Electronic Supplementary Material (ESI) for Analytical Methods

Supplementary data for

A proof-of-concept fluorescent strategy for highly selective detection of Cr(VI) based on inner filter effect using a hydrophilic ionic chemosensor

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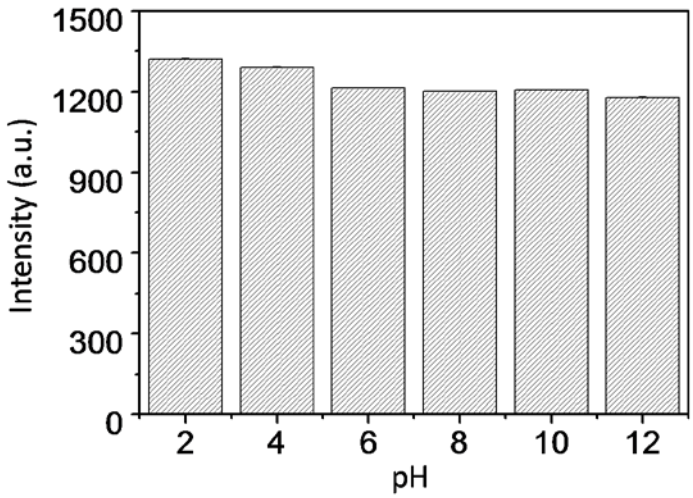

Fig. S1 Effect of pH on the fluorescence intensity at 437 nm of chemosensor **1** (5×10^{-6} M) in 100% aqueous solution. The pH values of the solution were adjusted by very small amount of HCl and KOH aqueous solution.

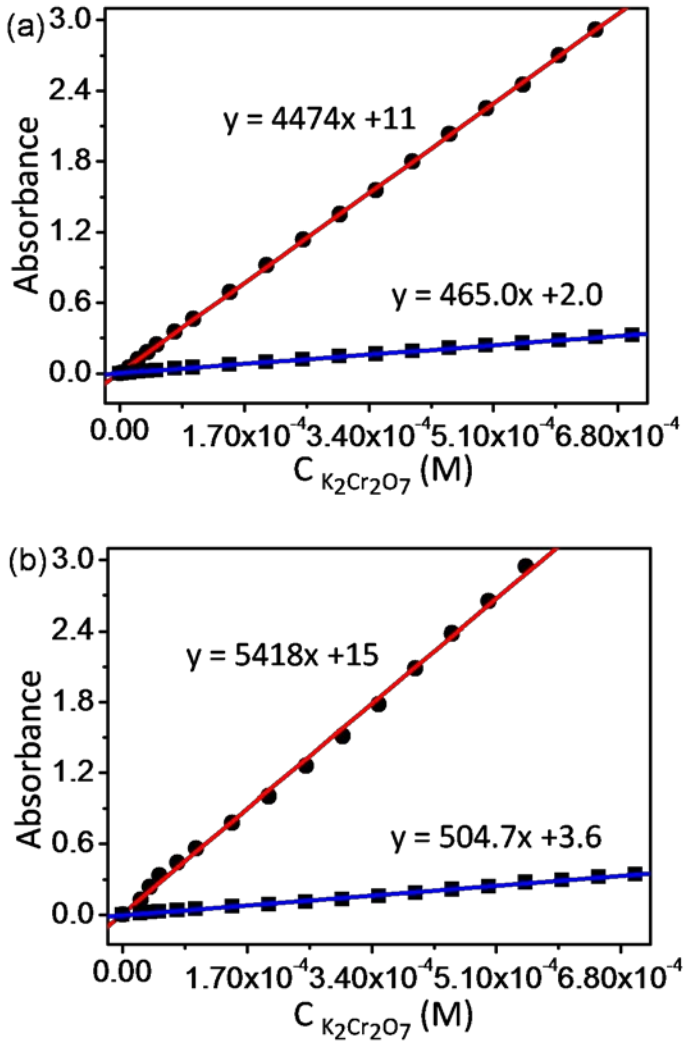

Fig. S2 Calculation of the extinction coefficients of $K_2Cr_2O_7$ at 259 nm (red lines) and 437 nm (blue lines) in water (a) and in 98% MeCN aqueous solution (b) respectively. The length of the cuvette used for UV measurement was 1 cm.

Table S1 Analytical performance data for Cr(VI) detection in MeCN aqueous system.

Percentage of MeCN	Liner range (M)	Detection limit (3σ, M)
50%	2.5×10^{-6}-2.5×10^{-5}	7.5×10^{-7}
90%	1.5×10^{-6}-1.25×10^{-5}	3.6×10^{-7}
98%	5.0×10^{-7}-1.0×10^{-5}	9.2×10^{-8}

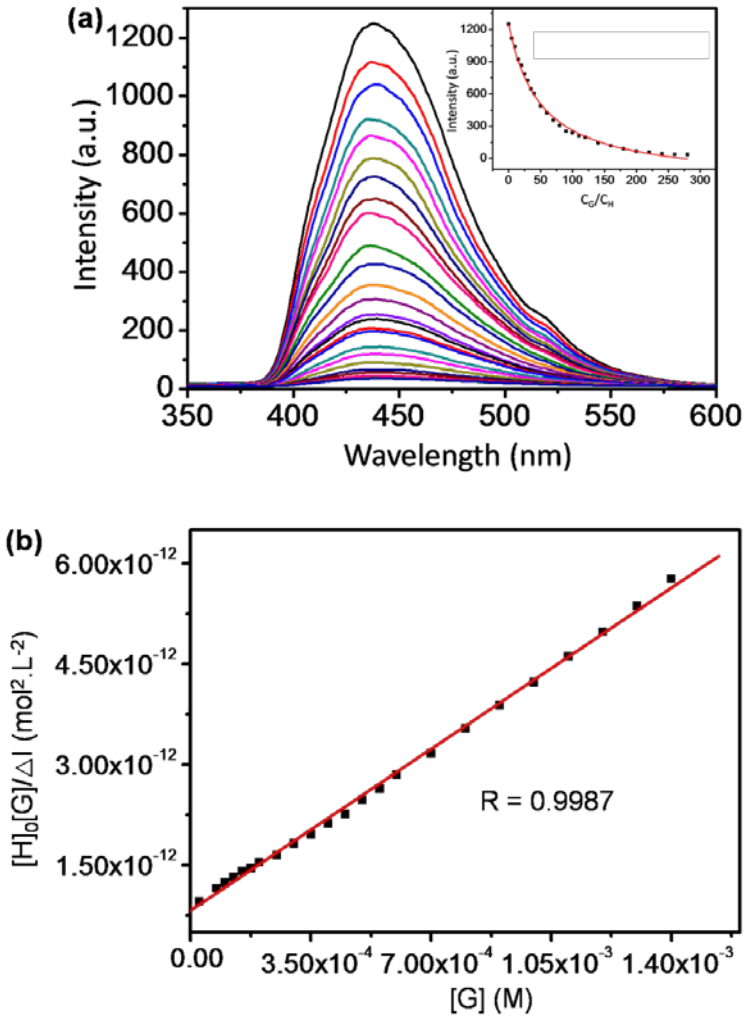

Fig. S3 (a) Fluorescence titration spectra of chemosensor **1** (5×10^{-6} M) upon addition of different equiv. of Cr(VI) (0 - 280 equiv.) in 100% aqueous solution at pH 4.0. Inset: fluorescence intensity development with the increasing equiv. of Cr(VI). (b) Plot of $[H]_0[G]/\Delta I$ *versus* [G] for calculating the inner filter constant of chemosensor **1** with Cr(VI) in 100% aqueous solution at pH 4.0.

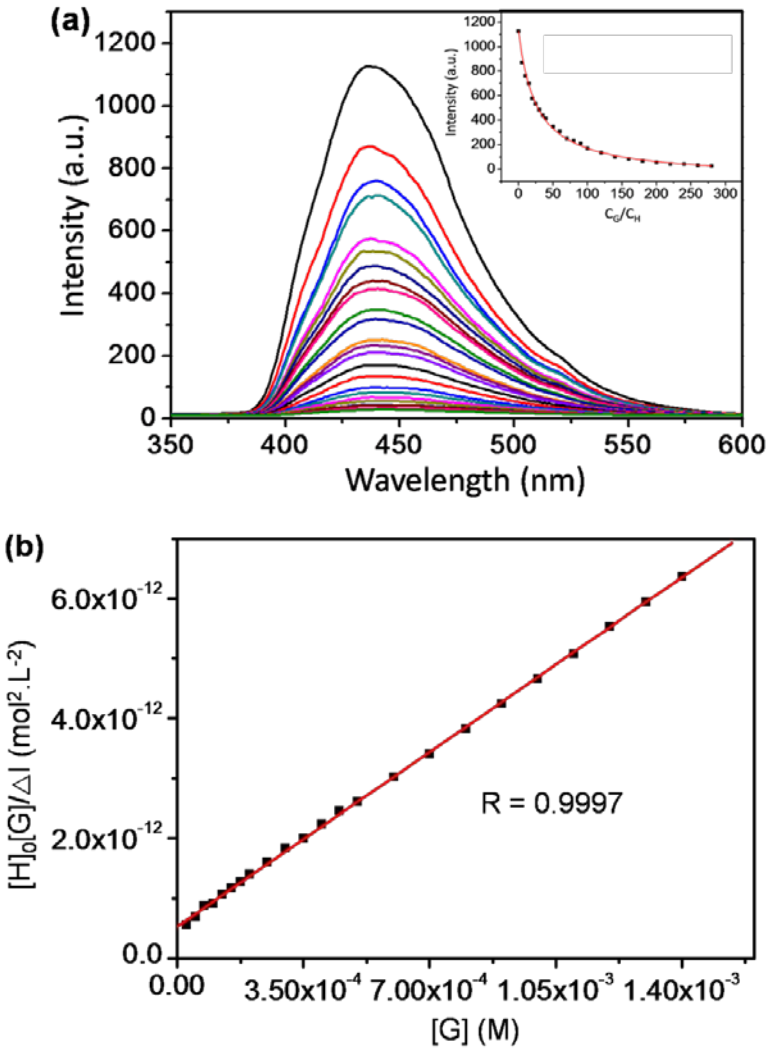

Fig. S4 (a) Fluorescence titration spectra of chemosensor **1** (5×10^{-6} M) upon addition of different equiv. of Cr(VI) (0 - 280 equiv.) in 100% aqueous solution at pH 10. Inset: fluorescence intensity development with the increasing equiv. of Cr(VI). (b) Plot of $[H]_0[G]/\Delta I$ *versus* [G] for calculating the inner filter constant of chemosensor **1** with Cr(VI) in 100% aqueous solution at pH 10.

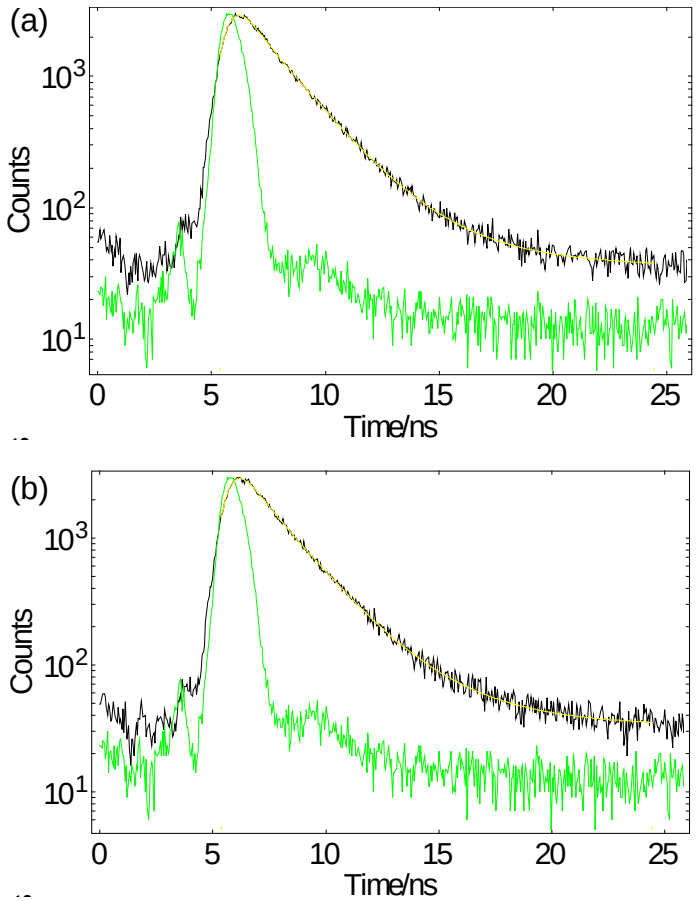

Fig. S5 (a) Fluorescence decay curve of the chemosensor **1** (5×10^{-6} M) in the absence of Cr(VI). (b) Fluorescence decay curve of chemosensor **1** (5×10^{-6} M) in the presence of 100 equiv. of Cr(VI). The decay curves were fitted to the biexponential function with acceptable χ^2 (1.2 and 1.1 respectively).

Table S2 Fluorescence lifetime of chemosensor **1** in 100% aqueous solution in the absence and presence of Cr(VI) upon excitation at 259 nm

Complex	τ_1, ns (%)	τ_2, ns (%)	χ^2
1[a]	1.75 (86.34)	3.44 (13.66)	1.2
1+100eq. Cr(VI)	1.81 (82.84)	3.57 (17.16)	1.1

[a] [**1**] = 5×10^{-6} M

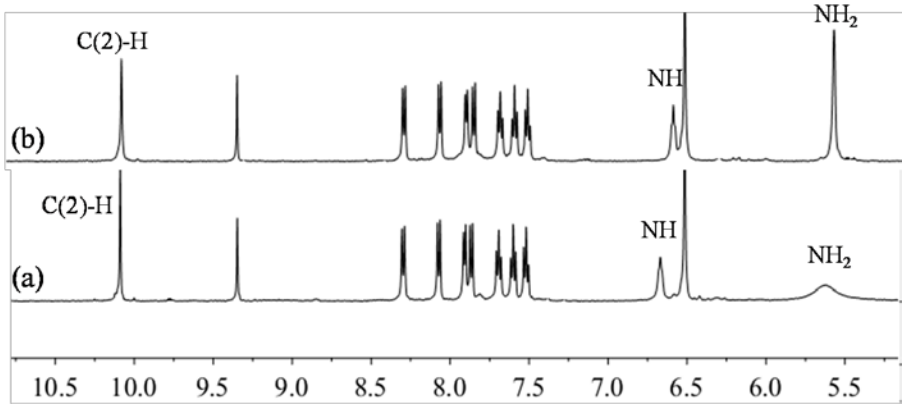

Fig. S6 Partial ^{1}H NMR spectra of chemosensor **1** (10 mM) in the absence (a) and presence (b) of Cr(VI) (1 equiv.) in DMSO-d_6.

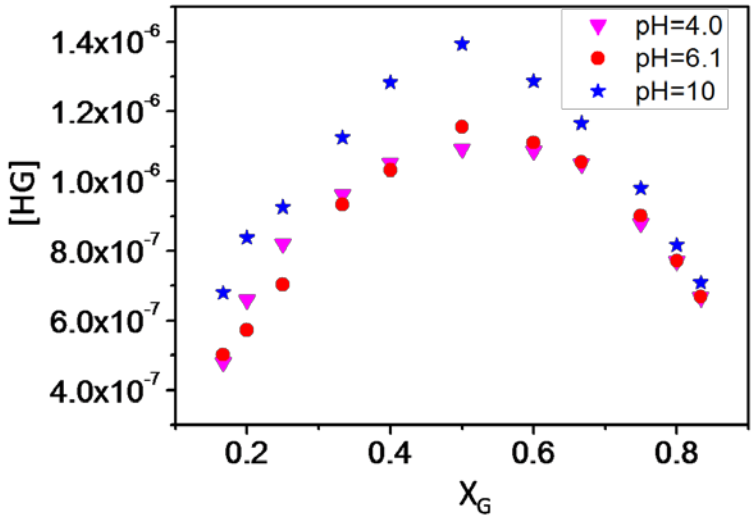

Fig. S7 Fluorescence Job's plot of chemosensor **1** with Cr(VI) in 100% aqueous solution at pH 4.0 (▼), 6.1(●) and 10 (★) respectively, where [G]+[H] = 5×10^{-6} M.

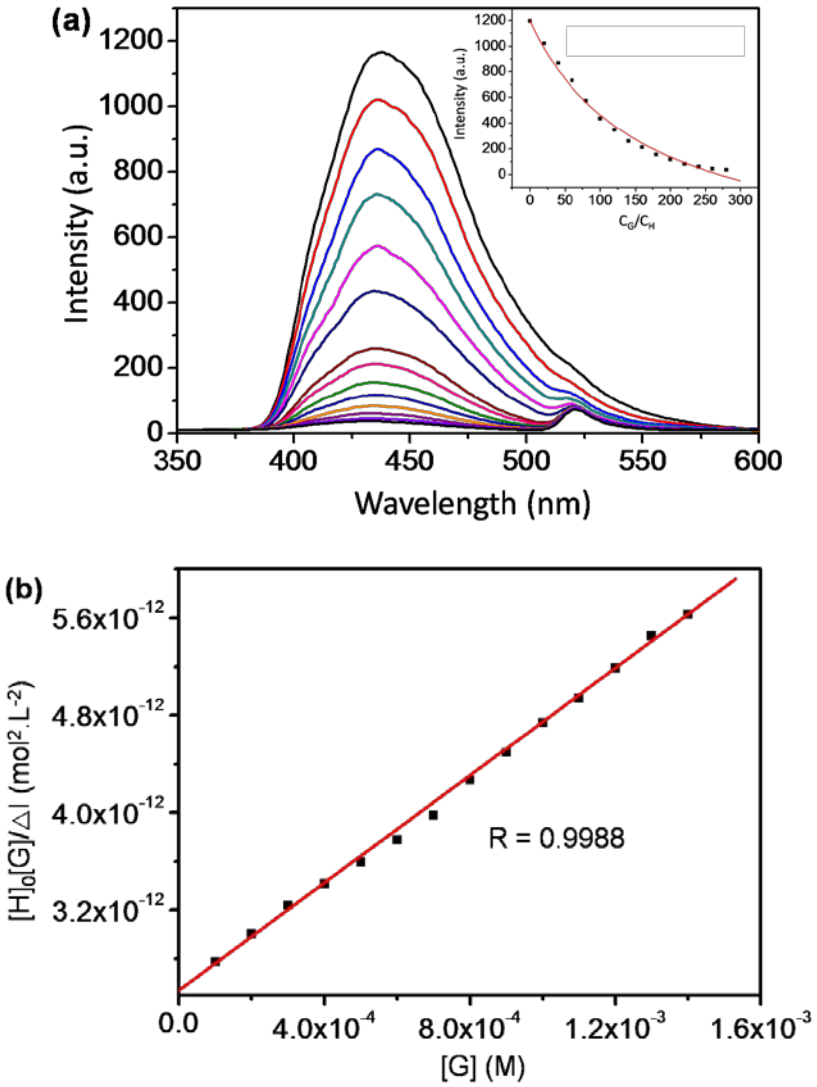

Fig. S8 (a) Fluorescence titration spectra of chemosensor **1** (5×10^{-6} M) upon addition of different equiv. of MnO_4^- (0 - 280 equiv.) in 100% aqueous solution at pH 6.1. Inset: fluorescence intensity development with the increasing equiv. of MnO_4^-. (b) Plot of $[H]_0[G]/\Delta I$ *versus* [G] for calculating the inner filter constant of chemosensor **1** with MnO_4^- in 100% aqueous solution at pH 6.1.

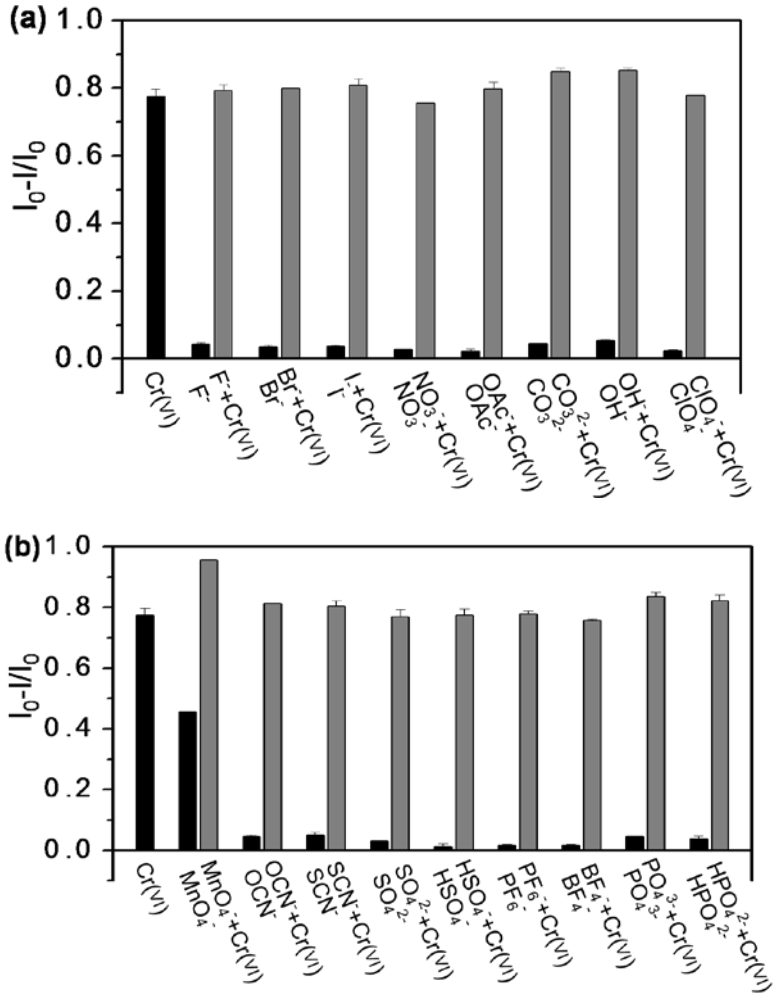

Fig. S9 Quenching rate at 437 nm of 5×10^{-6} M chemosensor **1** in aqueous solution at pH = 4.0. Dark bars represent the addition of 100 equiv. of anions, and gray bars represent the subsequent addition of 100 equiv. of Cr(VI) to the solution.

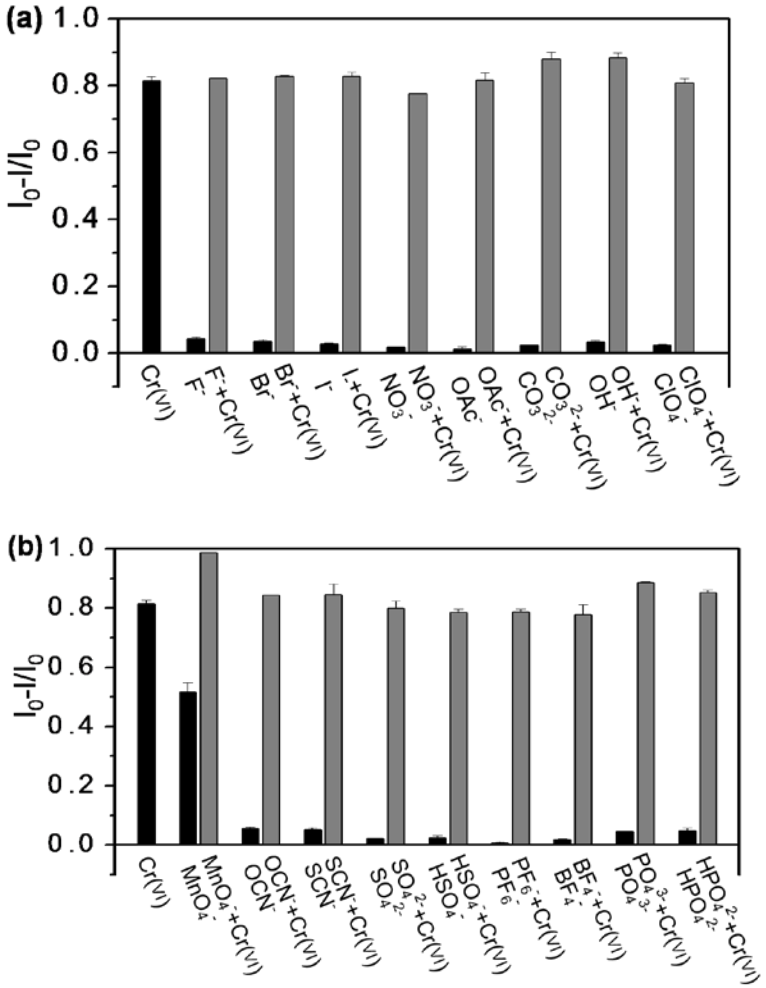

Fig. S10 Quenching rate at 437 nm of 5×10^{-6} M chemosensor **1** in aqueous solution at pH = 10. Dark bars represent the addition of 100 equiv. of anions, and gray bars represent the subsequent addition of 100 equiv. of Cr(VI) to the solution.

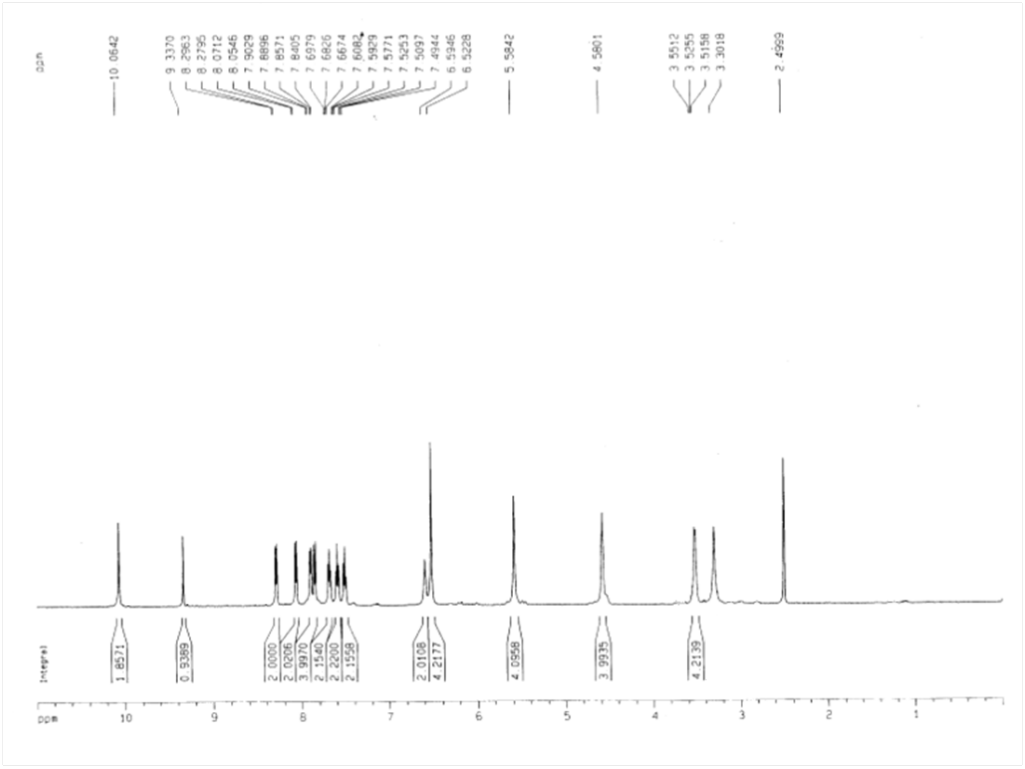

Fig. S11 ^{1}H NMR of chemosensor **1** in DMSO-d_6.

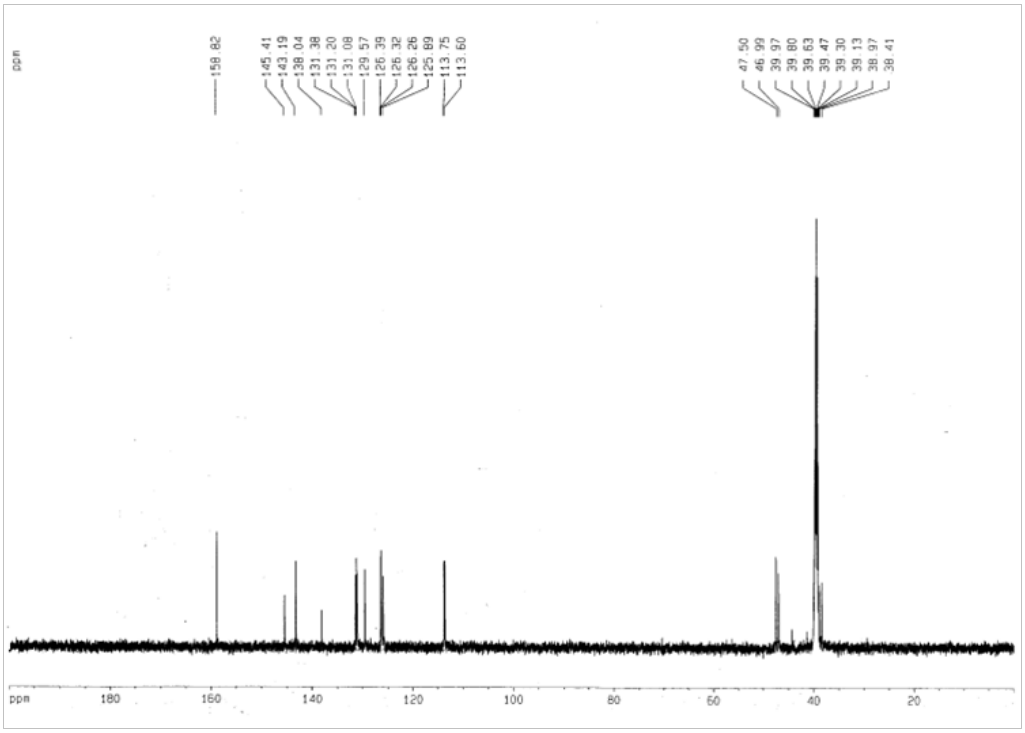

Fig. S12 ^{13}C NMR of chemosensor **1** in DMSO-d_6.