STRUCTURAL
CHEMISTRY

Volume 74 (2018)

Supporting information for article:

Synthesis, structural characterization and fluorescence enhancement of chromophore-modified polyoxometalates

Gizaw D. Fura, Yong Long, Jun Yan, Wei Chen, Chang-Gen Lin and Yu-Fei Song

Synthesis of $C_{14}H_9CH_2NHC(CH_2OH)_3$ (**5**): The desired compound 5 was synthesized according to published method (Song *et al.*, 2007) Yield: 56.4 %. ^{1}H-NMR (DMSO-d_6, ppm): δ = 1.71 (s, 1H), 3.60 (d, 6H), 4.51 (t, 3H), 4.72 (s, 2H), 7.52 (m, 4H), 8.06 (d, 2H), 8.49 (d, 2H), 8.52 (s, 1H). ^{13}C-NMR (DMSO-d_6, ppm): δ = 132.89, 131.10, 129.86, 128.70, 126.33, 125.87, 125.04, 124.71, 61.61, 60.31, 38.04. ESI-MS (positive mode, CH_3OH): 311.71 ($[M+H]^+$).

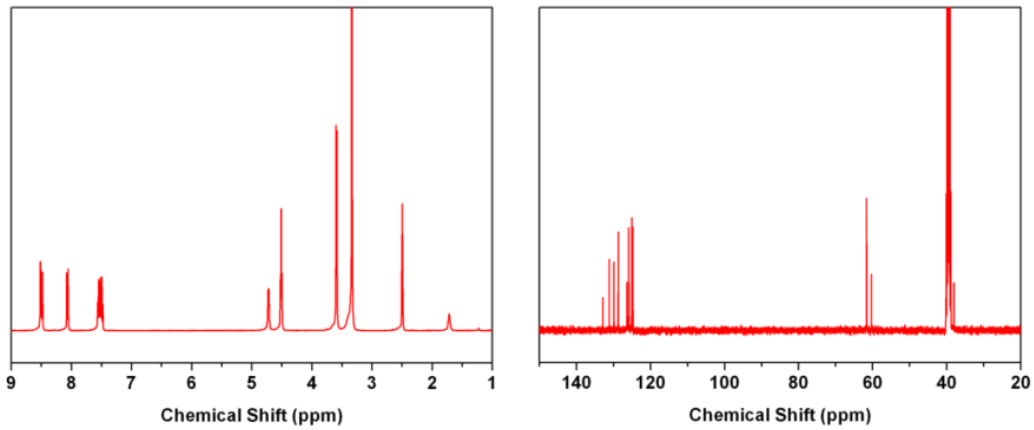

Figure S1 ^{1}H-NMR (left) and ^{13}C-NMR (right) spectra of **5**.

Synthesis of $C_{13}H_9CH_2NHC(CH_2OH)_3$ (**6**): Yield: 81.8 %. ^{1}H-NMR (DMSO-d_6, ppm): δ = 3.60 (d, 6H), 4.51 (t, 3H), 4.72 (s, 2H), 7.33 (t, 1H), 7.40 (t, 1H), 7.49 (d, 1H), 7.61 (d, 1H), 7.70 (s, 1H), 7.91 (m, 2H). ^{13}C-NMR (DMSO-d_6, ppm): δ = 143.15, 142.93, 140.67, 128.46, 126.90, 126.79, 125.87, 126.46, 125.19, 61.06, 59.19, 58.68, 45.60, 36.28. ESI-MS (positive mode, CH_3OH): 300.51 ($[M+H]^+$).

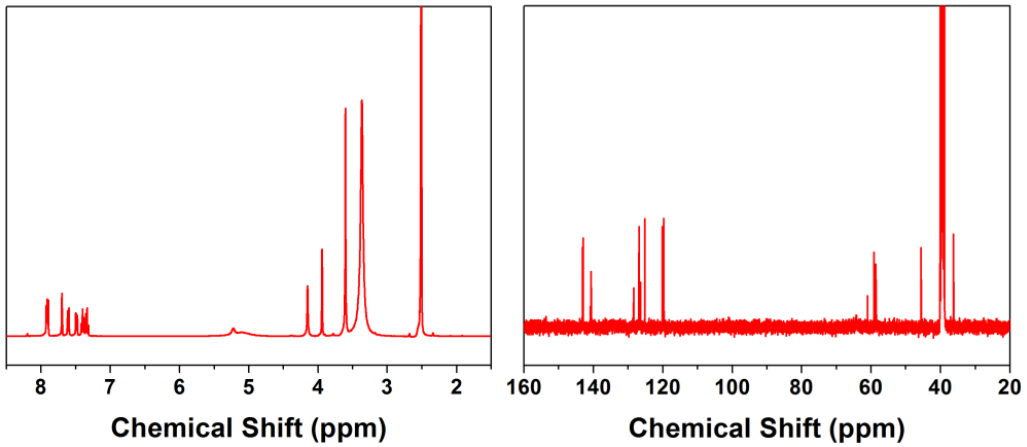

Figure S2 ^{1}H-NMR (left) and ^{13}C-NMR (right) spectra of **6**.

Synthesis of $C_{10}H_7CH_2NHC(CH_2OH)_3$ (**7**): Yield: 79.6 %. ^{1}H-NMR (DMSO-d_6, ppm): δ = 3.68 (d, 6H), 4.37 (s, 2H), 5.35 (m, 3H), 7.56 (m, 2H), 7.68 (t, 1H), 7.95 (m, 3H), 8.05 (m, 1H). ^{13}C-NMR (DMSO-

d_6, ppm): δ = 132.69, 132.51, 131.06, 129.38, 127.87, 127.78, 127.73, 127.56, 126.49, 126.39, 66.00, 57.74, 45.54. ESI-MS (positive mode, CH_3OH): 262.44 ($[M+H]^+$).

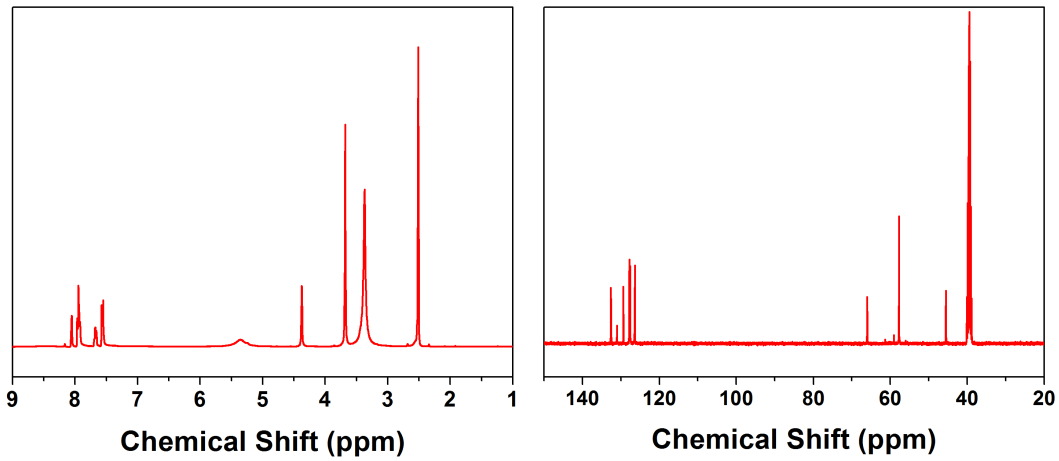

Figure S3 ^{1}H-NMR (left) and ^{13}C-NMR (right) spectra of **7**.

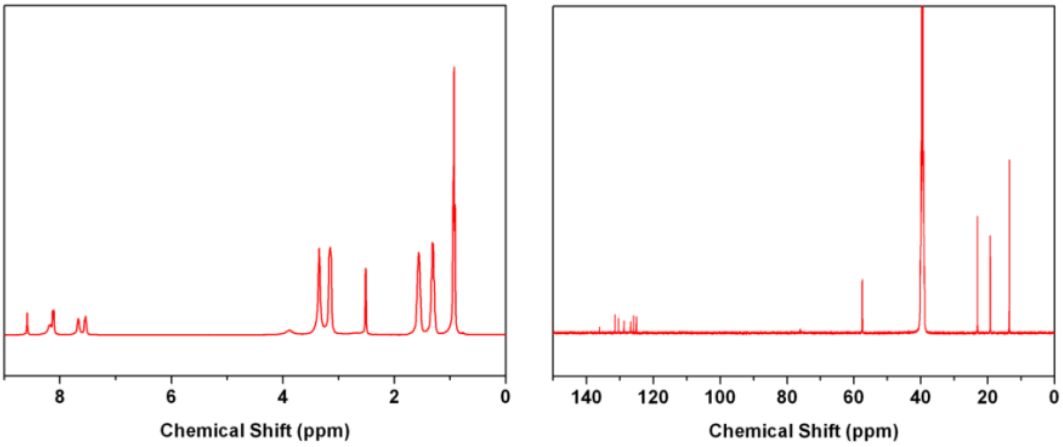

Figure S4 ^{1}H-NMR (left) and ^{13}C-NMR (right) spectra of **1**.

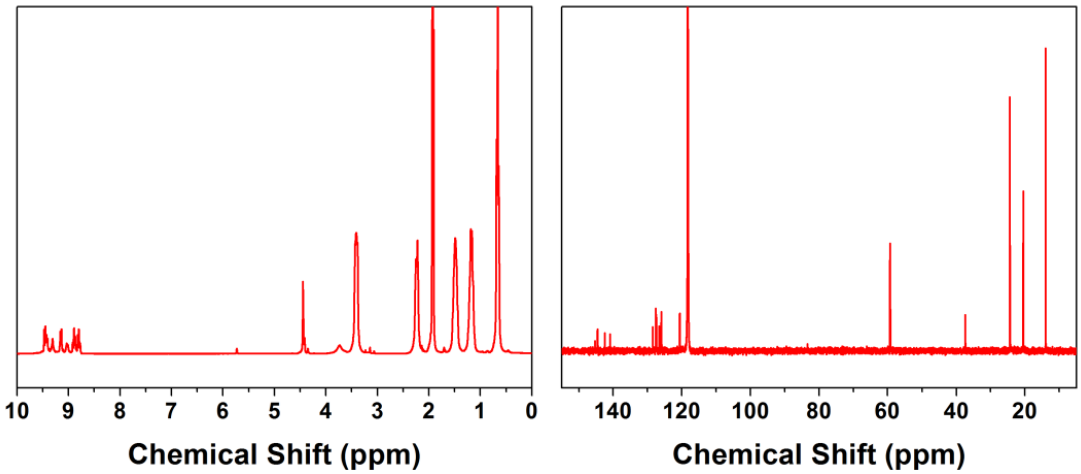

Figure S5 ^{1}H-NMR (left) and ^{13}C-NMR (right) spectra of **2**.

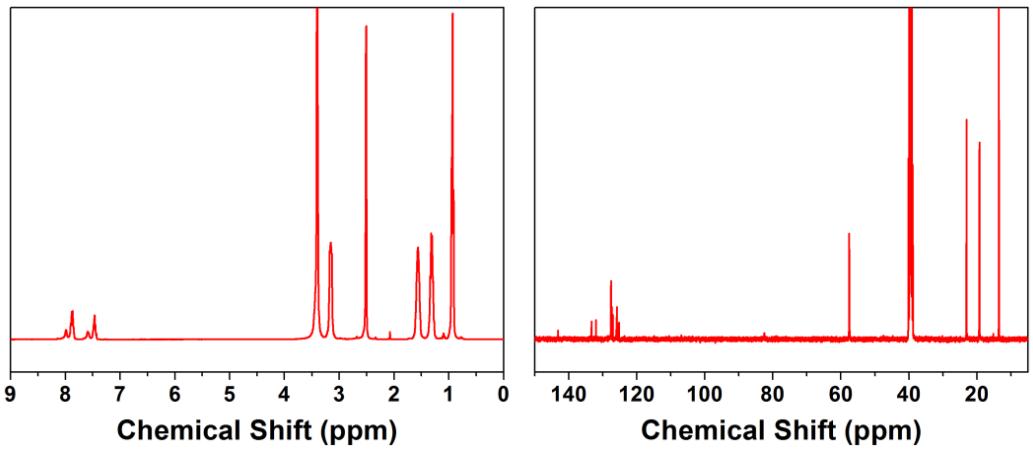

Figure S6 ^{1}H-NMR (left) and ^{13}C-NMR (right) spectra of **3**.

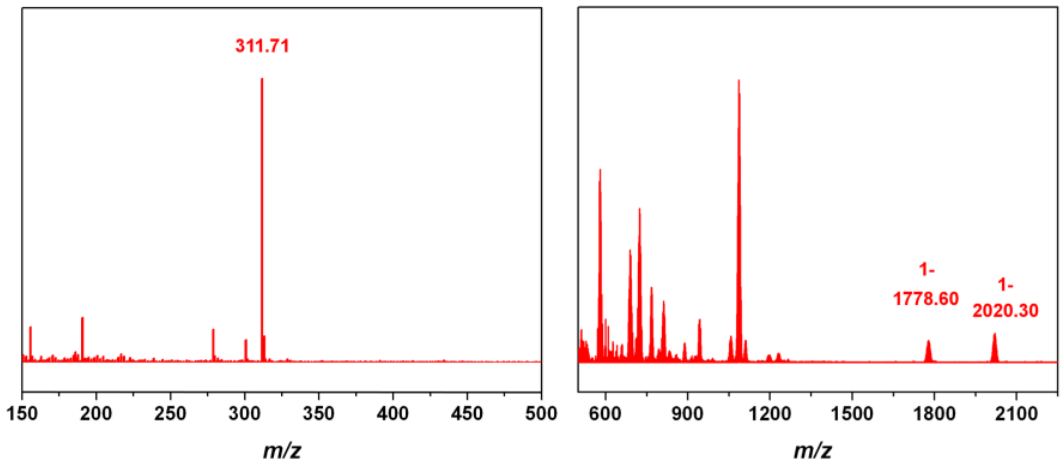

Figure S7 ESI-MS spectra of **5** (left) in positive mode and **1** (right) in negative mode.

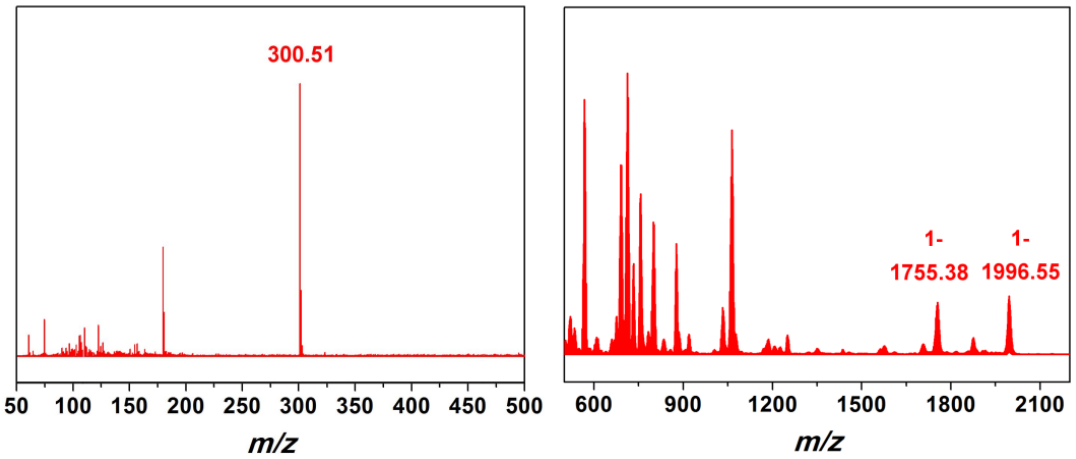

Figure S8 ESI-MS spectra of **6** (left) in positive mode and **2** (right) in negative mode.

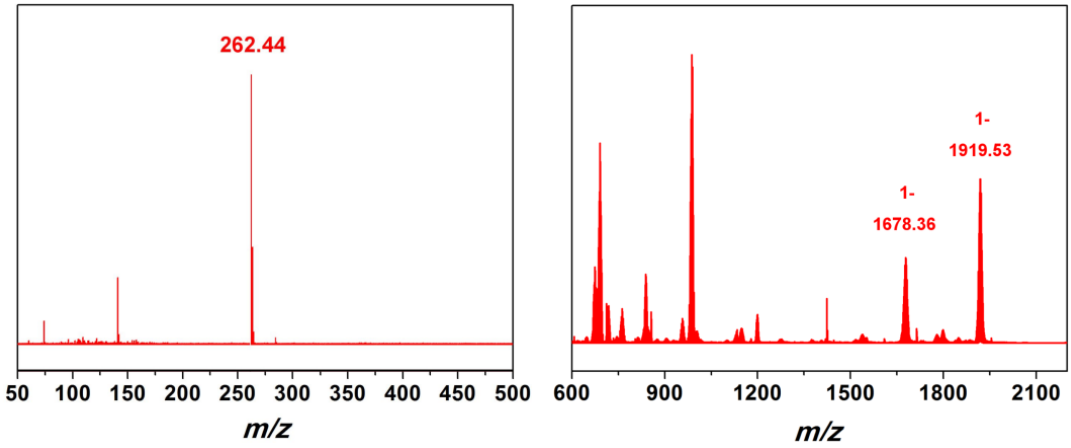

Figure S9 ESI-MS spectra of **7** (left) in positive mode and **3** (right) in negative mode.

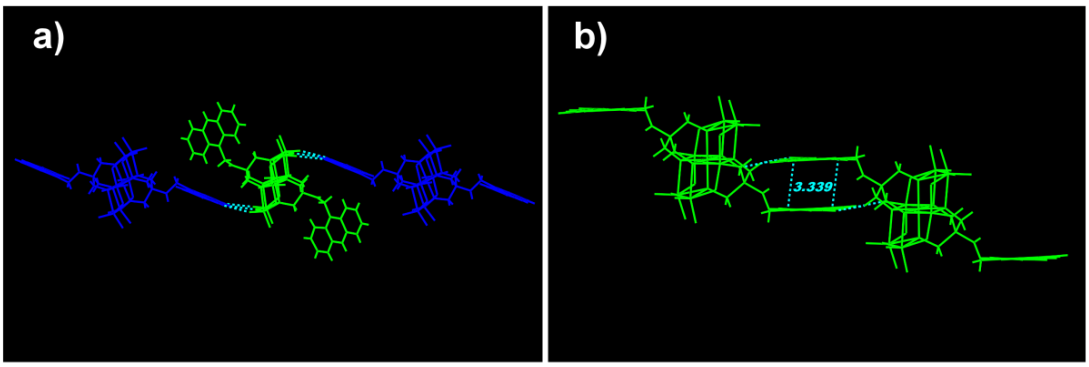

Figure S10 a) Hydrogen bonding and b) π-π stacking of **1** in crystal structure. TBA cations and acetonitrile molecules have been omitted for clarity.

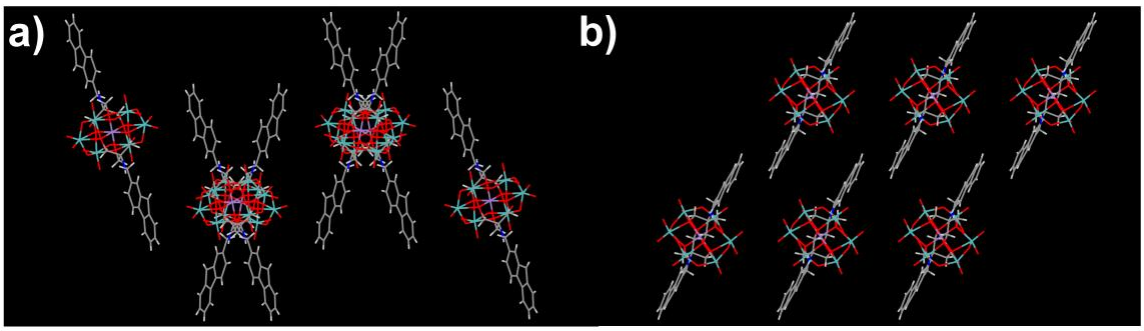

Figure S11 X-ray crystal packing structure of **2** a) viewed from 'a^*' direction, and b) viewed from 'b' direction. TBA cations have been omitted for clarity (Mn purple, Mo light teal, O red, N blue, C grey, H white).

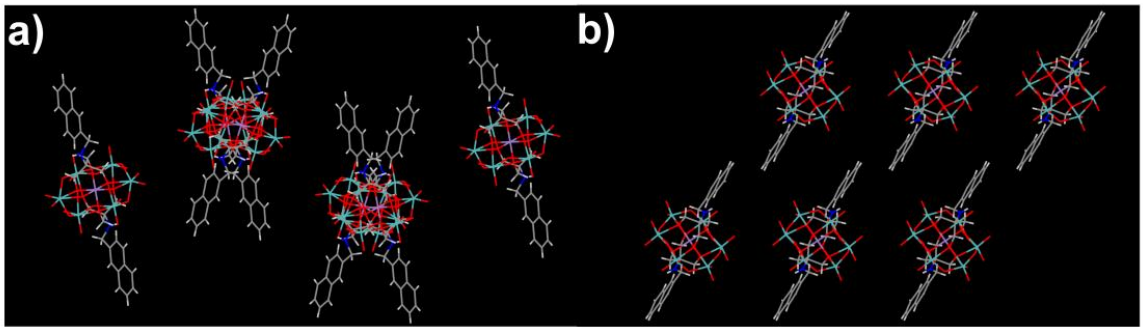

Figure S12 X-ray crystal packing structure of **3** a) viewed from 'a^*' direction, and b) viewed from 'b' direction. TBA cations have been omitted for clarity (Mn purple, Mo light teal, O red, N blue, C grey, H white).

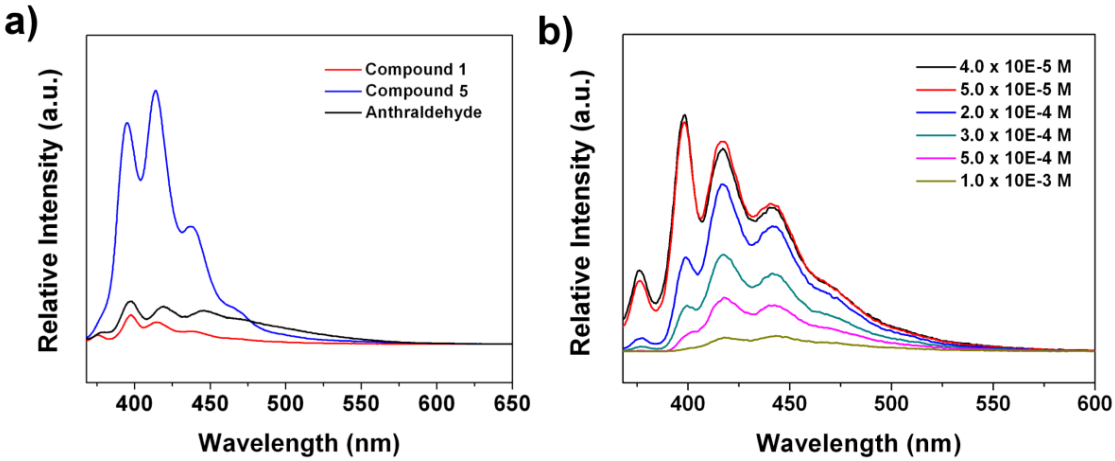

Figure S13 Fluorescence spectra of a) **1**, **5**, and anthraldehyde in DMF solutions, and b) **1** at different concentritions in DMF solution. Chromophore concentration: 1×10^{-4} M.

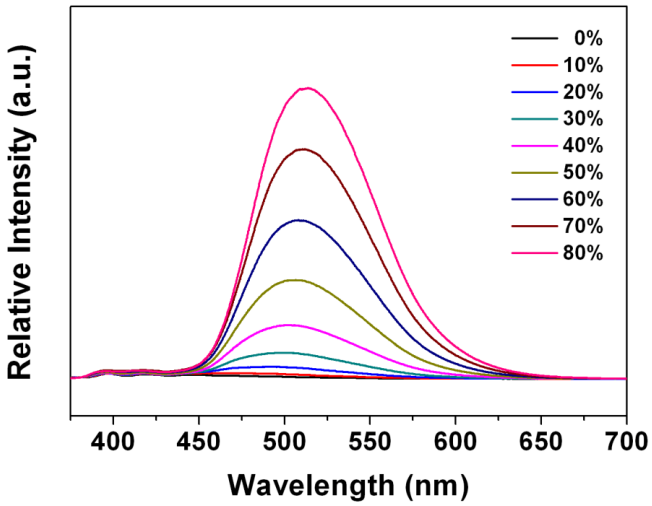

Figure S14 Fluorescence spectra of 9-anthraldehyde in H_2O/DMF mixture with different H_2O contents (v%). Chromophore concentration: 1×10^{-4} M. As can be observed, when H_2O is added into DMF solution of 9-anthraldehyde, a broad excimer peak centered at λ = 490.2 nm appears and gradually

shifts to 515.0 nm. The formation of excimer is considered to be detrimental and induces the quenching process.

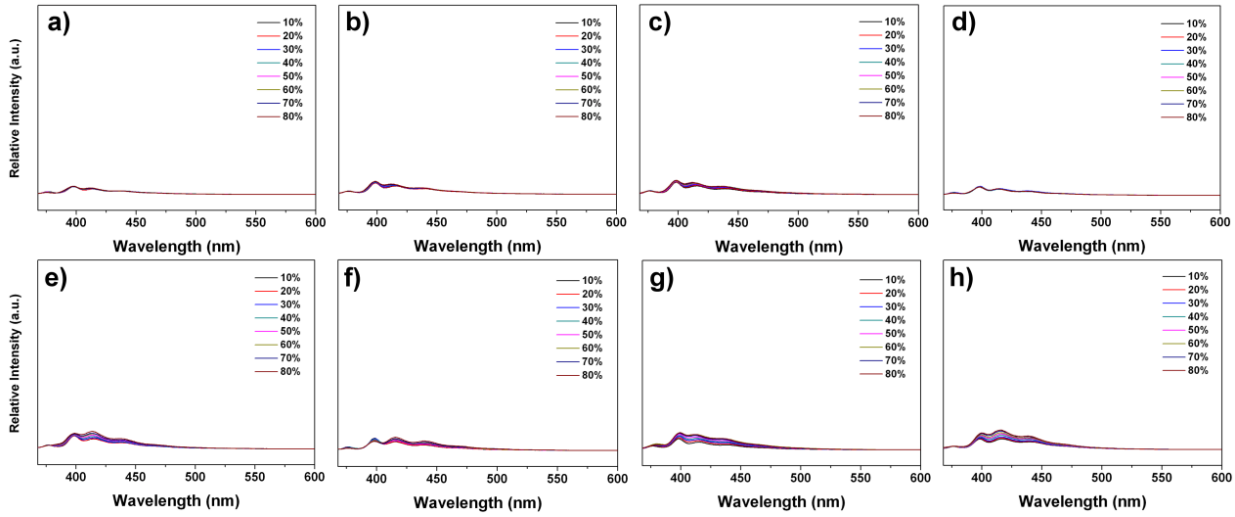

Figure S15 Fluorescence spectra of **1** in a) CH_3OH/DMF, b) C_2H_5OH/DMF, c) *i*-Propanol/DMF, d) Acetone/DMF, e) Dichloromethane/DMF, f) Chloroform/DMF, g) THF/DMF, and h) Toluene/DMF mixtures (v%). Chromophore concentration: 1×10^{-4} M.

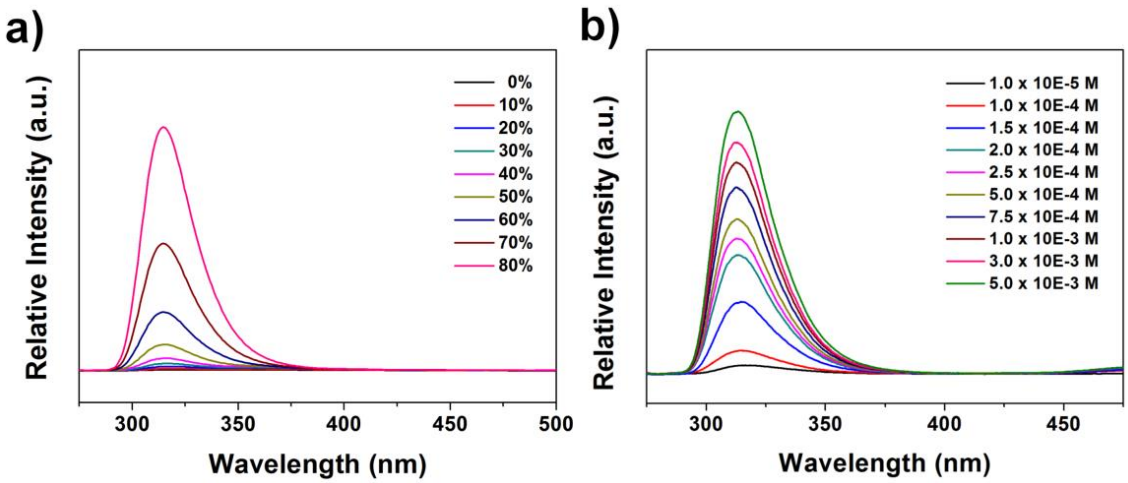

Figure S16 Fluorescence spectra of **2** in a) H_2O/DMF with different H_2O contents (v%), and b) HCl/DMF mixture (HCl content: 10 v%) with different HCl concentrations. Chromophore concentration: 1×10^{-4} M.

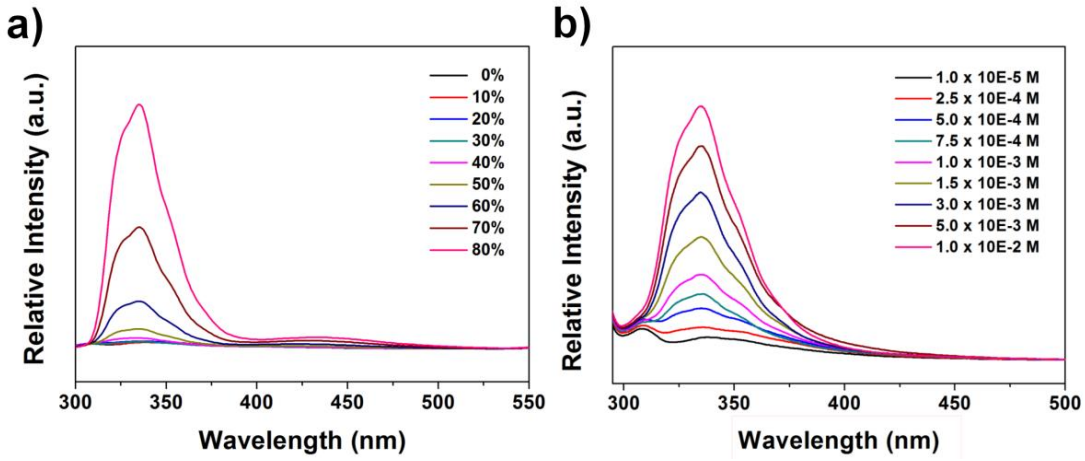

Figure S17 Fluorescence spectra of **3** in a) H_2O/DMF with different H_2O contents (v%), and b) HCl/DMF mixture (HCl content: 10 v%) with different HCl concentrations. Chromophore concentration: 1×10^{-4} M.

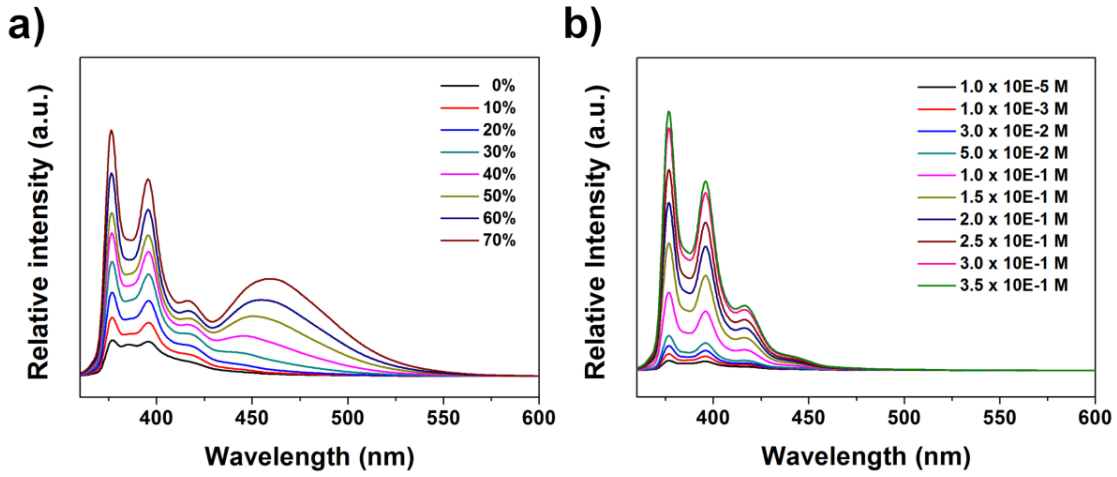

Figure S18 Fluorescence spectra of **4** in a) H_2O/DMF with different H_2O contents (v%), and b) HCl/DMF mixture (HCl content: 10 v%) with different HCl concentrations. Chromophore concentration: 1×10^{-4} M.