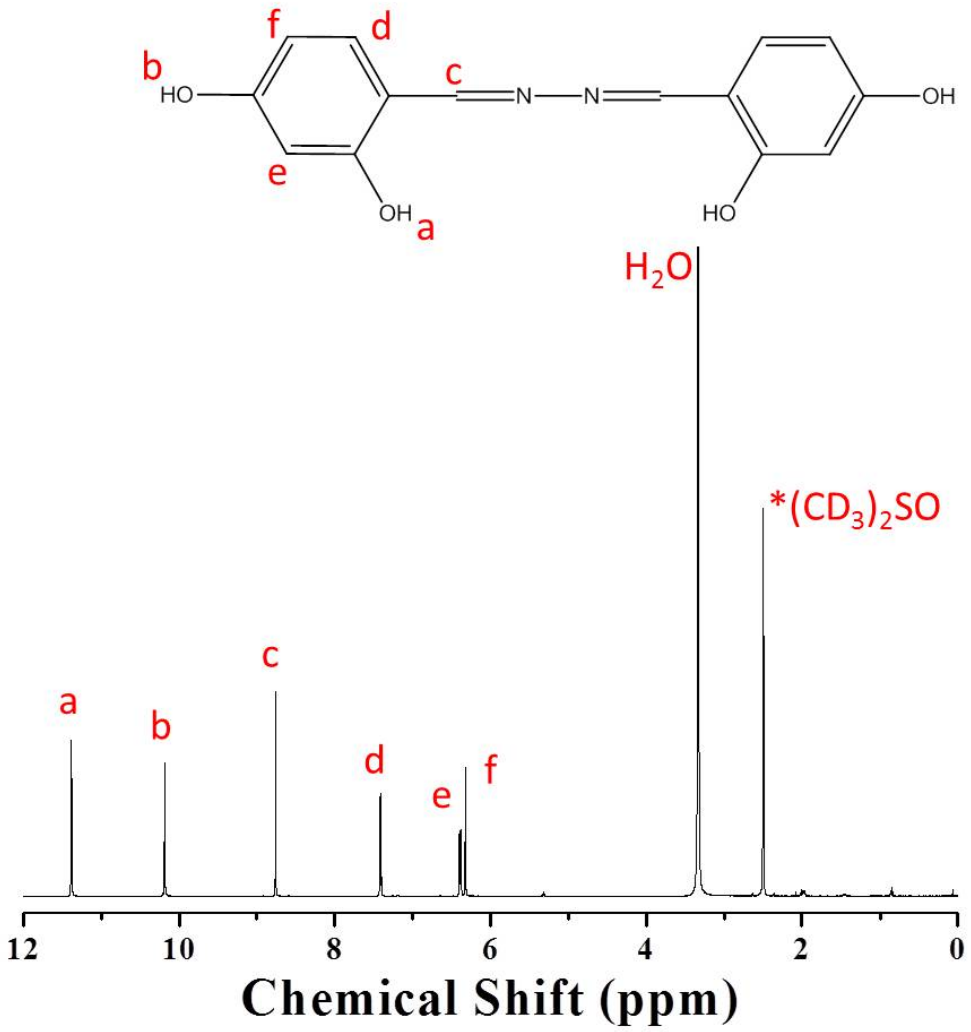

Figure S1 ^{1}H NMR of CN4OH (d_6-DMSO).

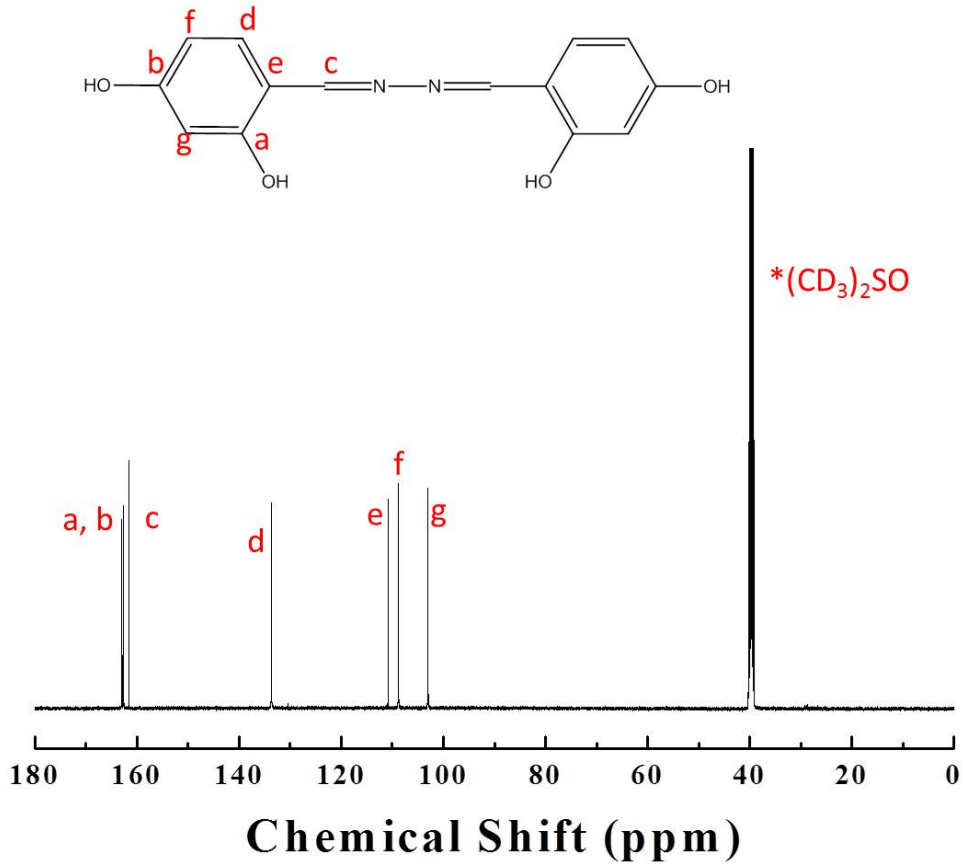

Figure S2 ^{13}C NMR of CN4OH (d_6-DMSO).

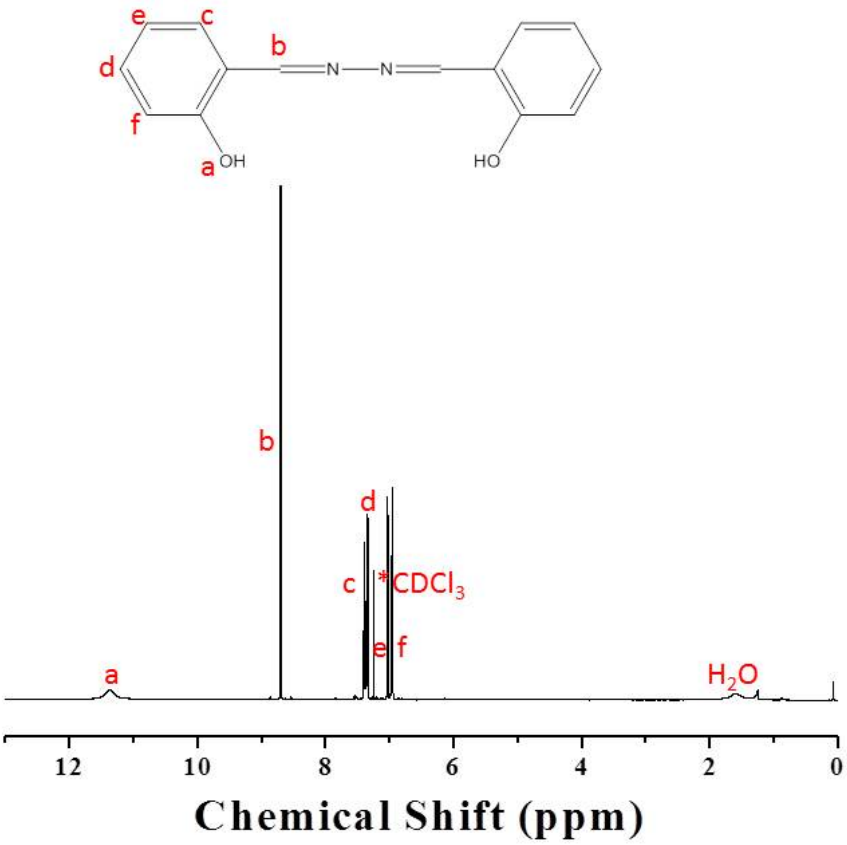

Figure S3 ^{1}H NMR of CN2OH ($CDCl_3$).

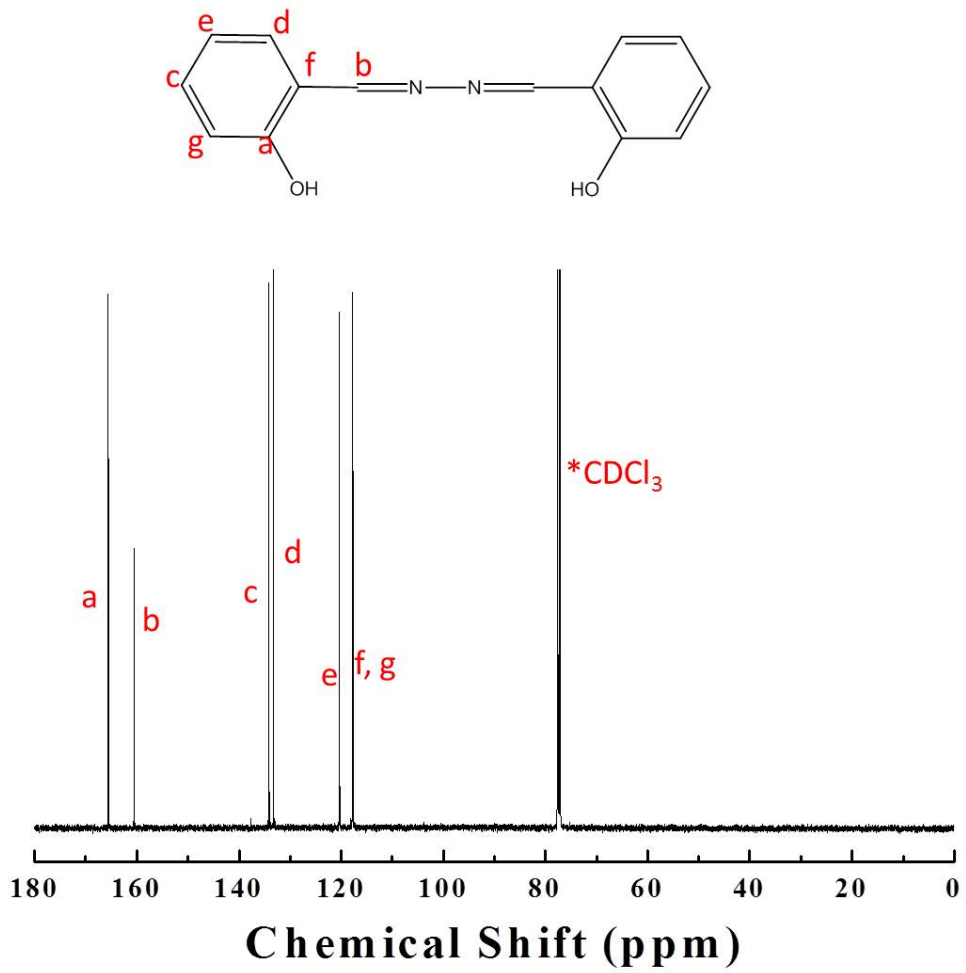

Figure S4 ^{13}C NMr of CN2OH ($CDCl_3$).

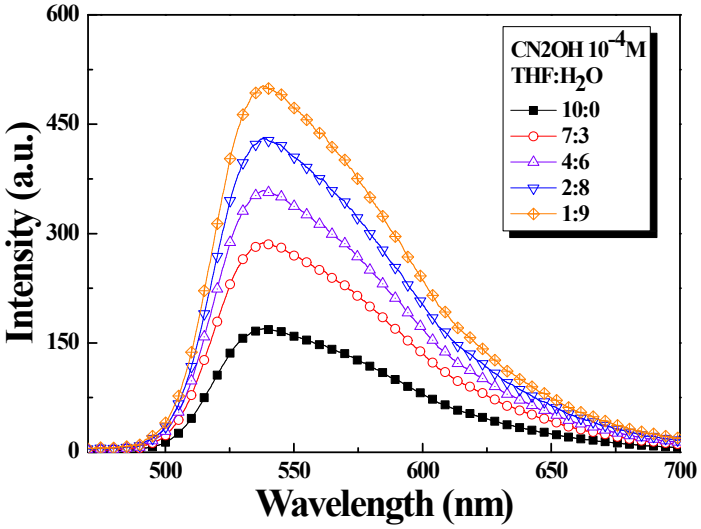

Figure S5 Solution (10^{-4} M) PL emission spectra of CN2OH in THF containing different amounts of water (λ_{ex} = 360 nm).

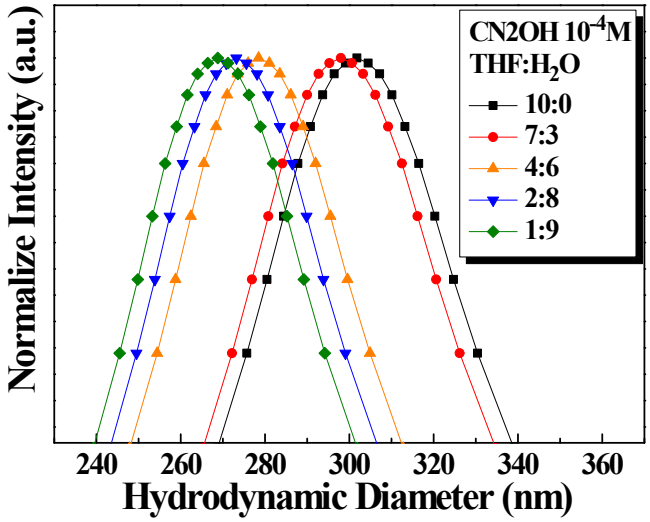

Figure S6 Histograms of hydrodynamic diameters of CN2OH in THF containing different amounts of water.

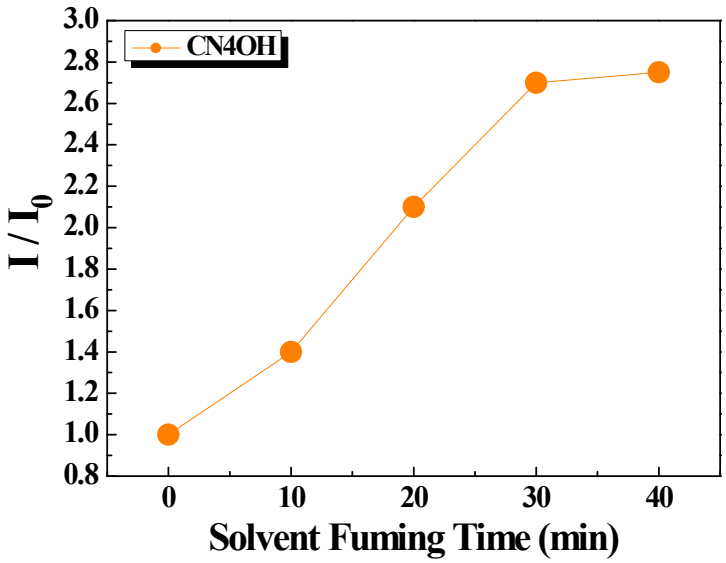

Figure S7 Variation of the emission intensity ratio I/I_0 during solvent-annealing of CN4OH (I and I_0 are the peak intensities after and before solvent-annealing, respectively) (excited at 365 nm).

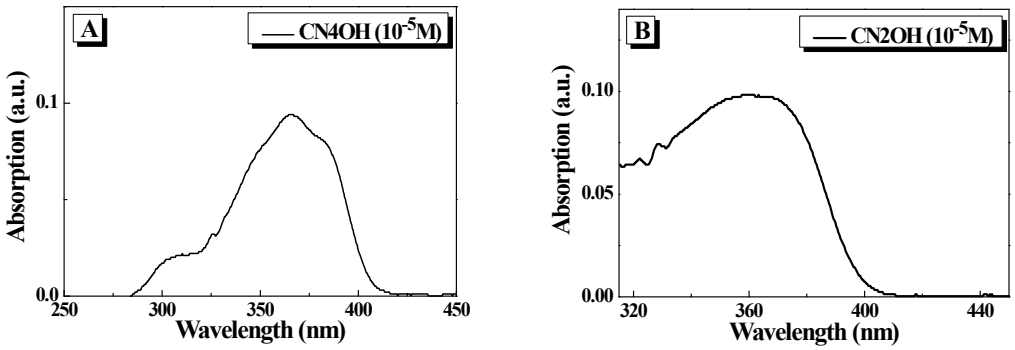

Figure S8 Solution UV-Vis spectra of (A) CN4OH (10^{-5} M) and (B) CN2OH (10^{-5} M) in THF.