Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information For:

Rational Design of a Functionalized Aluminum Metal-Organic Framework as a Turn-Off Fluorescence Sensor for *α*-Ketoglutaric Acid

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Materials and Characterization Methods

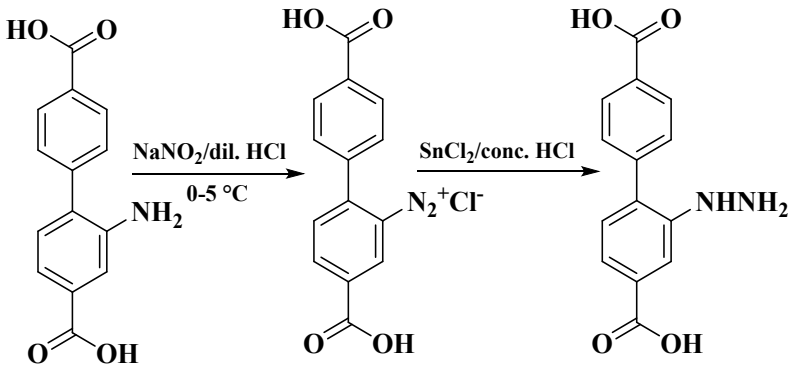
The hydrazinyl functionalized biphenyl-4,4′-dicarboxylic acid linker ($H_2BPDC\text{-}N_2H_3$) was synthesized by following the reported procedure[1] with few modifications. The synthesis and characterization (Figures S1-S4) details of the linker are presented in Supporting Information. All the chemicals were purchased from commercial sources and used without further purification. Fourier transform infrared spectroscopy data were recorded in the region 400-4000 cm^{-1} at room temperature with the Perkin Elmer Spectrum Two FT-IR spectrometer. The following indications were used to indicate the corresponding absorption bands: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh) and broad (br). Thermogravimetric (TG) experiments were carried out with a heating rate of 10 °C min^{-1} under flow of argon using a SDT Q600 thermogravimetric analyzer. XRPD data were collected in transmission mode using a Bruker D2 Phaser X-ray diffractometer (30 kV, 10 mA) using Cu-Kα (λ = 1.5406 Å) radiation. The EDX experiments were carried out with a Hitachi S3400N SEM-EDX equipment. The surface morphology of the materials was analyzed via field-emission scanning electron microscopy (FE-SEM) experiments using a Zeiss Supra 55VP SEM-EDX (SEM = scanning electron microscope) equipment. The UV-Vis spectra were measured with a PerkinElmer Lambda 25 UV-Vis spectrometer. An Edinburgh Instrument Life-Spec II equipment was used to measure the fluorescence lifetimes by employing time-correlated single-photon counting (TCSPC) procedure. The N_2 sorption experiments were calculated on a Quantachrome Autosorb iQMP gas sorption analyzer at -196 °C. Fluorescence emission studies were performed at room temperature using a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. The compound was directly activated at 160 °C for 24 h under dynamic vacuum.

Synthesis of $H_2BPDC\text{-}N_2H_3$ linker:

The synthesis of the $H_2BPDC\text{-}N_2H_3$ linker involves two steps (Scheme 1). It was synthesized by using 2-amino-[1,1'-biphenyl]-4,4'-dicarboxylic acid ($H_2BPDC\text{-}NH_2$) as the starting material.

First step: $H_2BPDC\text{-}NH_2$ linker (515 mg, 2 mmol) was dissolved in 20 mL of conc. HCl and stirred at 0 °C until complete dissolution was achieved. After that an aqueous solution of $NaNO_2$ (1.15 g, 16.66 mmol in 10 mL water) was added slowly to the mixture and kept under stirring conditions at 0 °C for 2 h.

Second step: After completion of 2 h, a mixture of $SnCl_2{\cdot}2H_2O$ (1.1 gm, 4.83 mmol) in 5 mL conc. HCl was added slowly to the solution obtained in the first step. The resulting mixture was stirred for 12 h at room temperature. The precipitate was filtered and repeatedly washed with water until neutral pH is obtained. The pale yellow colored product was finally washed with ethanol (2 × 3 mL) and diethyl ether (2 × 3 mL) and dried in a conventional oven at 80 °C for 4 h. Yield: 272 mg (0.5 mmol, 50%). ^1H NMR (400 MHz, DMSO-d_6): δ = 8.04 (d, 2H), 7.69 (s, 1H), 7.63 (d, 2H), 7.51 (d, 1H), 7.30 (d, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.55, 167.45, 142.61, 140.04, 132.94, 131.70, 131.30, 130.47, 130.27, 129.45, 122.13, 119.90 ppm. ESI-MS (m/z): 272.08 for M+ ion (M = mass of $H_2BPDC\text{-}N_2H_3$ linker). In Figures S1-S3 (Supporting Information), the NMR and mass spectra o the $H_2BPDC\text{-}N_2H_3$ linker are shown.



Scheme S1. Reaction scheme for the preparation of $H_2BPDC\text{-}N_2H_3$ linker.

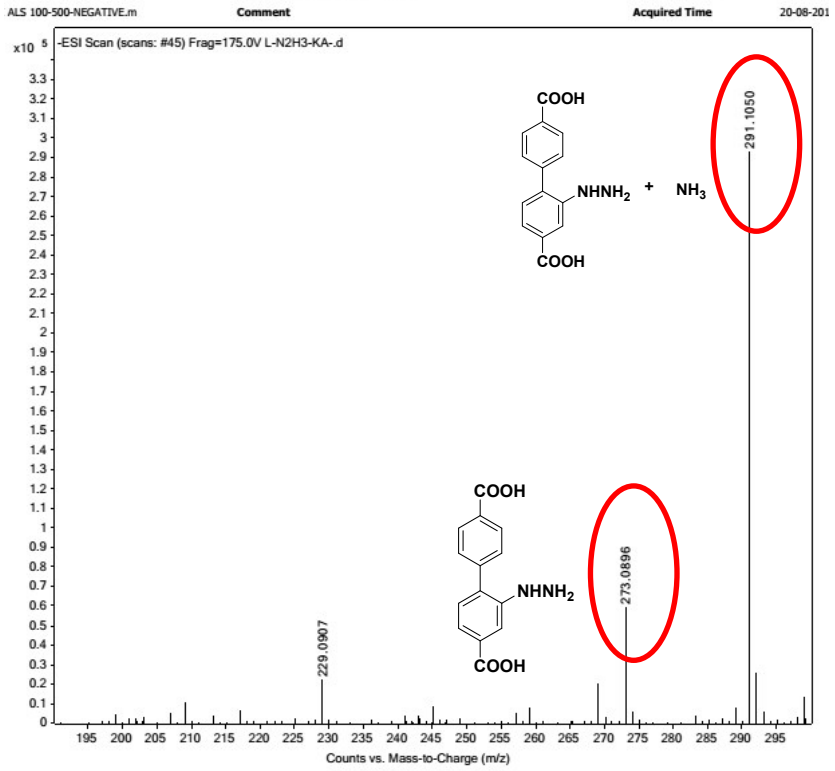


Figure S1. ESI-MS spectrum of $H_2BPDC\text{-}N_2H_3$ linker in methanol. The spectrum shows m/z (positive ion mode) peak at 273.0896, which corresponds to $(M+H)^+$ ion (M = mass of $H_2BPDC\text{-}N_2H_3$ linker).

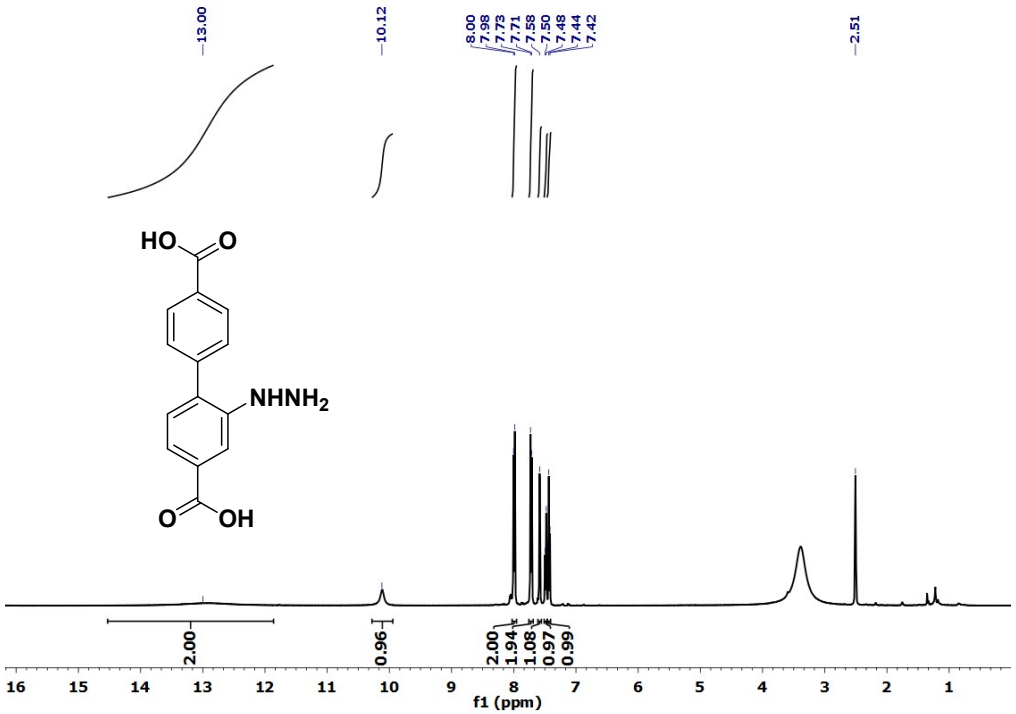


Figure S2. ^{1}H NMR spectrum of $H_2BPDC\text{-}N_2H_3$ linker in DMSO-d_6.

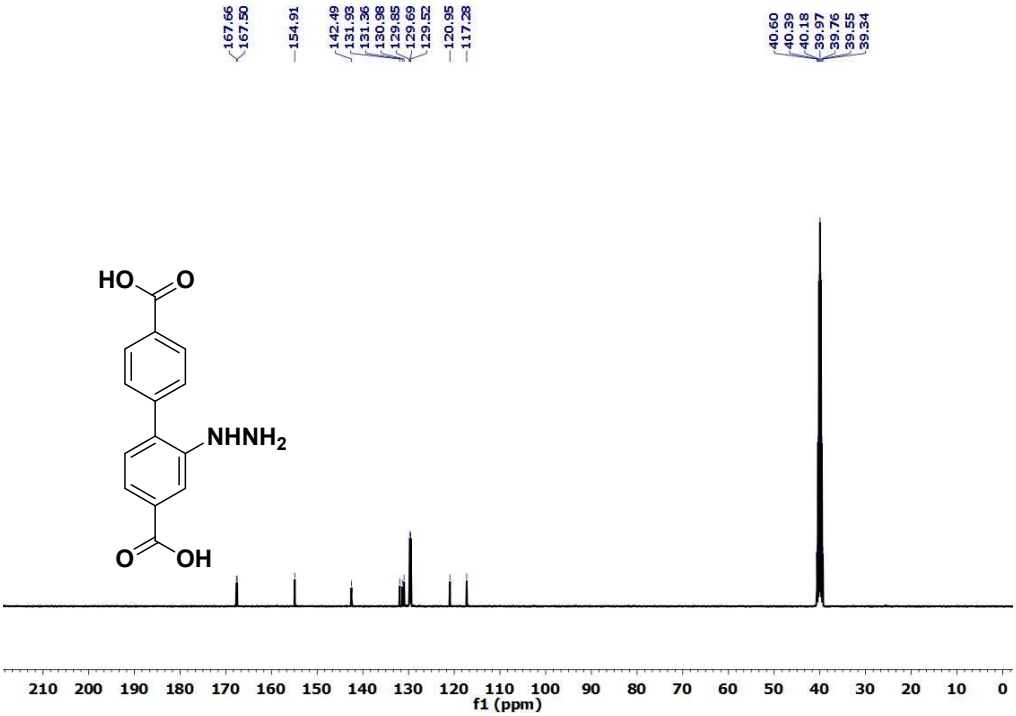


Figure S3. ^{13}C NMR spectrum of $H_2BDPC\text{-}N_2H_3$ linker in DMSO-d_6.

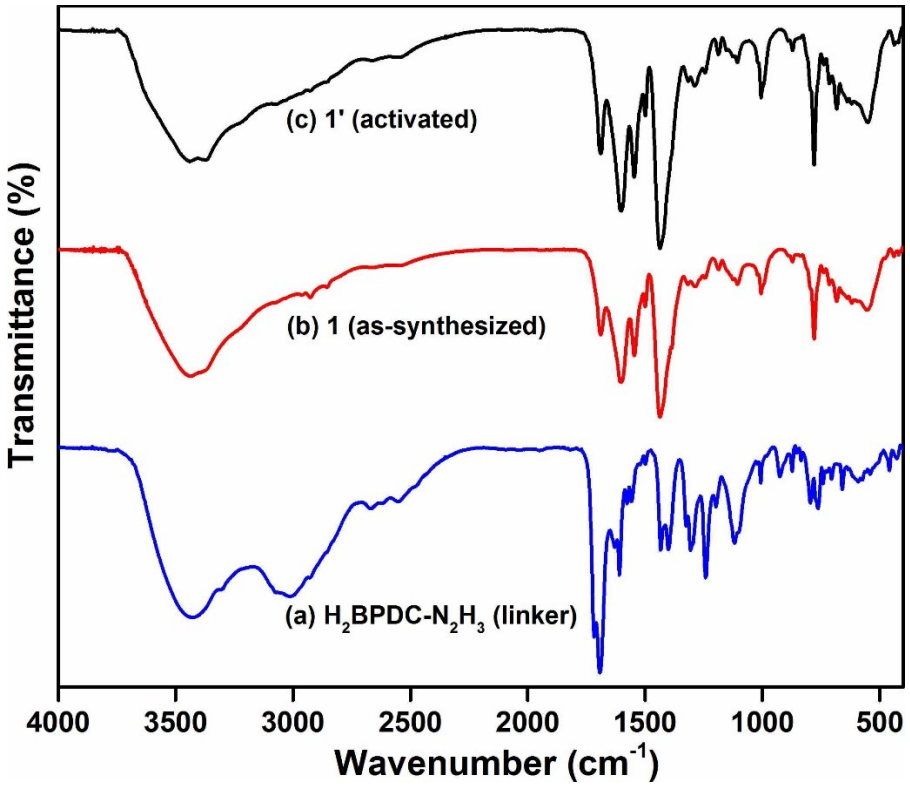


Figure S4. FT-IR spectra of (a) H_2BPDC-N_2H_3 linker, (b) as-synthesized **1** and (c) activated **1′**.

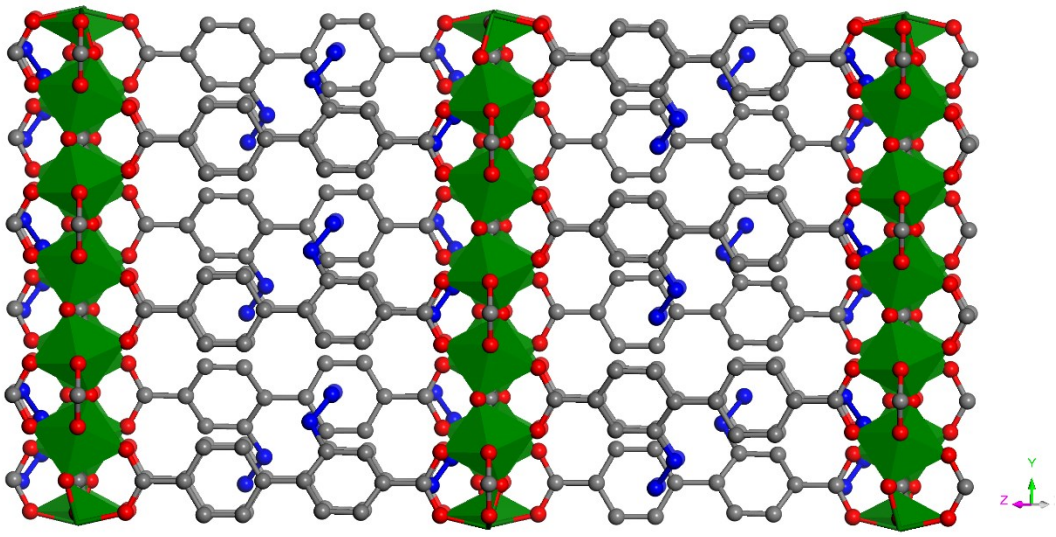


Figure S5. 3D view of structure of **1** along *y*-axis. Color codes: Al, green polyhedra; C, gray; O, red; N, blue. H atoms are removed for clarification.

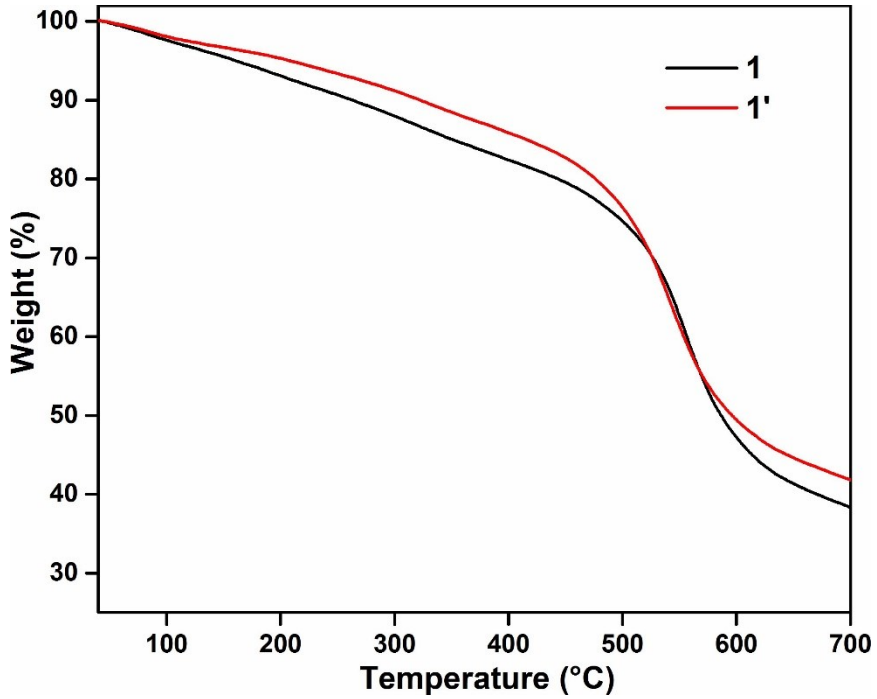


Figure S6. TG curves of as-synthesized **1** (black) and thermally activated **1′** (red) recorded in an argon atmosphere in the temperature range of 25-700 °C with a heating rate of 10 °C min^{-1}.

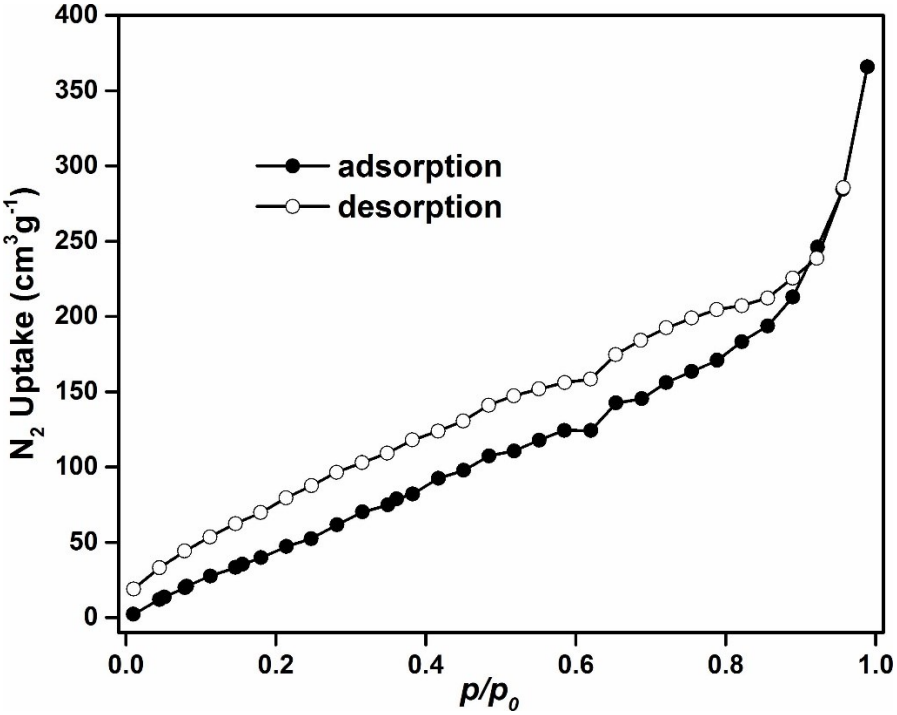


Figure S7. N_2 adsorption (solid circles) and desorption (open circles) isotherms of **1′** measured at –196 °C.

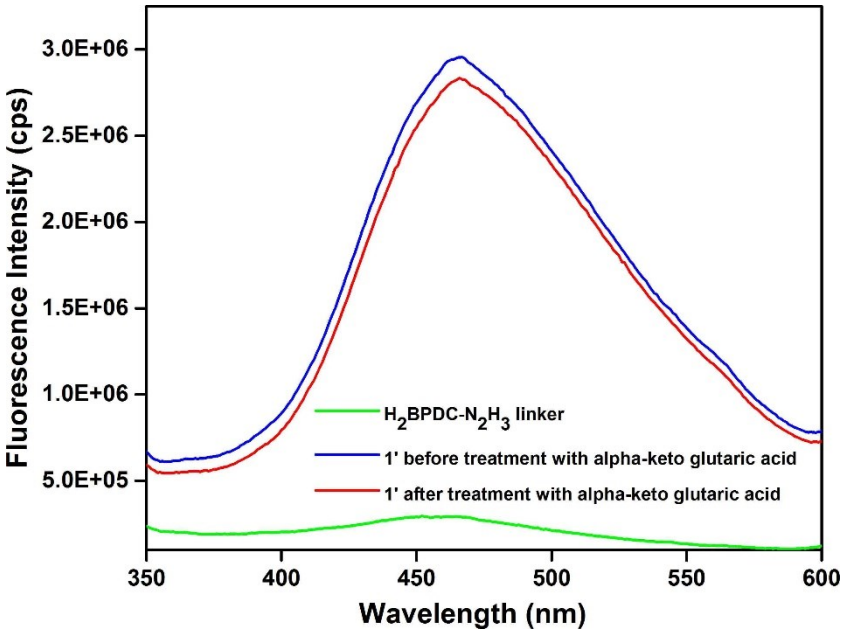


Figure S8. Solid-state luminescence spectra of free $H_2BPDC\text{-}N_2H_3$ linker (green), **1′** before treatment with α-KG (blue) and **1′** after treatment with α-KG (red).

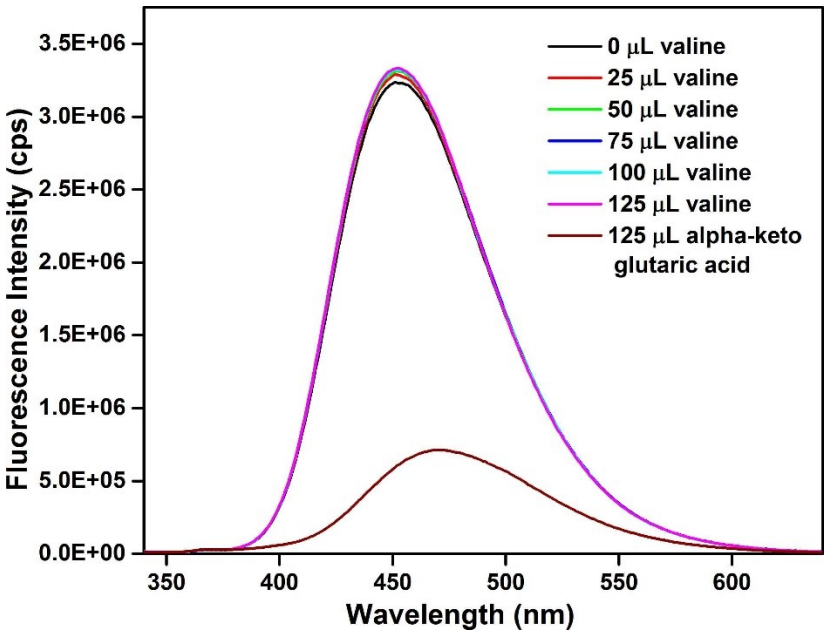


Figure S9. Quenching of the fluoresecnce intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 µL of 5 mM α-KG solution in presence of 125 µL of 5 mM valine solution in methanol/water (v/v = 5:1) mixture.

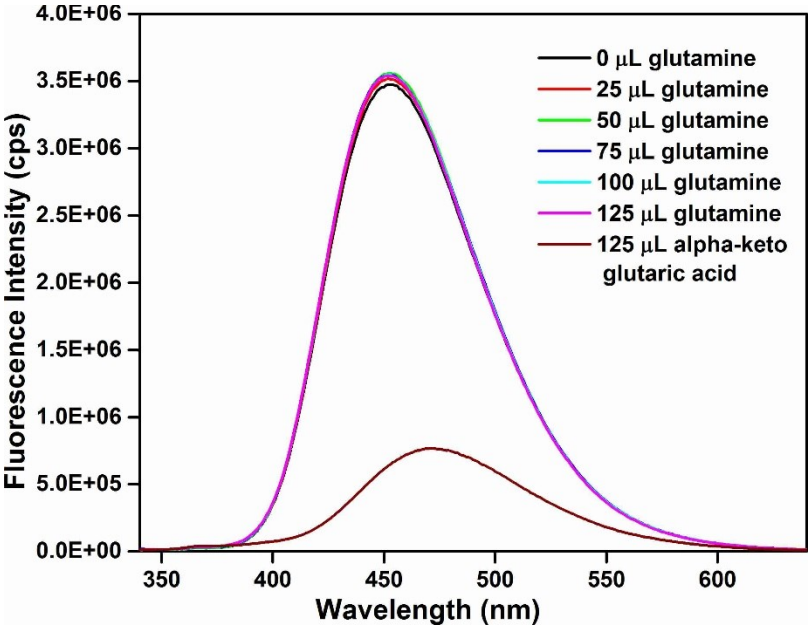


Figure S10. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM glutamine solution in methanol/water (v/v = 5:1) mixture.

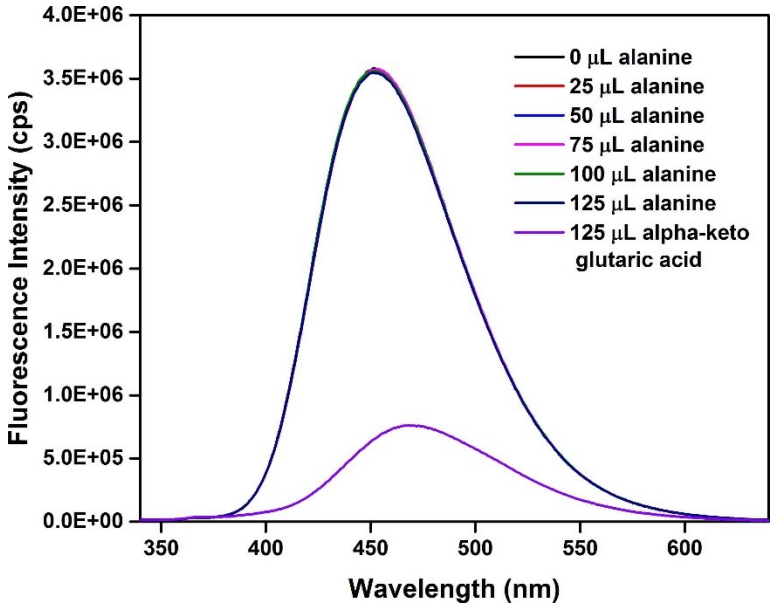


Figure S11. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM alanine solution in methanol/water (v/v = 5:1) mixture.

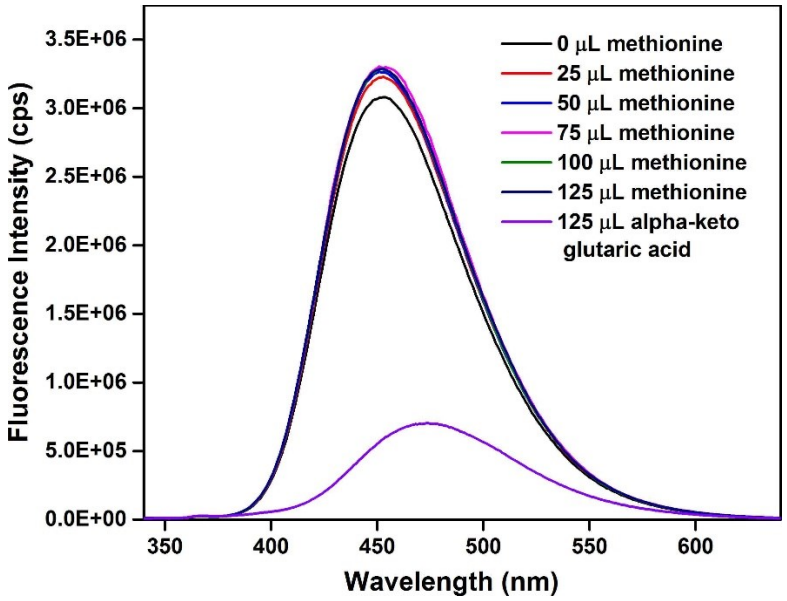


Figure S12. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM methionine solution in methanol/water (v/v = 5:1) mixture.

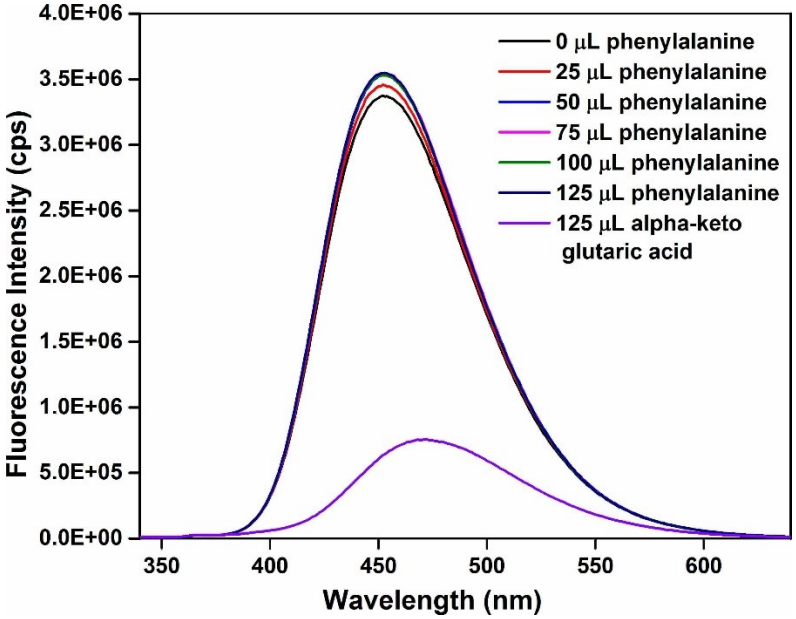


Figure 13. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM phenylalanine solution in methanol/water (v/v = 5:1) mixture.

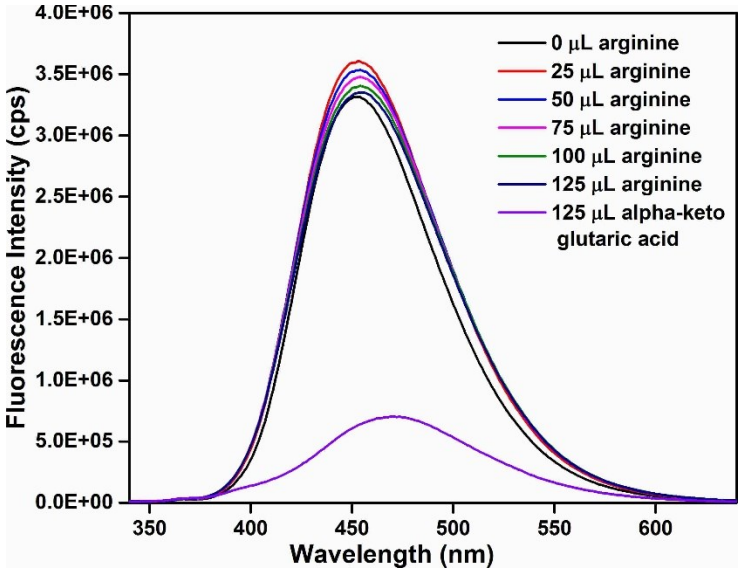


Figure S14. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM arginine solution in methanol/water (v/v = 5:1) mixture.

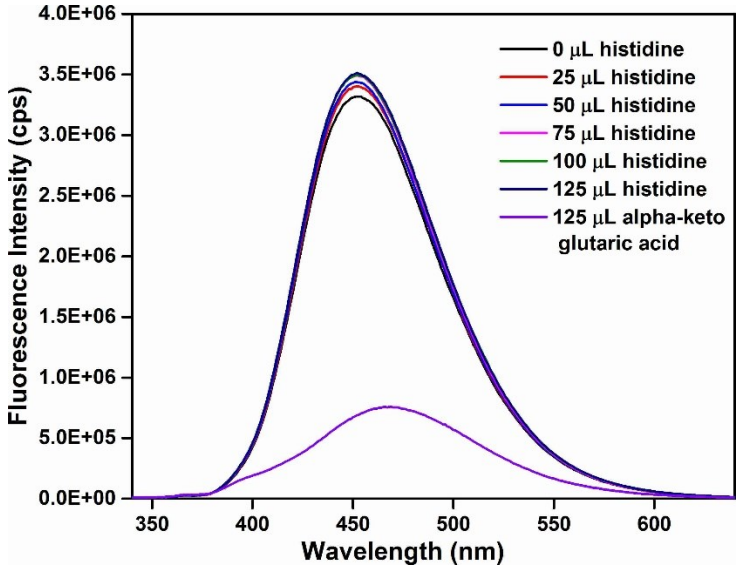


Figure S15. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM histidine solution in methanol/water (v/v = 5:1) mixture.

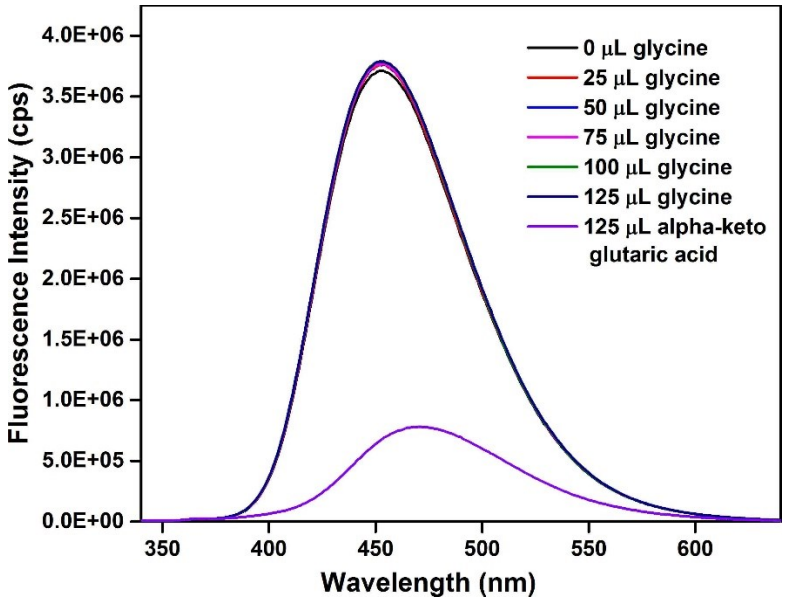


Figure S16. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM glycine solution in methanol/water (v/v = 5:1) mixture.

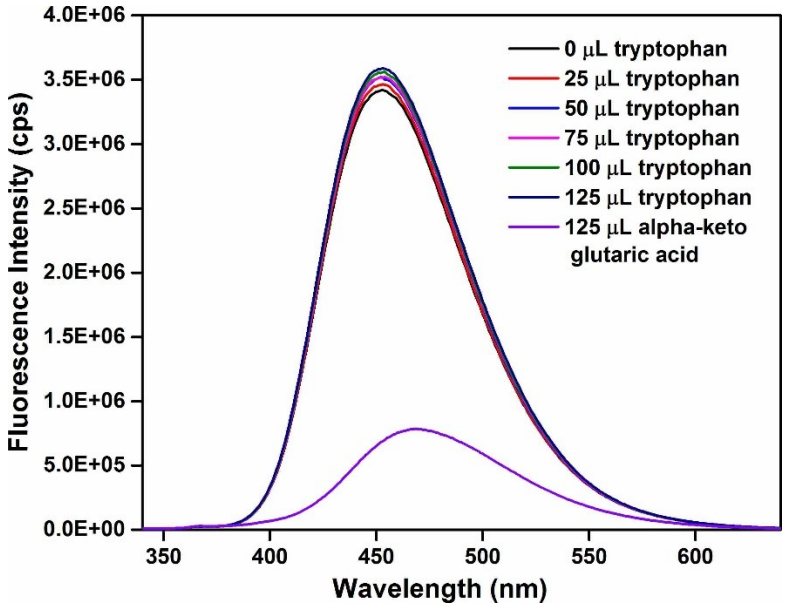


Figure S17. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM tryptophan solution in methanol/water (v/v = 5:1) mixture.

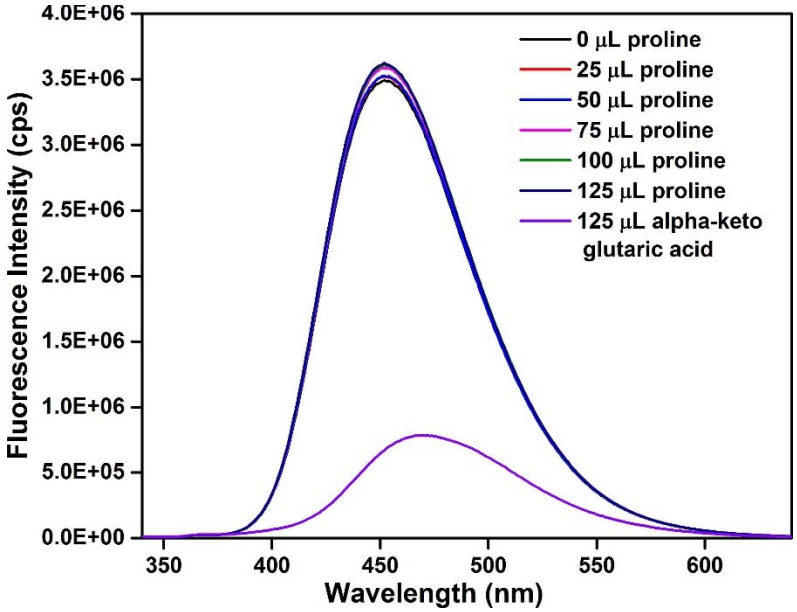


Figure S18. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM proline solution in methanol/water (v/v = 5:1) mixture.

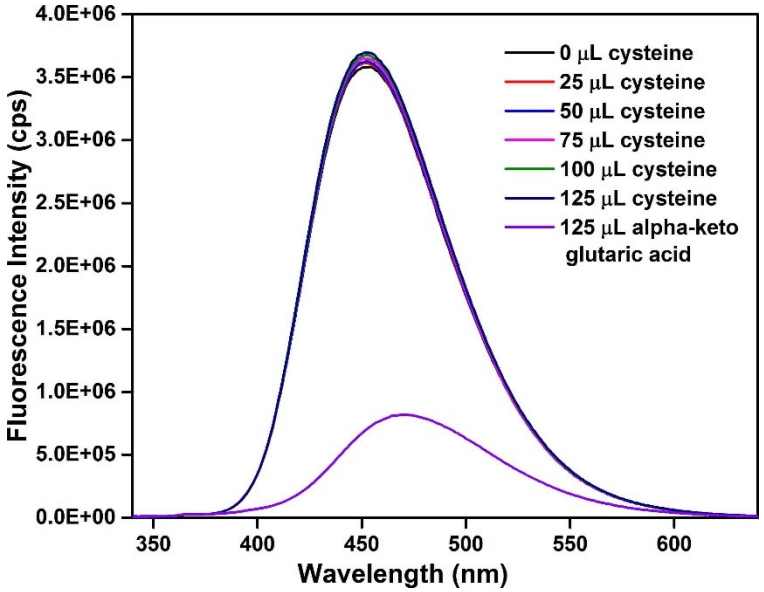


Figure S19. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM cysteine solution in methanol/water (v/v = 5:1) mixture.

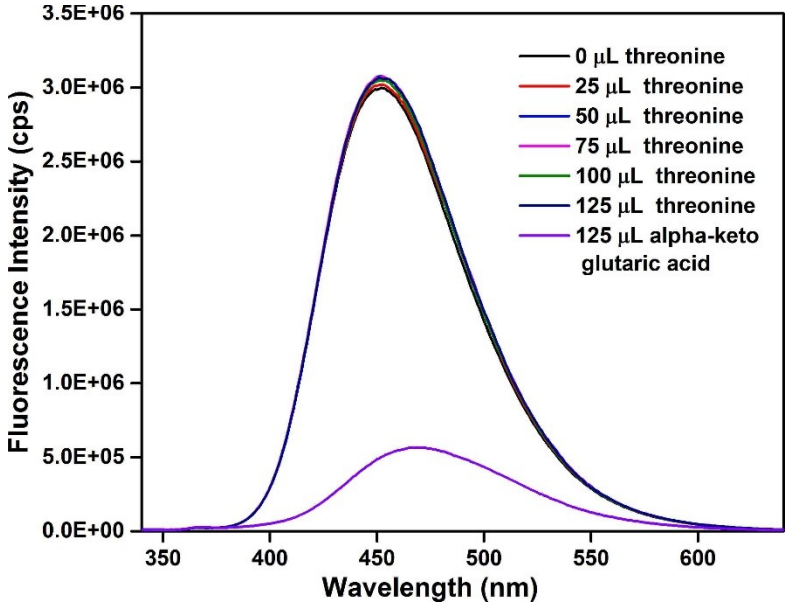


Figure S20. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM threonine solution in methanol/water (v/v = 5:1) mixture.

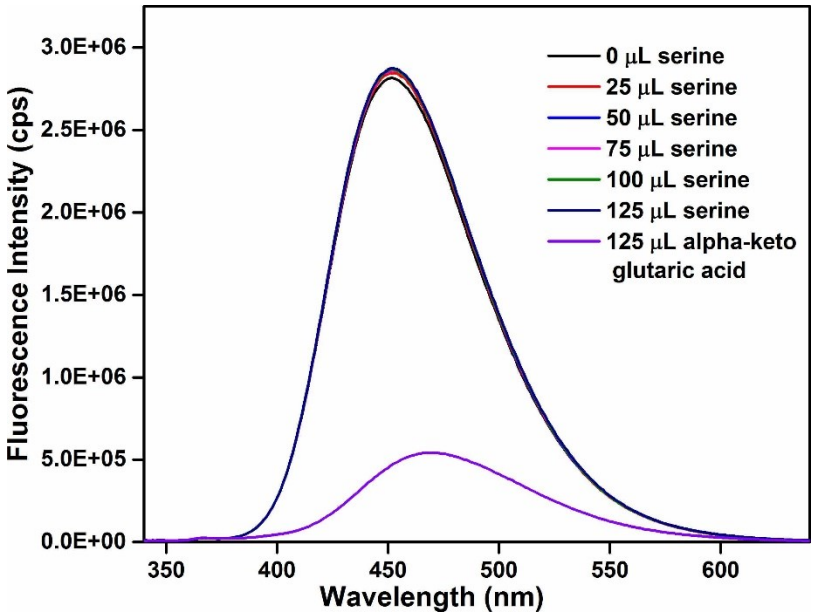


Figure S21. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM serine solution in methanol/water (v/v = 5:1) mixture.

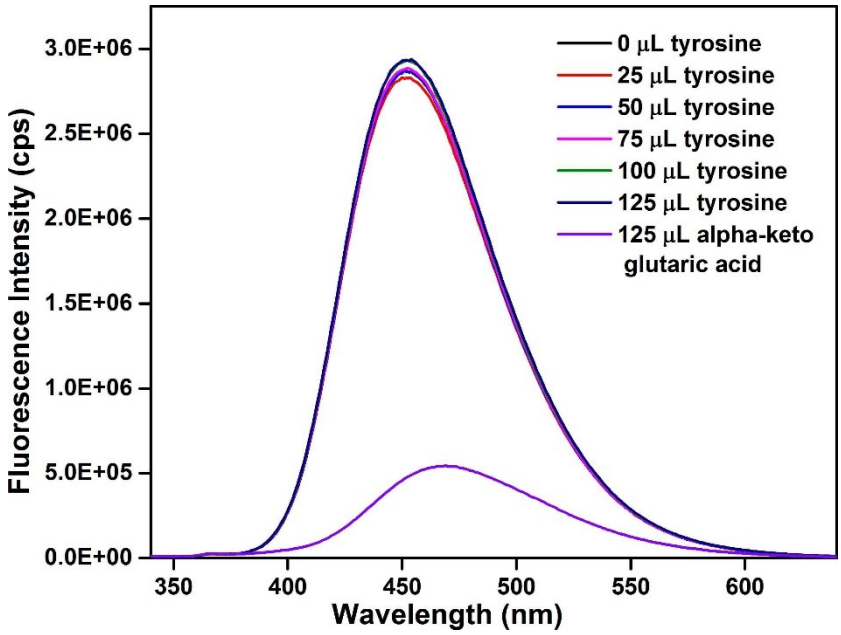


Figure S22. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM tyrosine solution in methanol/water (v/v = 5:1) mixture.

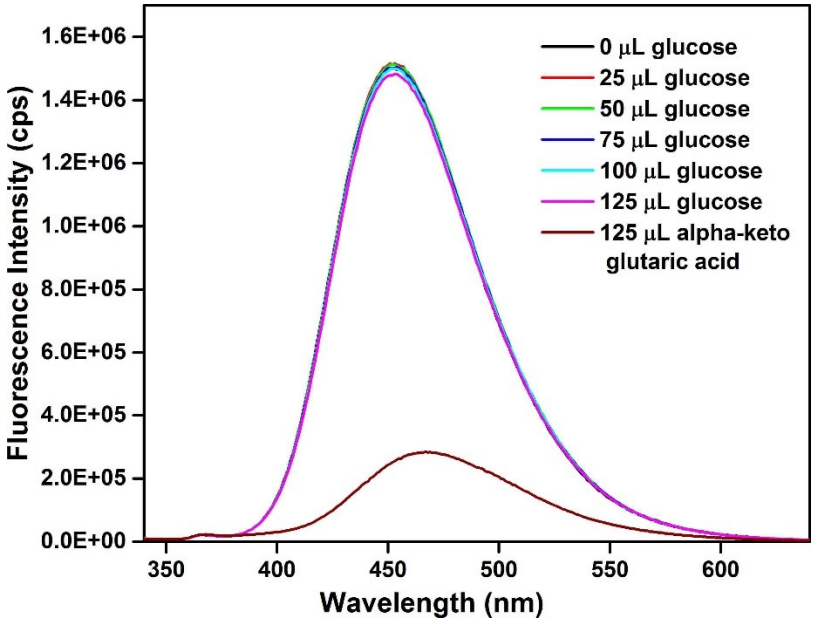


Figure S23. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM glucose solution in methanol/water (v/v = 5:1) mixture.

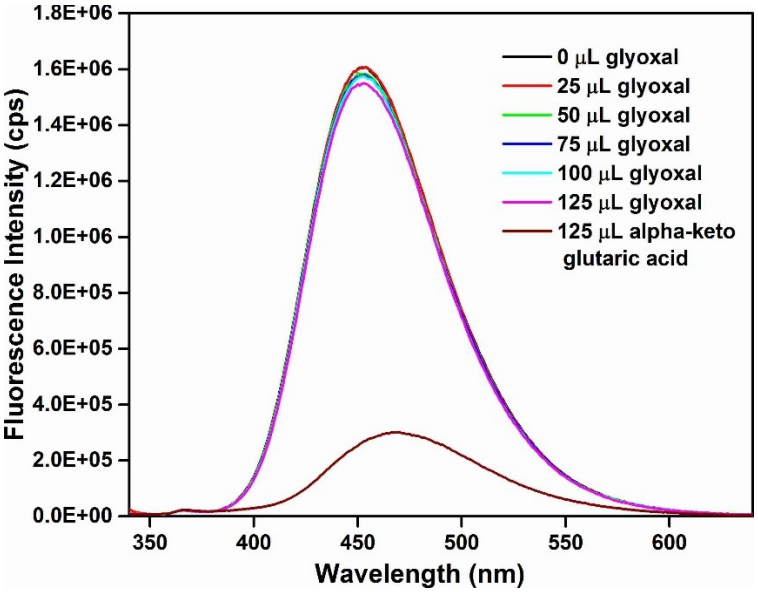


Figure S24. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM glyoxal solution in methanol/water (v/v = 5:1) mixture.

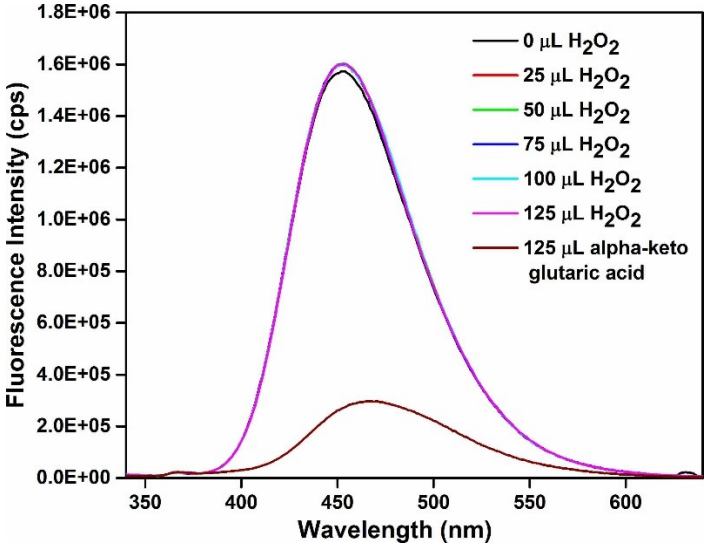


Figure S25. Quenching of the fluorescence intensity of the suspension of **1′** (in methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in presence of 125 μL of 5 mM H_2O_2 solution in methanol/water (v/v = 5:1) mixture.

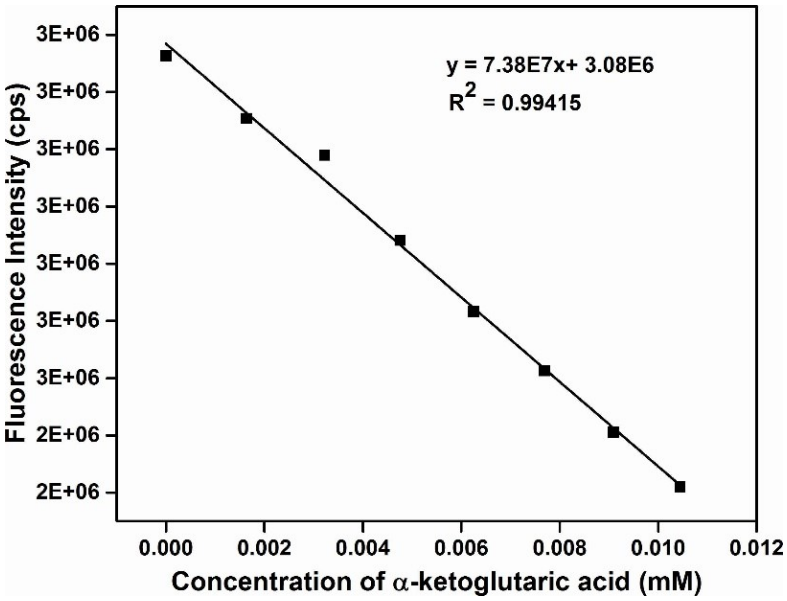


Figure S26. Change in the fluorescence intensity of **1′** in methanol/water (v/v = 5:1) mixture as a function of α-KG concentration.

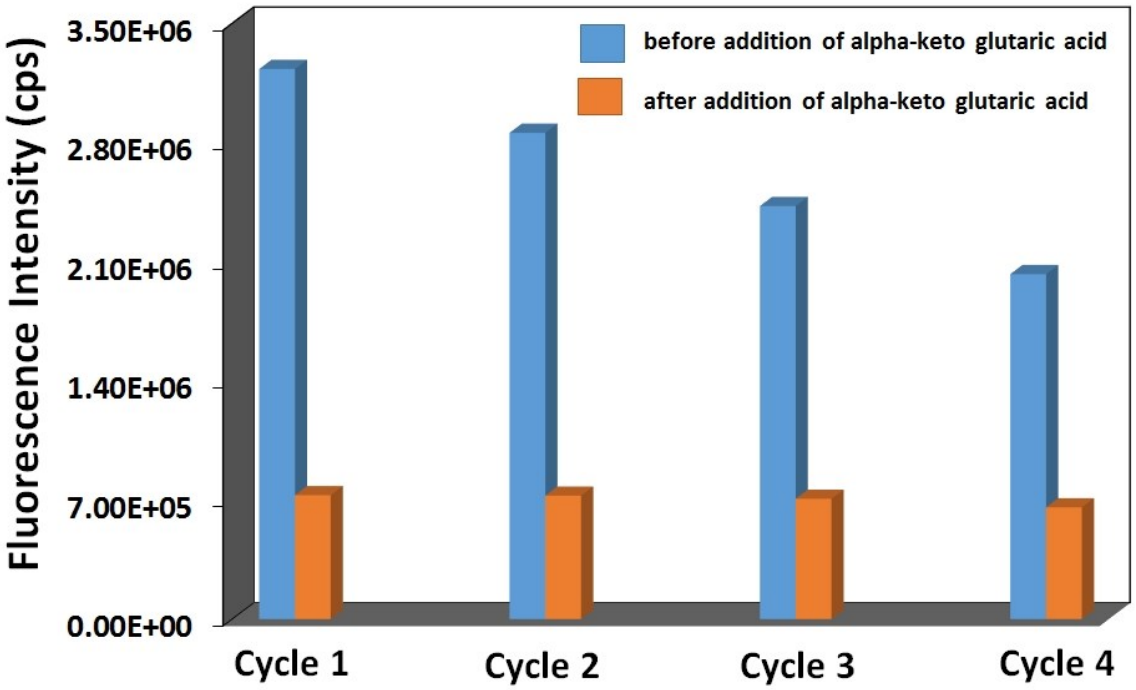


Figure S27. Recyclability test for the fluorescence turn-off response of the suspension of **1′** towards 5 mM α-KG solution (methanol/water mixture, v/v = 5:1).

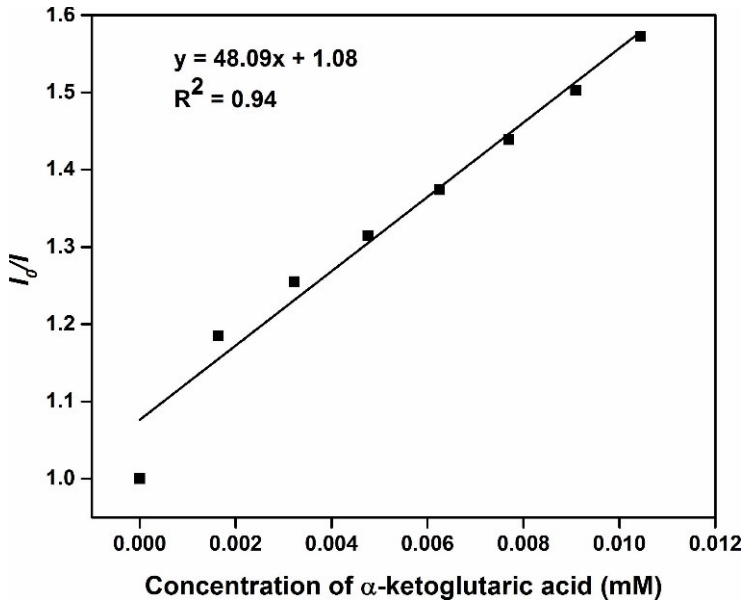


Figure S28. Stern-Volmer plot for the fluorescence quenching of **1′** in methanol/water (v/v, 5:1) mixture upon addition of α-KG.

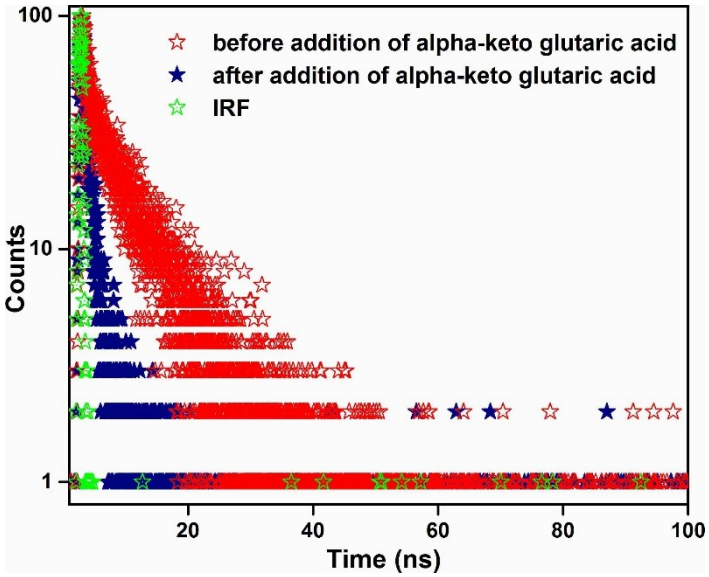


Figure S29. Lifetime decay profile of **1′** before and after the addition of 125 μL of 5 mM *α*-KG solution in methanol/water (v/v = 5:1) mixture.

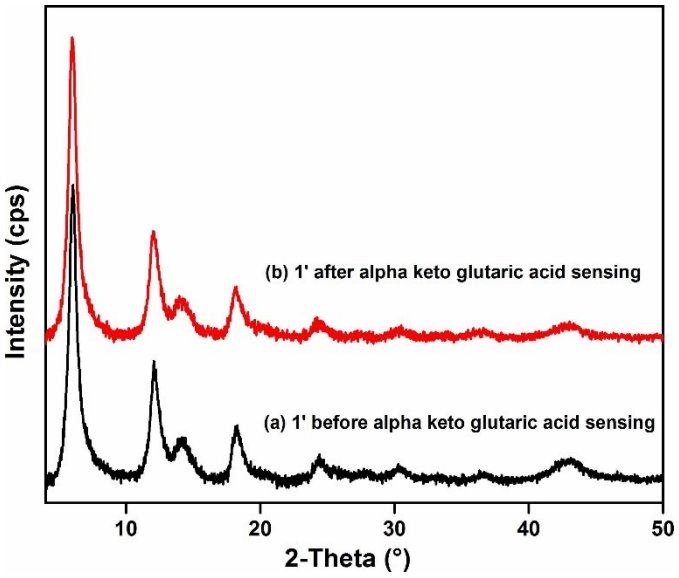


Figure S30. XRPD patterns of **1′** in methanol/water (v/v, 5:1) mixture (a) before and (b) after sensing of α-KG.

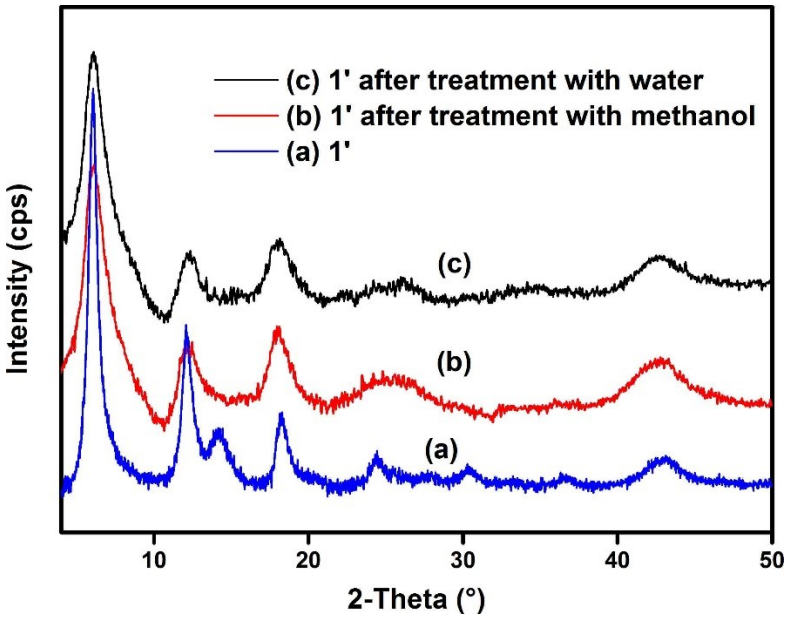


Figure S31. XRPD pattern of **1′**: (a) activated only, stirred in (b) methanol and (c) water.

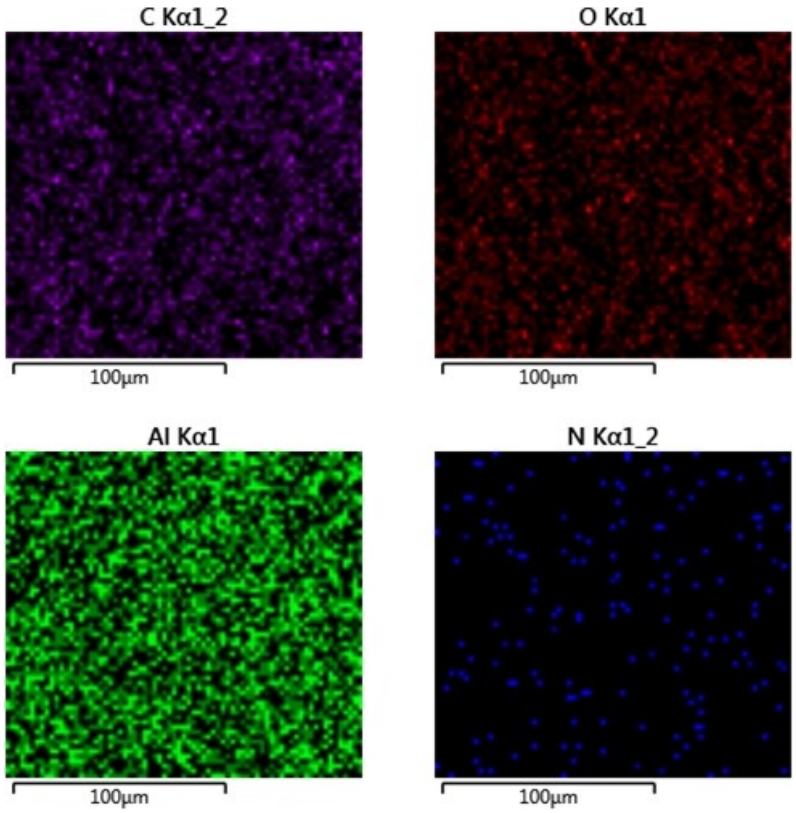


Figure S32. EDX elemental mapping of **1′** before sensing of α-KG.

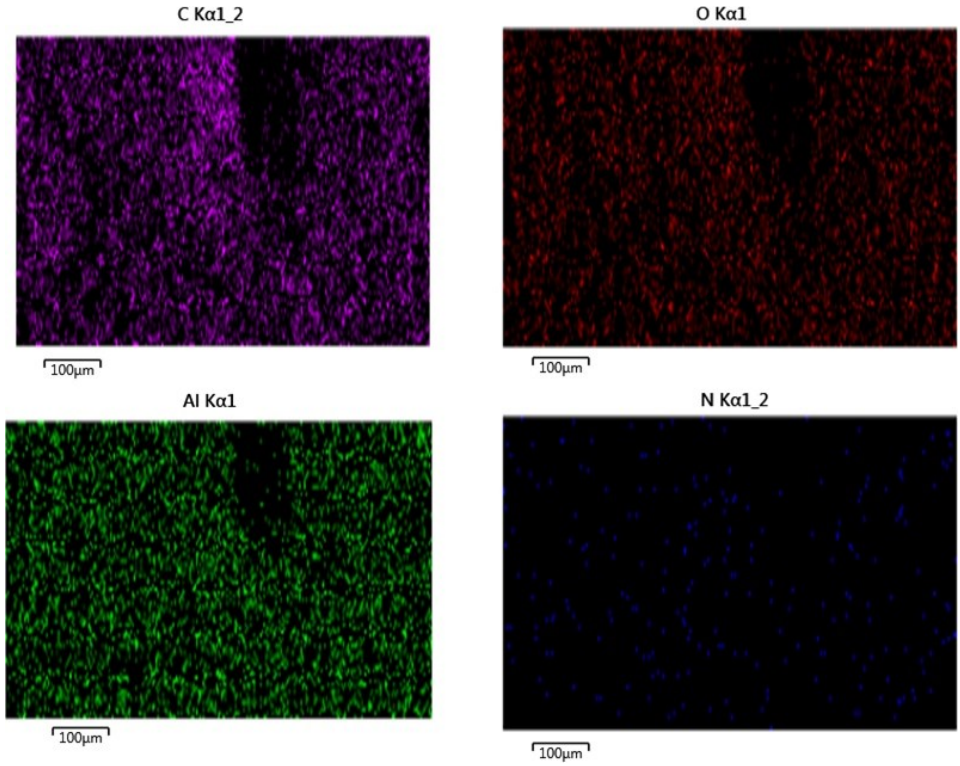


Figure S33. EDX elemental mapping of **1′** after sensing of α-KG.

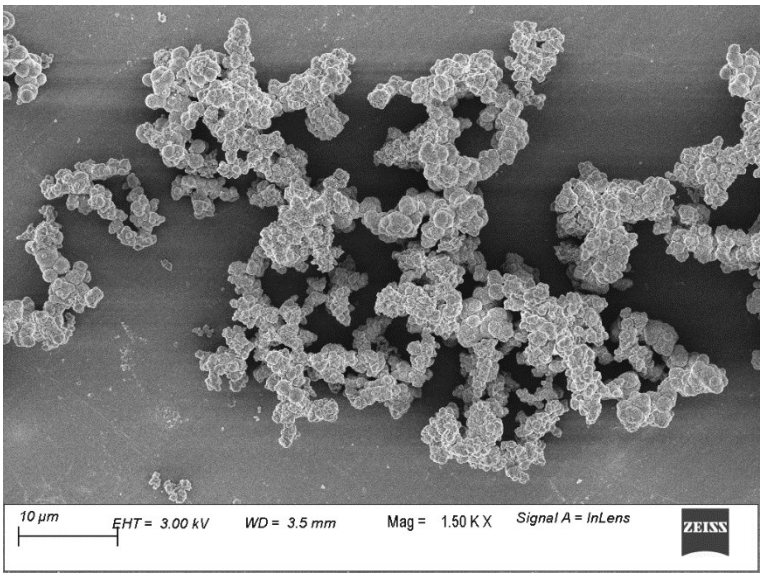


Figure S34. FE-SEM images of **1′** before α-KG sensing.

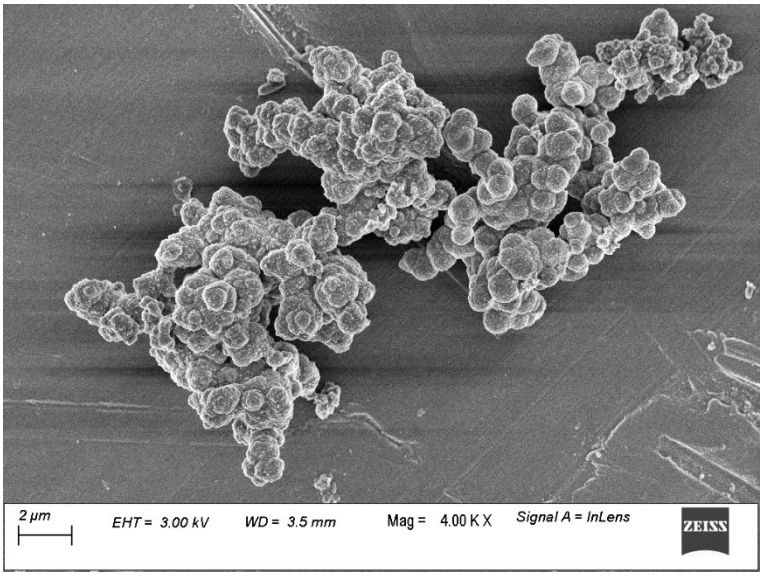


Figure S35. FE-SEM images of **1′** after α-KG sensing.

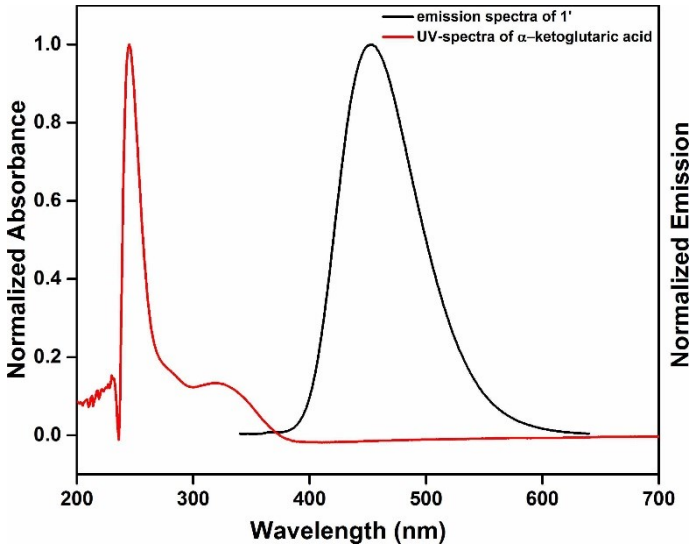


Figure S36. Spectral overlap between the absorption spectra of α-KG and the emission spectra of **1′** in methanol/water (v/v = 5:1) mixture.

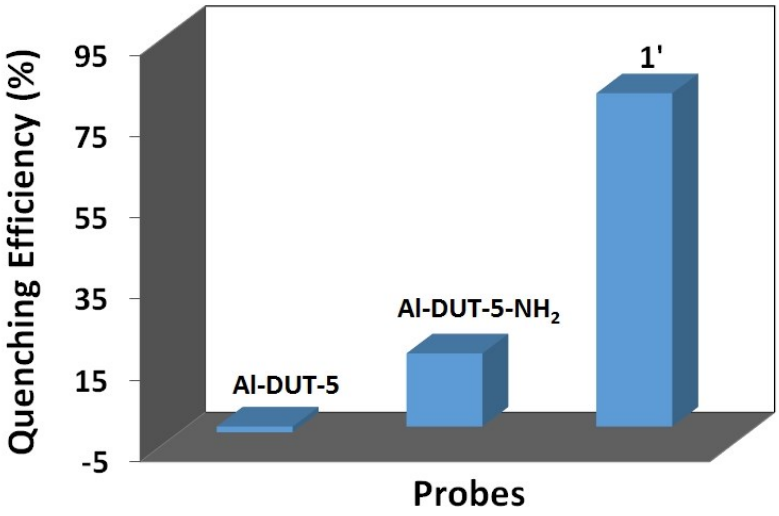


Figure S37. Comparison of quenching efficiency of the suspension of **1′** (methanol/water, v/v = 5:1) upon the addition of 125 μL of 5 mM α-KG solution in methanol/water (v/v = 5:1) mixture.

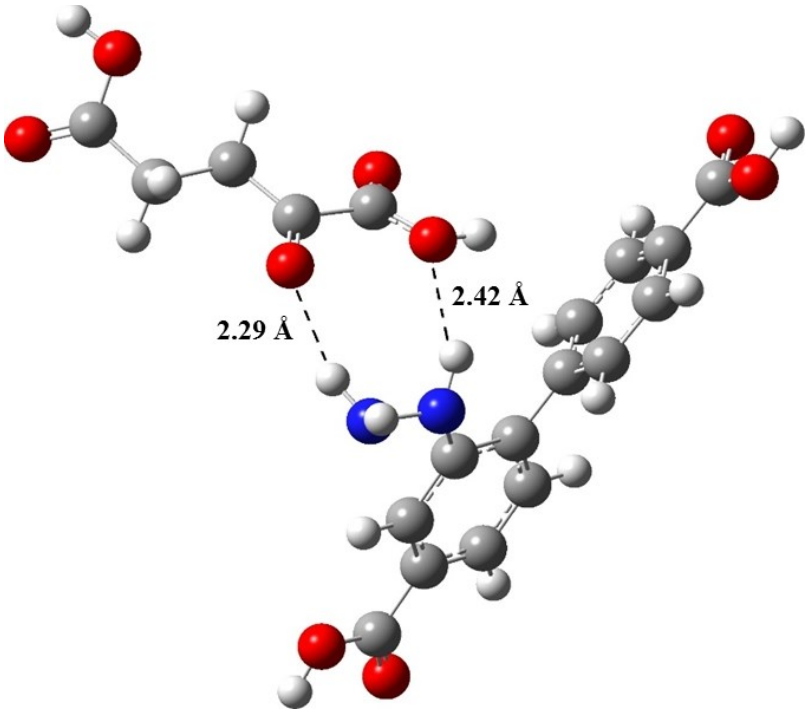


Figure S38. Plausible 'H' bond formation between H_2BPDC-$NHNH_2$ in **1′** and α-KG.

Table S1. Average excited-state lifetime (<τ>*) values of **1′** before and after the addition of 125 μL of 5 mM α-KG solution in methanol/water (v/v = 5:1) mixture.

Vol of α-KG (μl)	B_1	B_2	a_1	a_2	τ_1 (ns)	τ_2 (ns)	<τ>* (ns)	$\chi 2$	λ_{ex} (nm)	λ_{em} (nm)
0	0.0870	0.0221	0.259	0.741	0.652	7.331	5.601	1.017	330	450
125	0.0635	0.0121	0.598	0.402	0.531	1.883	1.074	1.009	330	470

Average life-time $<\tau>^* = a_1 \tau_1 + a_2 \tau_2$

References:

1. X. Tang, Z. Zhu, C. Qi, W. Wu and H. Jiang, *Org. Lett.*, 2016, **18**, 180-183.