Supporting Information

Rhenium(I) based irregular pentagonal-shaped metallacavitands

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Contents

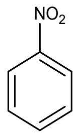
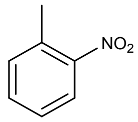
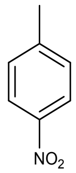
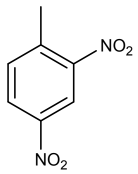
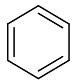
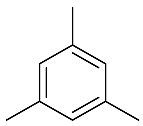
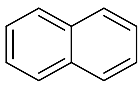
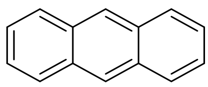
Host-Guest Studies. Quenching experiments of host **1** in the presence of aromatic nitro compounds (Nitrobenzene, NB; 2-Nitrotoluene, 2-NT; 4-Nitrotoluene, 4-NT; 2,4- dinitrotoluene, 2,4-DNT) and planar aromatic compounds (Benzene, Bn; Mesitylene, Ms; Naphthalene, Np; Anthracene, An) were carried out by fluorescence spectroscopic method. The solvent (DMSO) used in this study was of spectroscopic grade and used as received. Aromatic guests stock solutions (NB; 1.7×10^{-2} M for 2-NT, 4-NT and 2,4-DNT; 1.7×10^{-1} M for Bn and Ms; 0.14×10^{-2} M for Np; 0.17×10^{-3} M for An) were prepared in DMSO. Complex **1** stock solutions (1.92×10^{-4} M for NB, 2-NT, 4-NT and 2,4-DNT; 1.92×10^{-4} M for both Bn and Ms; 2.13×10^{-4} M for Np; 1.92×10^{-4} M for An) were prepared in DMSO. Test solutions were prepared by the addition of an appropriate aliquot (0.02-3mL) of each guest stock into 5ml standard volumetric flask followed by placing 1 mL of stock solution of host **1** and then diluting the solution to 5 mL with DMSO. The excitation wavelengths (λ_{ex}) were 336 nm for NB, 2-NT and 4-NT and 2,4-DNT; 350 nm for Bn; 325 nm for Ms; 290 nm for Np and 336 nm for An. The slit width was 5 nm for both the excitation and emission.

The binding characteristics of host **1** with guest molecules were determined by the emission spectroscopic method. The binding constants were calculated on the basis of the Benesi-Hildebrand equation.

$$1/\Delta I = 1/\Delta I_{max} + (1/\ K[G]\ \Delta I_{max})$$

Here $\Delta I = I - I_{min}$, $\Delta I_{max} = I_0 - I_{min}$, I_0 is the emission intensity of free host **1,** I is the intensity measured with guest, I_{min} is the intensity measured with an excess of guest, K is the binding constant, and [G] is the concentrations of guest molecules.

Table S1: Binding constant K [M^{-1}] of host **1** with guests in DMSO at 298K.

Guests	Binding constants (K, M^{-1})
	4.7×10^{2}
	1.1×10^{3}
	4.5×10^{2}
	2.5×10^{3}
	not detectable
	not detectable
	1.7×10^{3}
	1.3×10^{4}

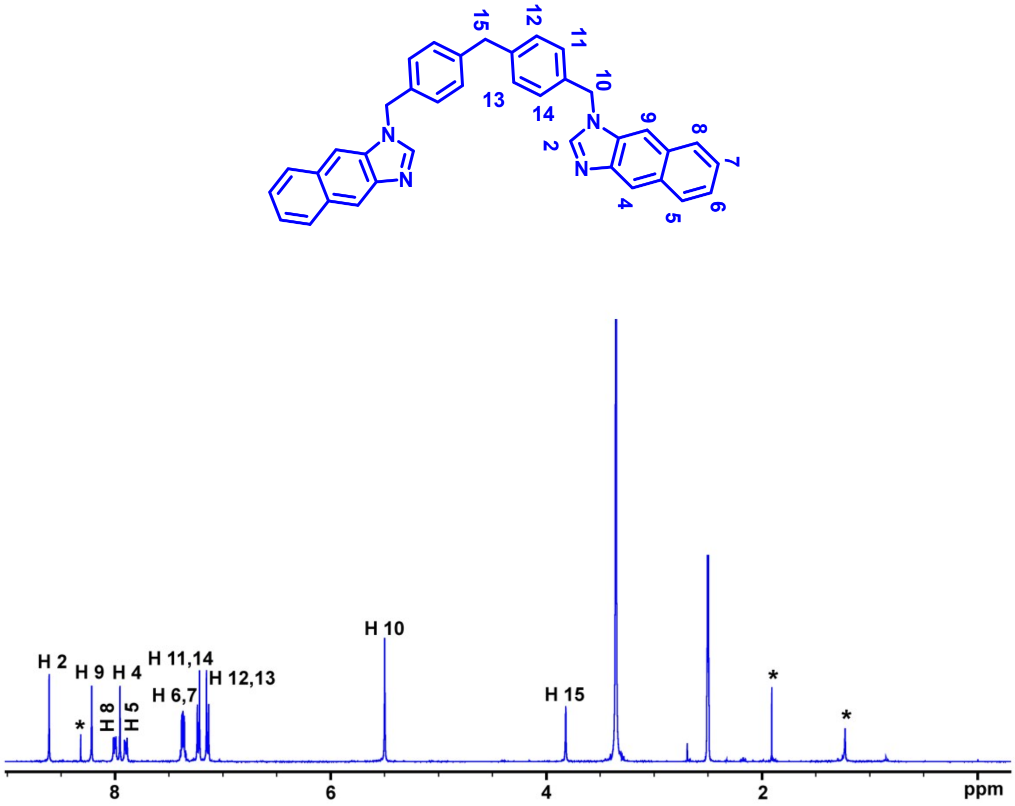


Fig. S1 ^{1}H NMR spectrum of L^1 in DMSO- d_6 (* is solvent).

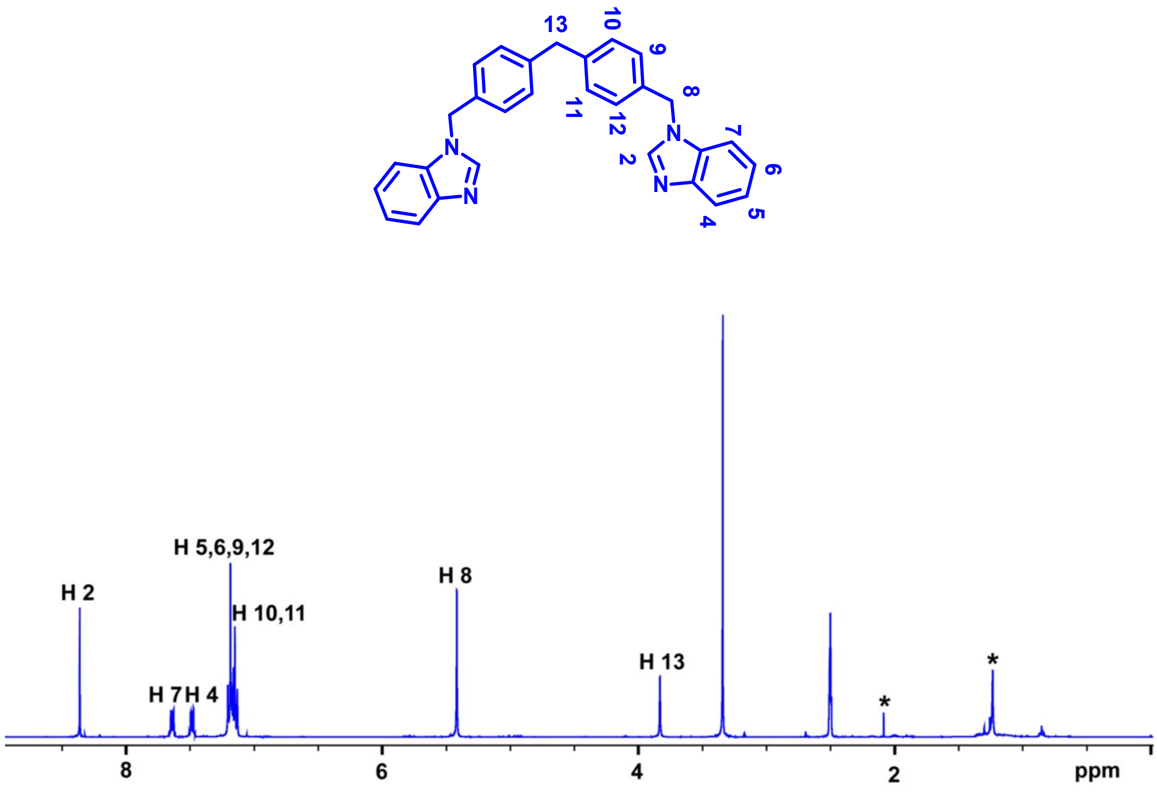
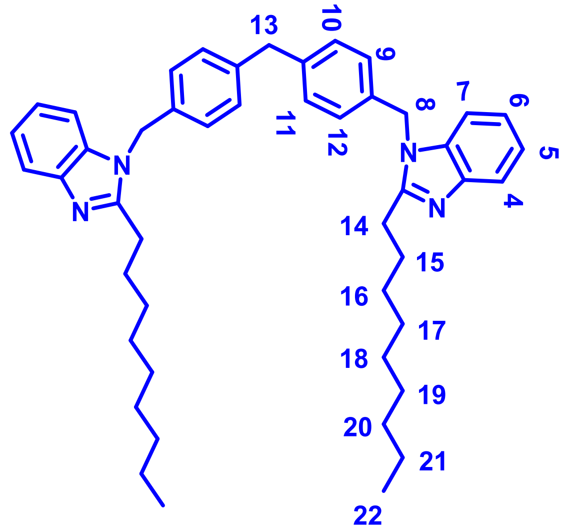


Fig. S2 ^{1}H NMR spectrum of L^2 in DMSO- d_6 (* is solvent).



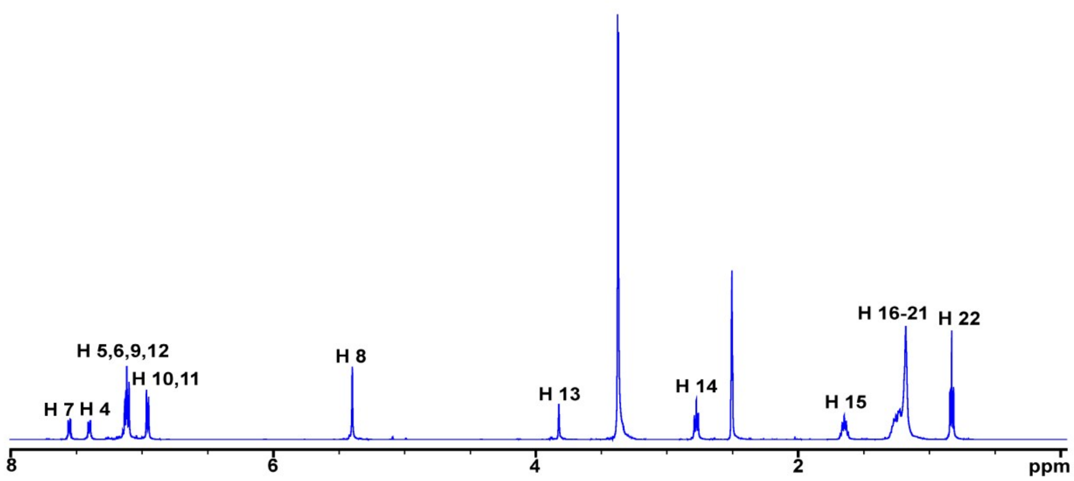
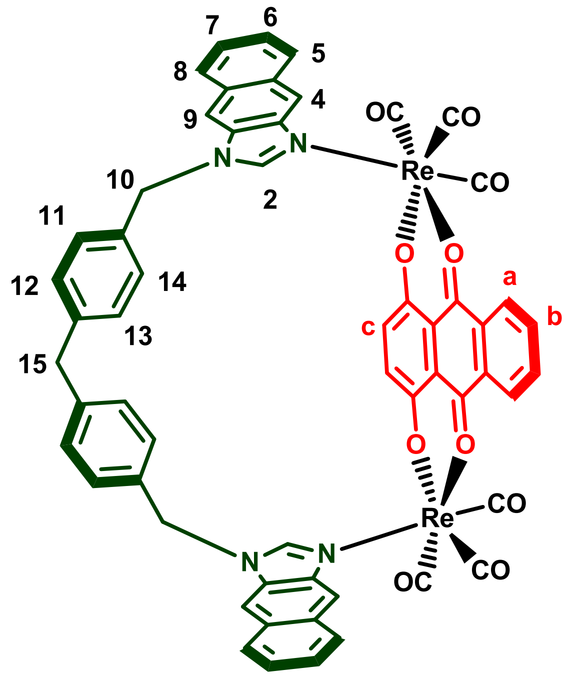


Fig. S3 ^{1}H NMR spectrum of L^3 in DMSO- d_6.



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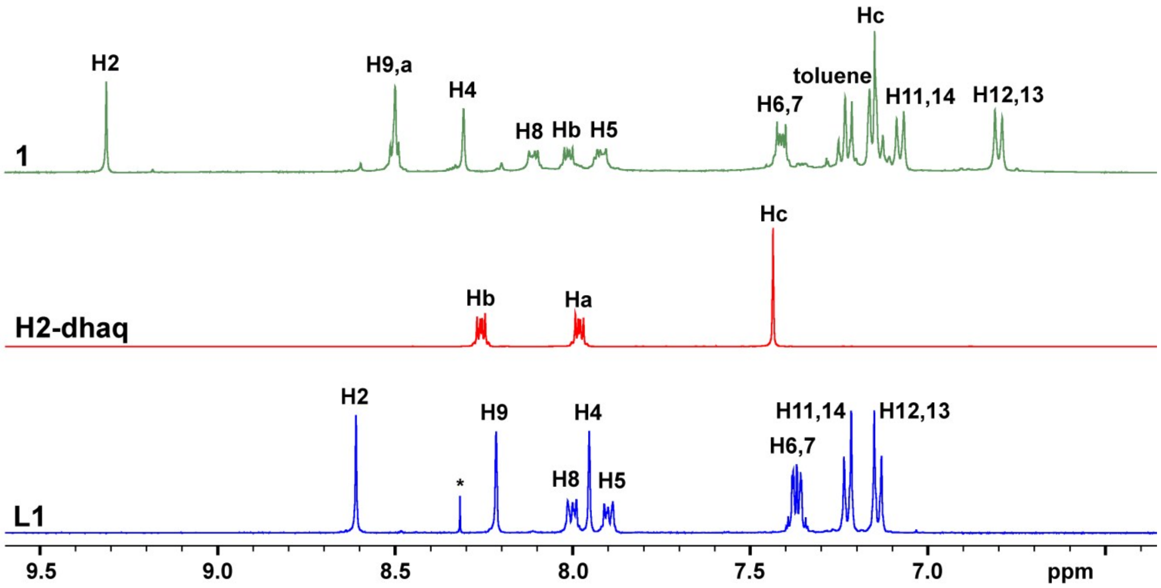
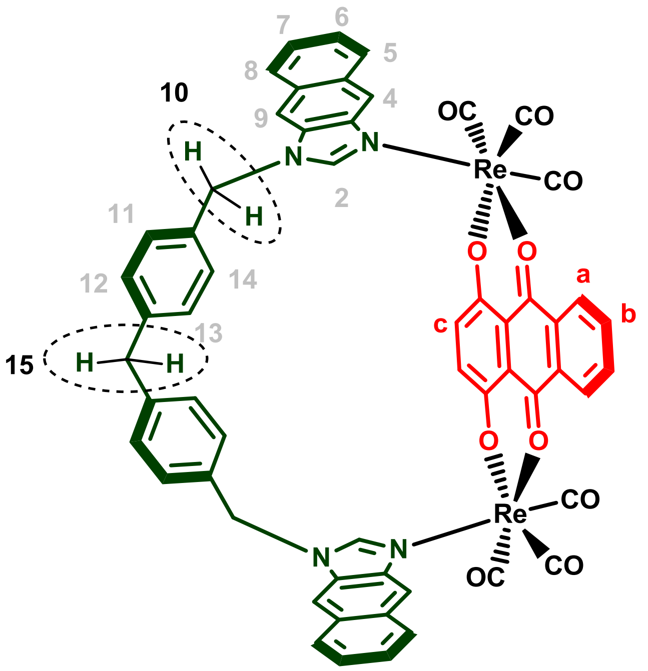


Fig. S4 Partial [1]H NMR spectra of **1**, H_2-dhaq and L[1] in DMSO-d_6.



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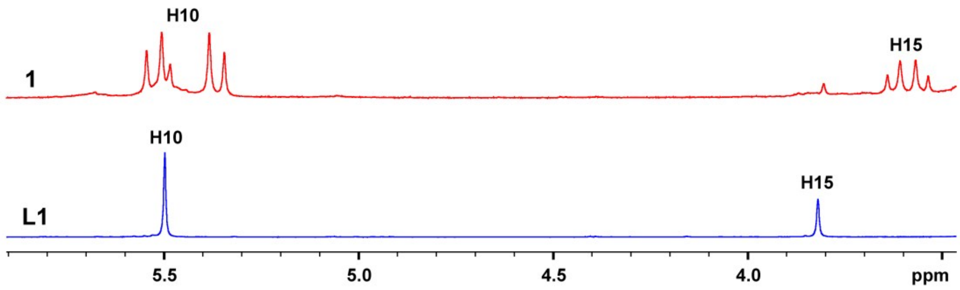
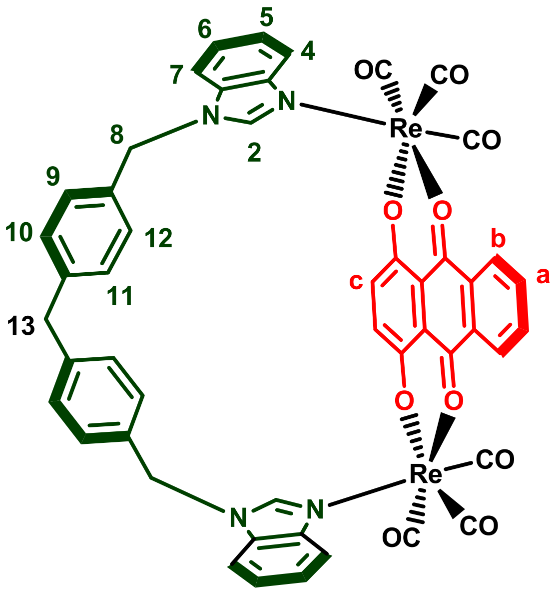


Fig. S5 Partial ^{1}H NMR spectra of **1**, and L^1 in DMSO-d_6.



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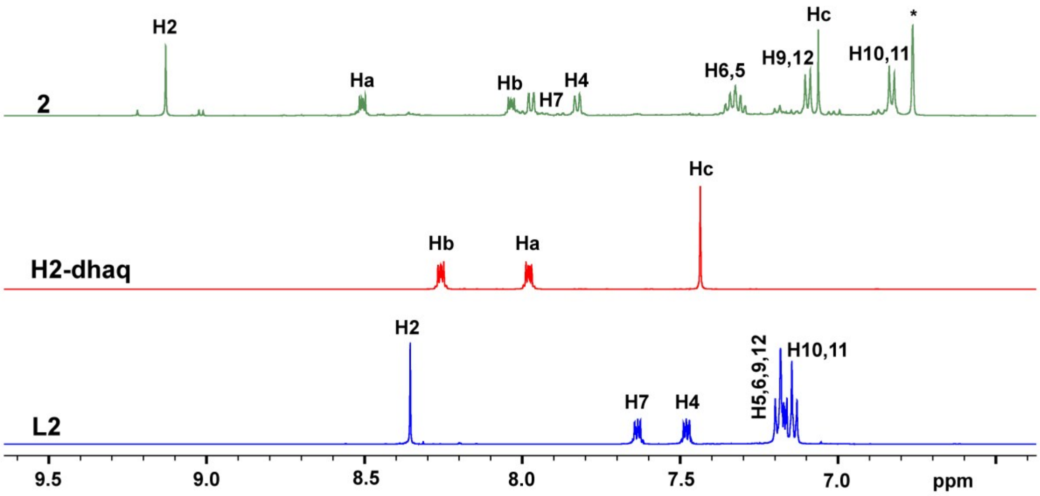
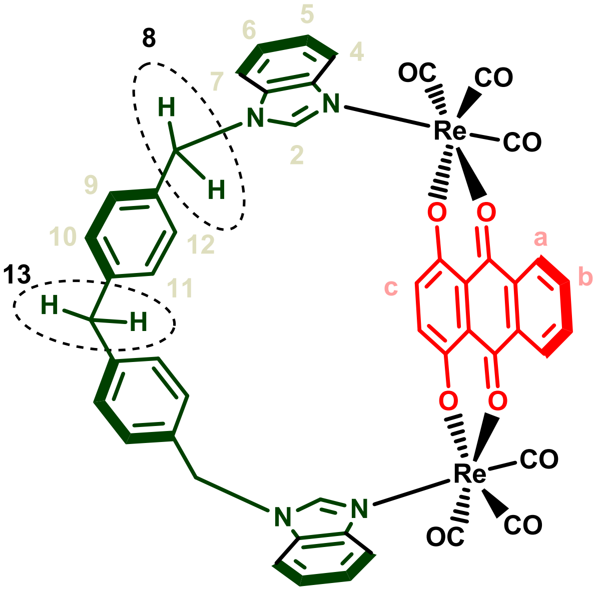


Fig. S6 Partial ^{1}H NMR spectra of **2**, H_2-dhaq and L^2 in DMSO-d_6 (* is solvent).



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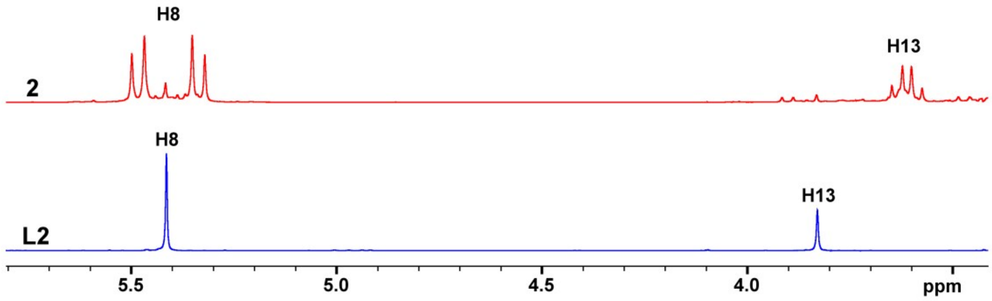
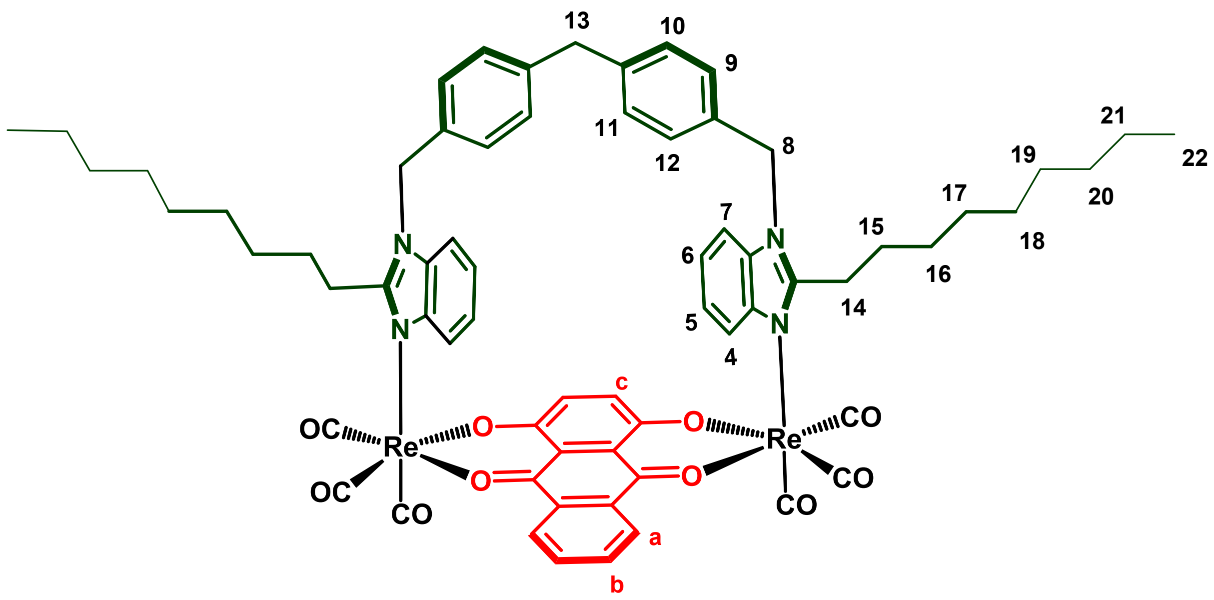


Fig. S7 Partial ^{1}H NMR spectra of **2**, and L^2 in DMSO-d_6.



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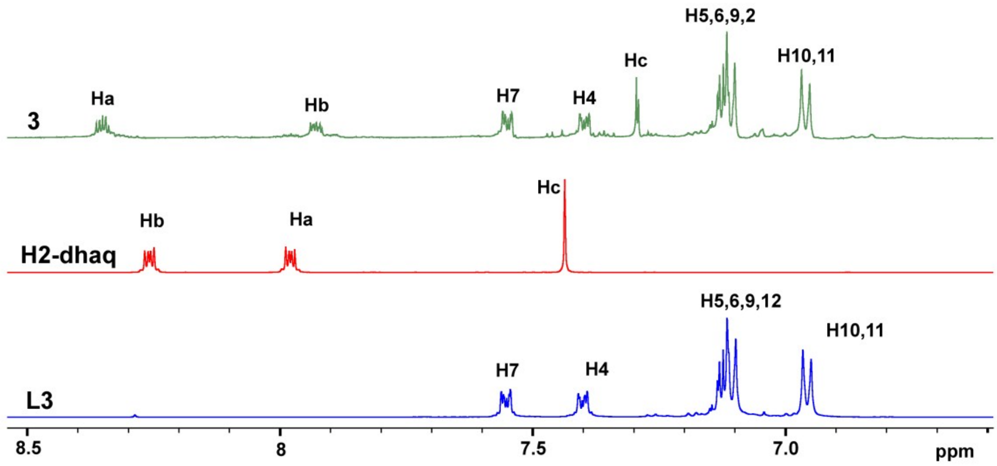
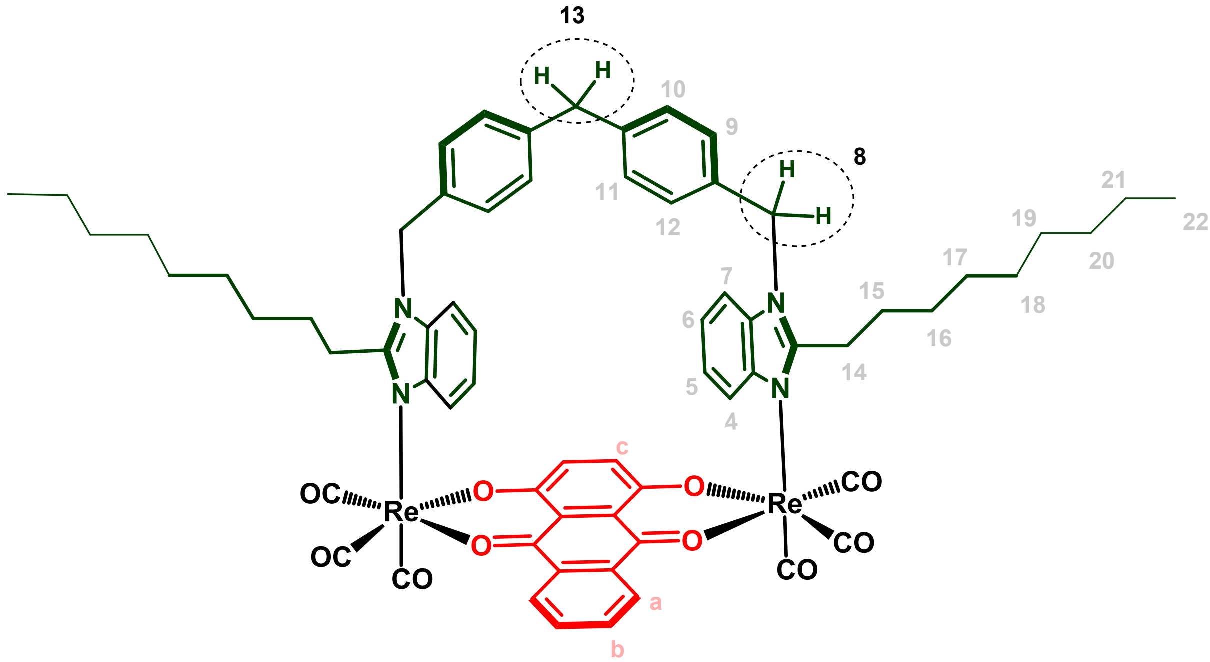


Fig. S8 ^{1}H NMR spectra of **3**, H_2-dhaq and L^3 in DMSO-d_6.



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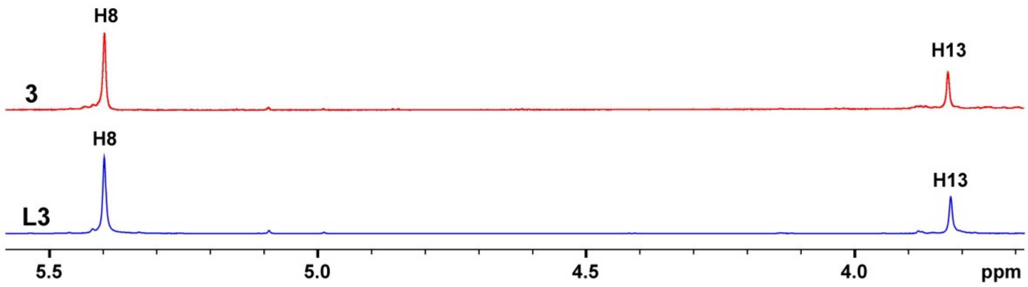
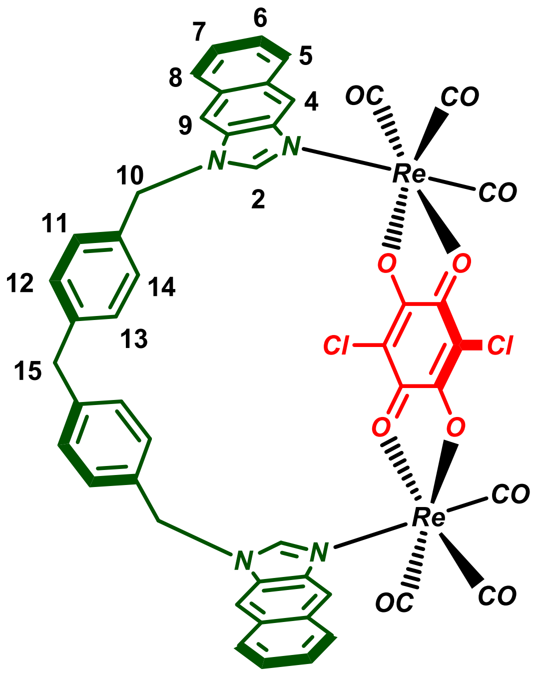


Fig. S9 Partial ^{1}H NMR spectra of **3**, and L^{3} in DMSO-d_6.



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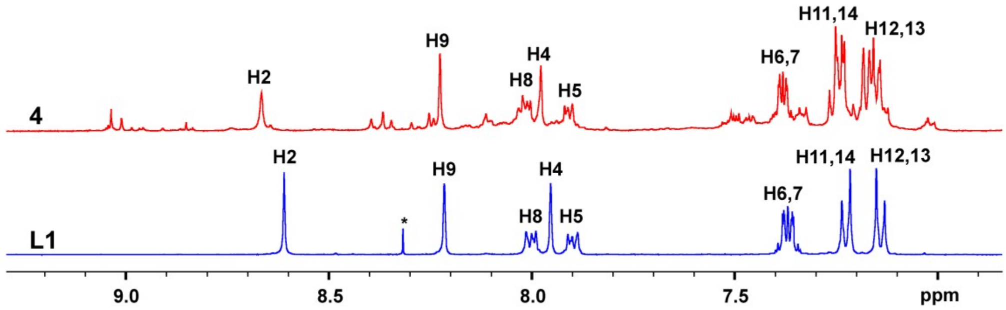
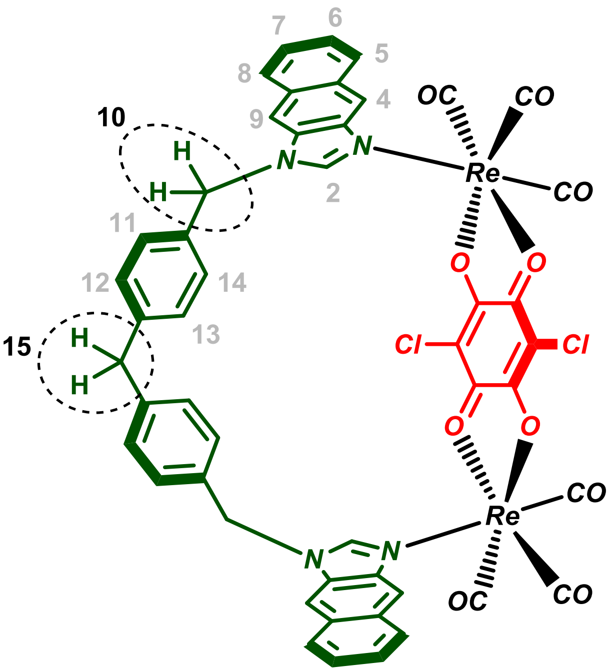


Fig. S10 Partial ^{1}H NMR spectra of **4**, and L^1 in DMSO-d_6.



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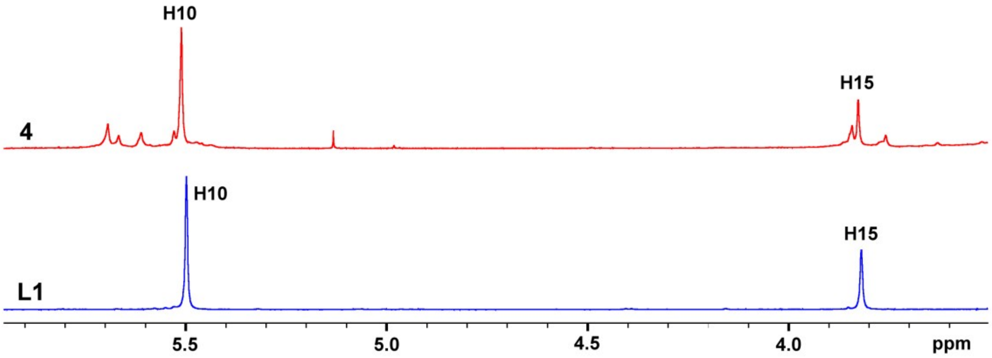

Fig. S11 Partial ^{1}H NMR spectra of **4**, and L^{1} in DMSO-d_6.

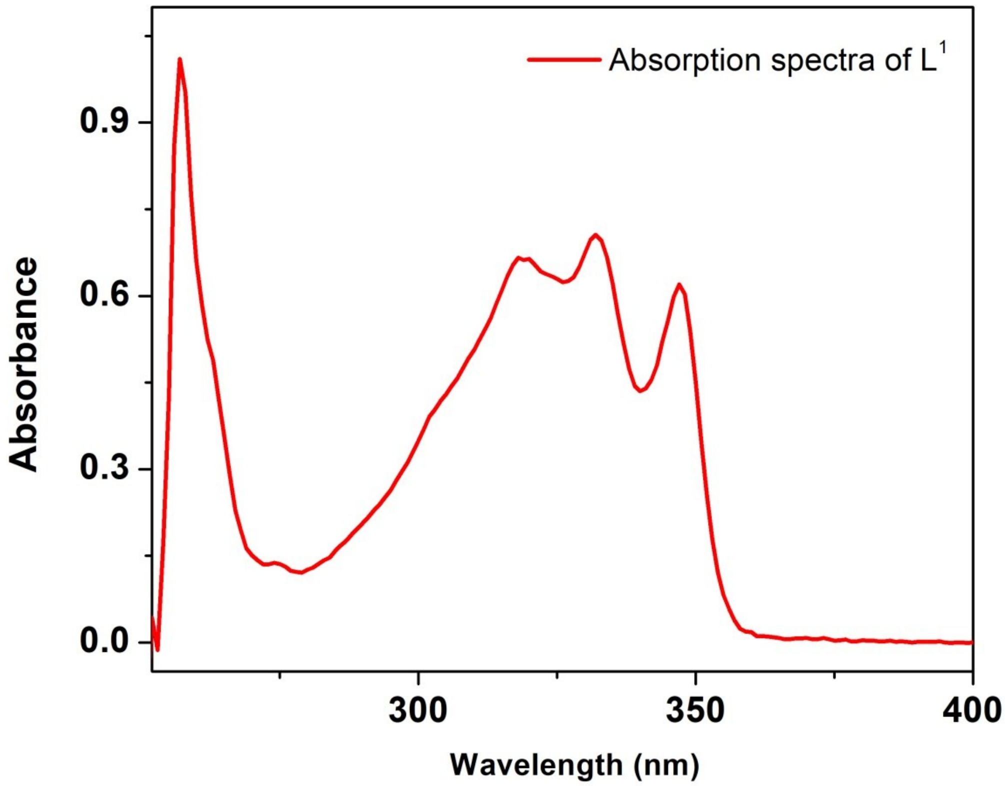

Fig. S12 Absorption spectra of L^1 in DMSO (concentration: 0.68×10^{-4} M).

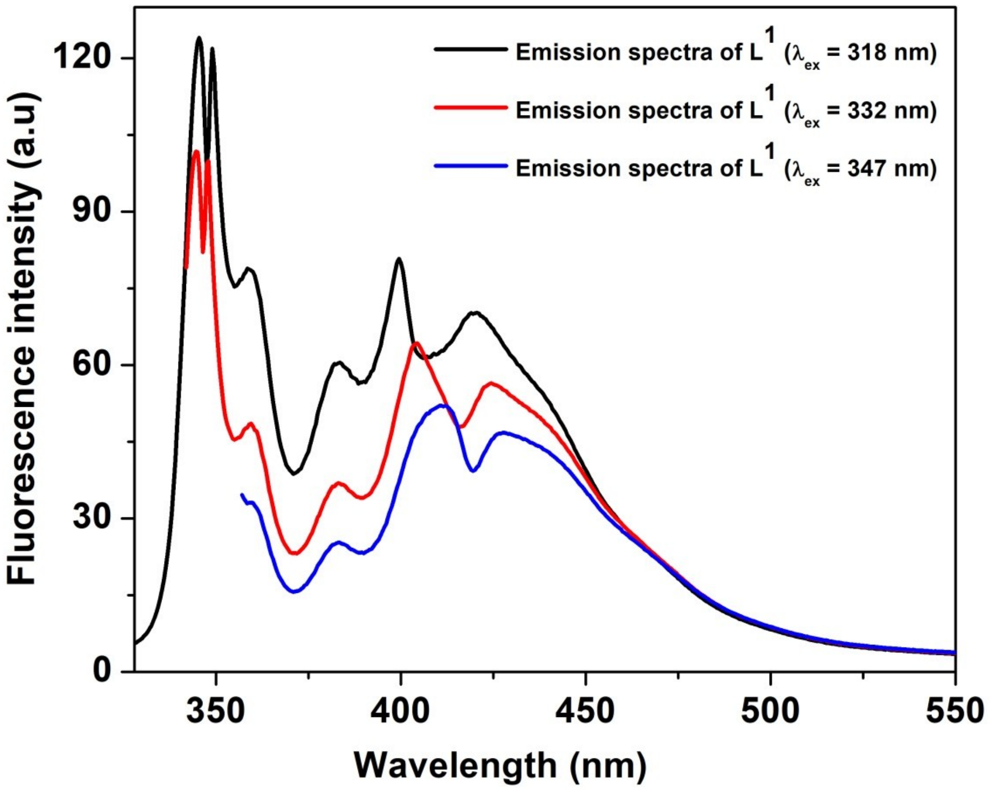

Fig. S13 Emission spectra of L^1 excited at UV region wavelength in DMSO (concentration: 0.68×10^{-4} M).

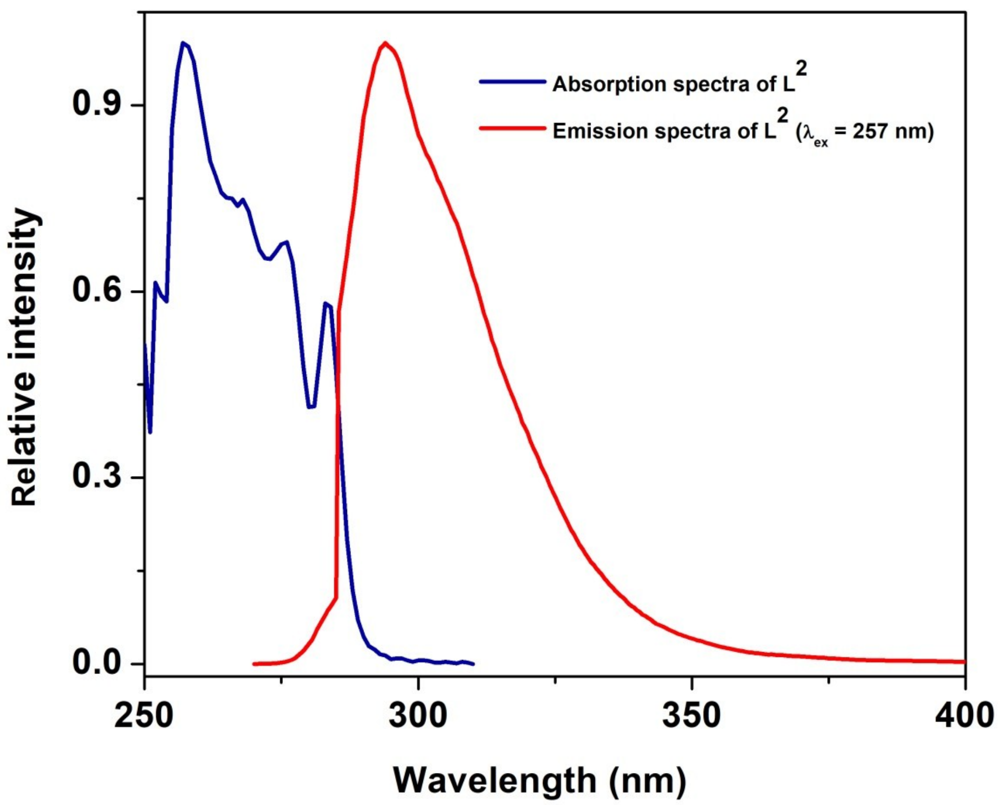

Fig. S14 Absorption and emission spectra of L^2 in DMSO (concentration: 10^{-4} M).

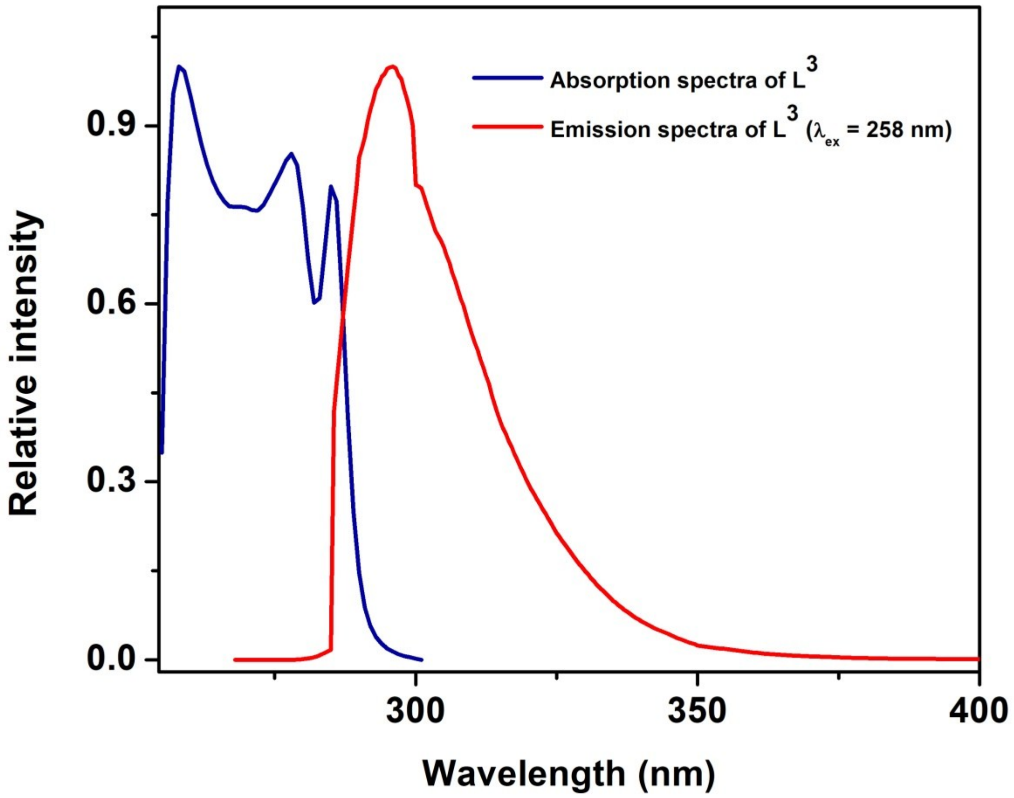

Fig. S15 Absorption and emission spectra of L^3 in DMSO (concentration: 0.2×10^{-4} M)

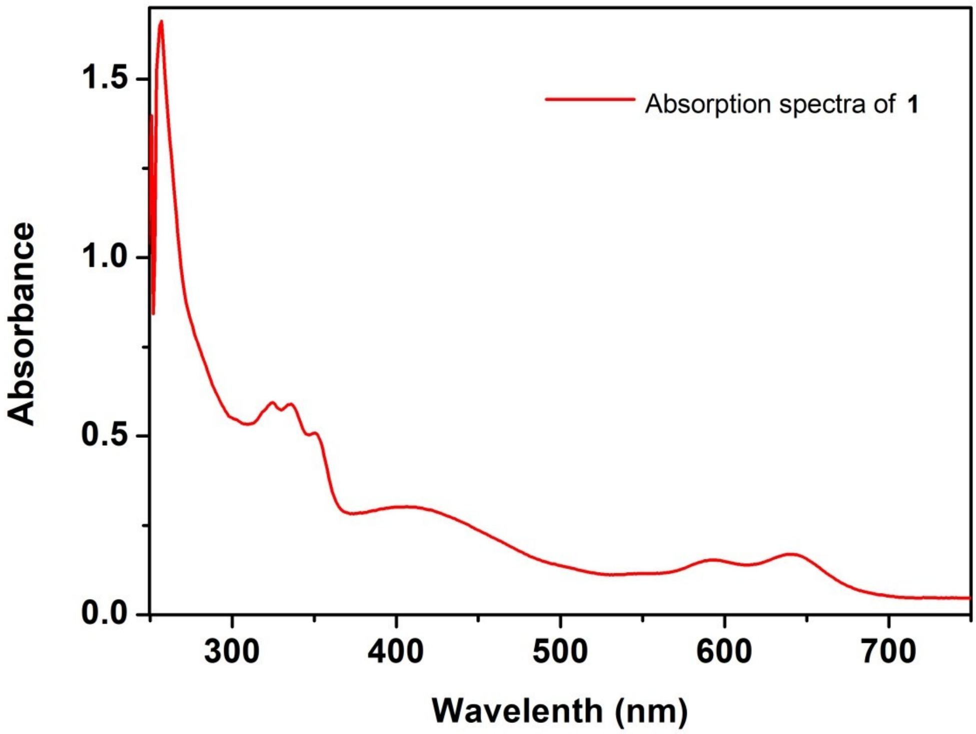

Fig. S16 Absorption spectra of **1** in DMSO (concentration: 0.60×10^{-3} M).

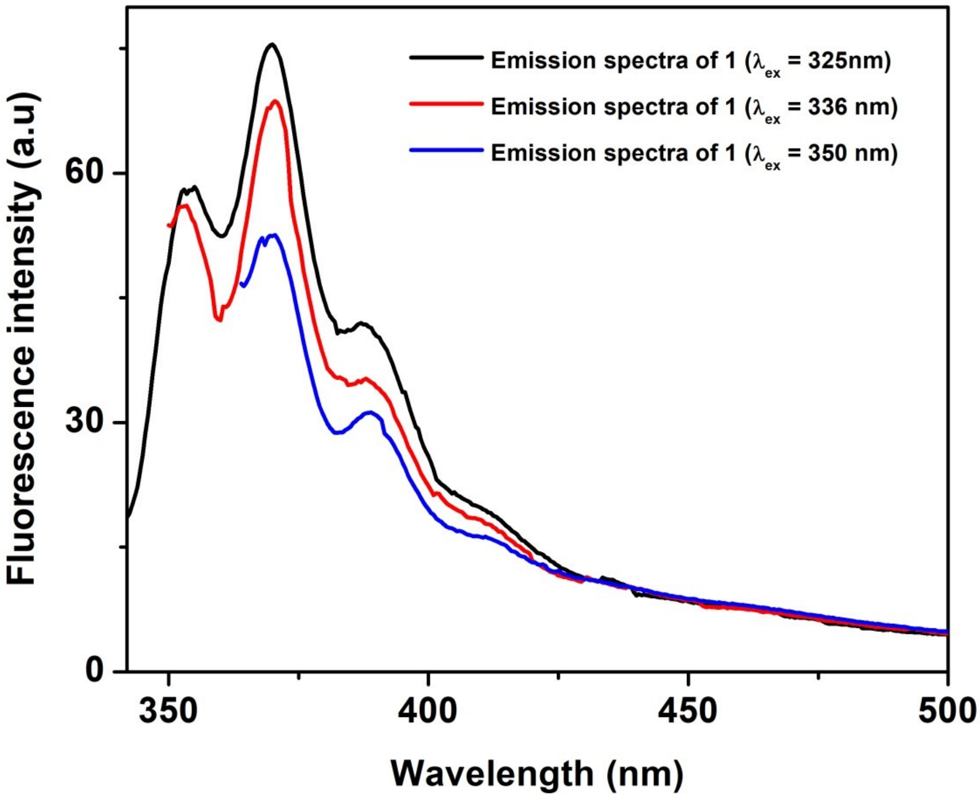

Fig. S17 Emission spectra of **1** in DMSO (concentration: 1.92×10^{-4} M).

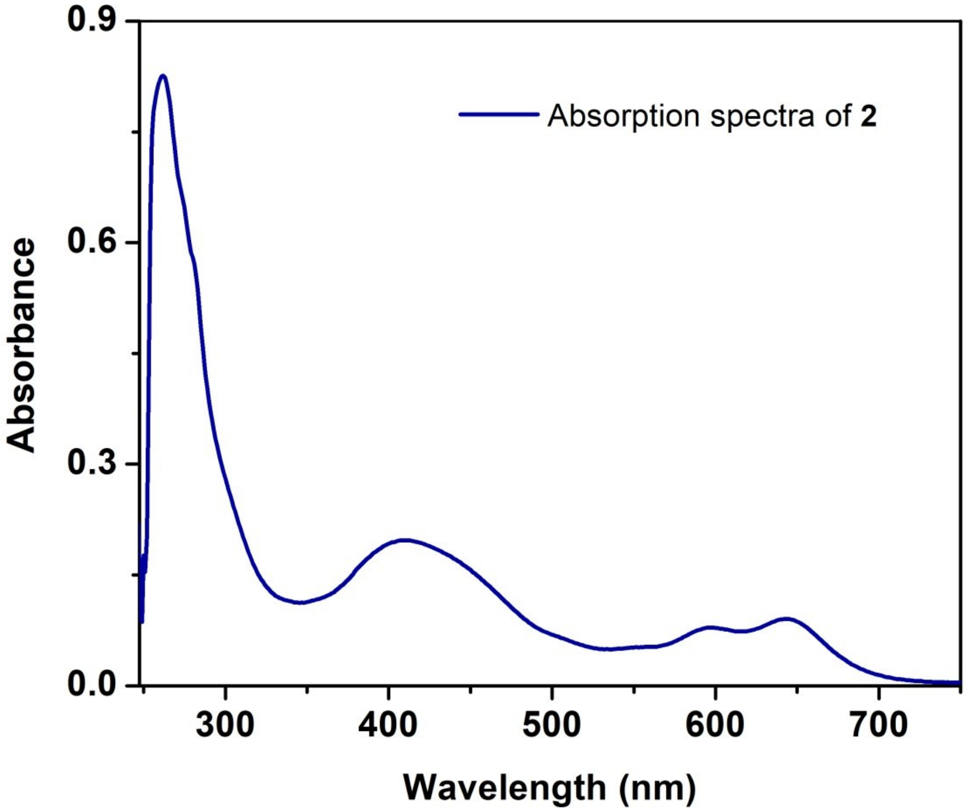

Fig. S18 Absorption spectra of **2** in DMSO (concentration: 0.3×10^{-5} M).

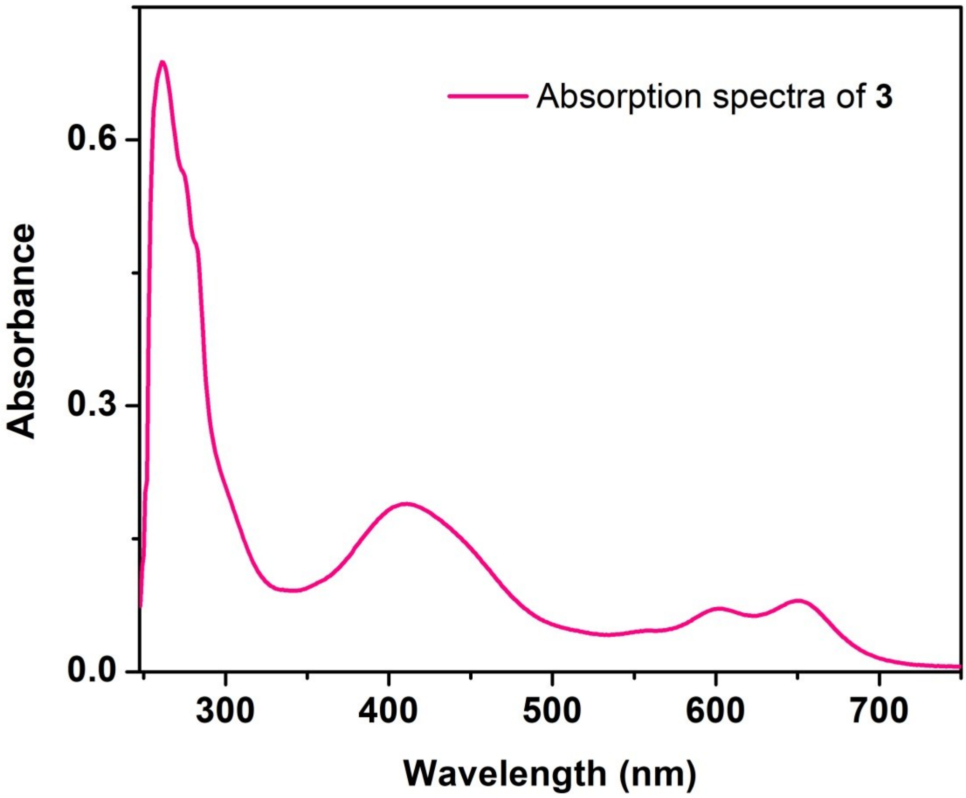

Fig. S19 Absorption spectra of **3** in DMSO (concentration: 0.4×10^{-5} M).

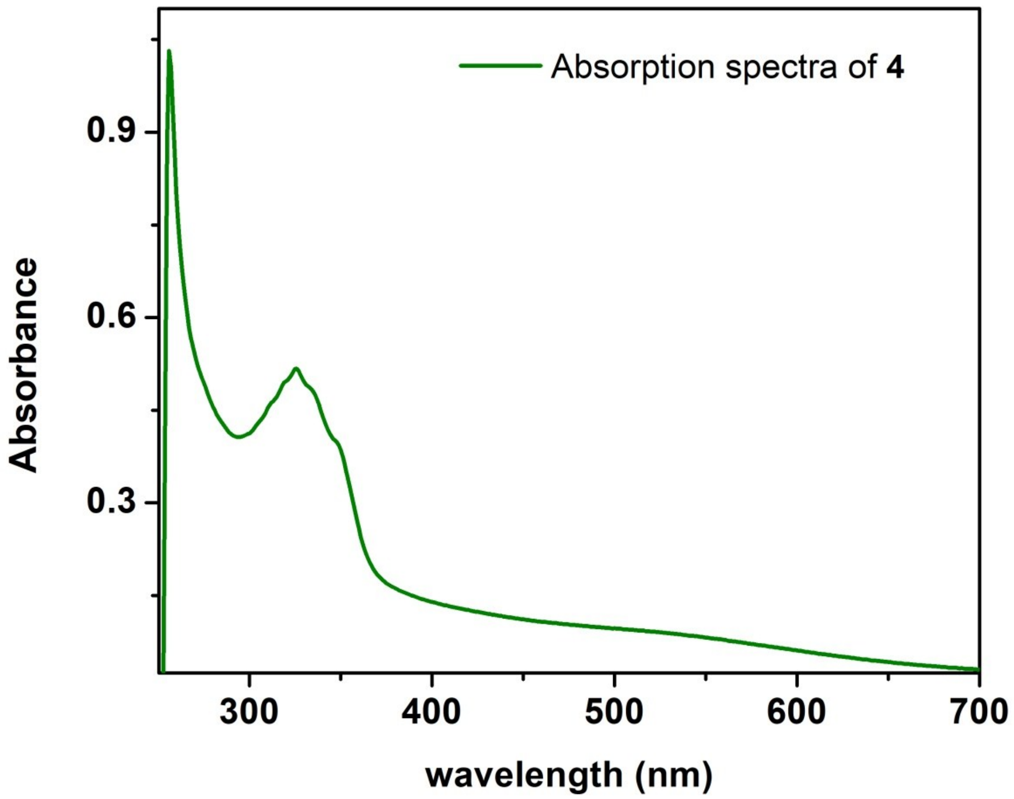

Fig. S20 Absorption spectra of **4** in DMSO (concentration: 0.2×10^{-4} M).

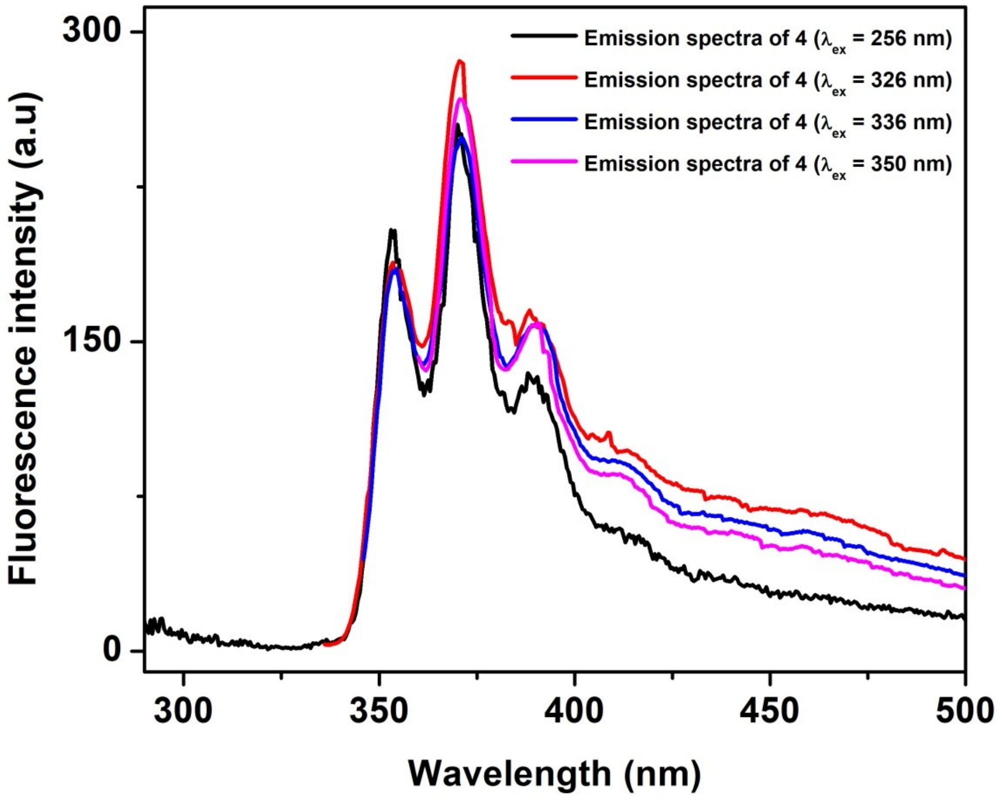

Fig. S21 Emission spectra of **4** in DMSO (concentration: 1.0×10^{-4} M).

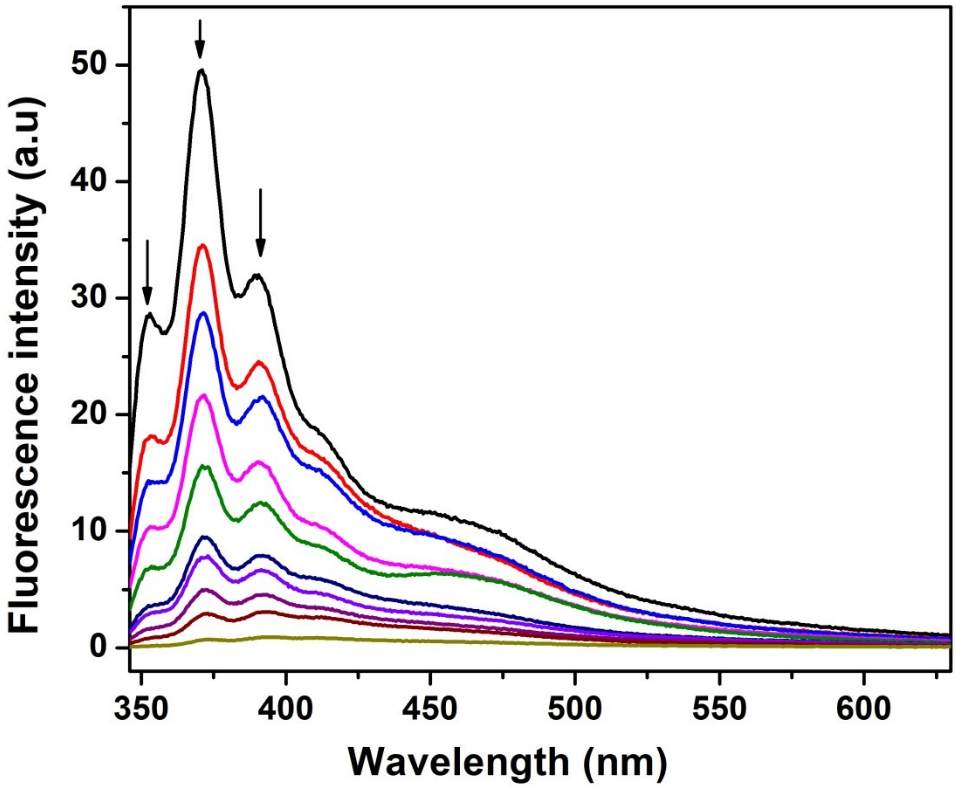

Fig. S22 Changes in the emission spectra of **1** (3.84×10^{-5} M, λ_{ex}= 336 nm) with the addition of nitro benzene in DMSO. The arrows indicate the changes in the fluorescence intensity by addition of an appropriate aliquot of nitrobenzene.

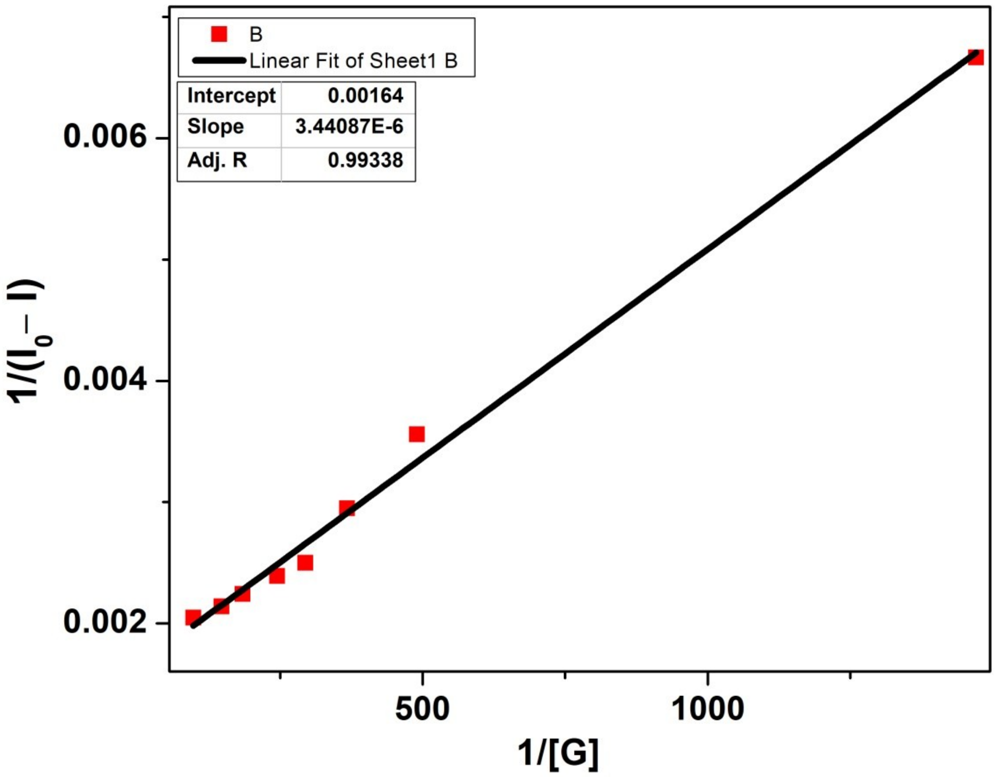

Fig. S23 Benesi-Hildebrand plot for the emission quenching of host **1** (at 371 nm) with an increase in the concentration of nitrobenzene in DMSO.

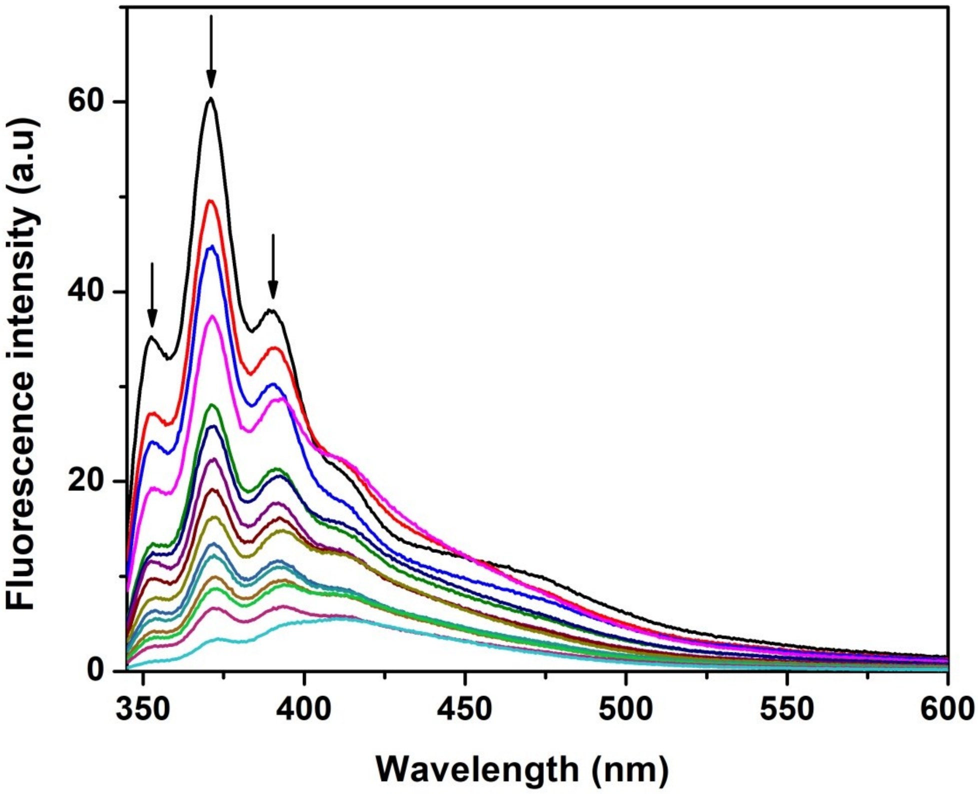

Fig. S24 Changes in the emission spectra of **1** (3.84×10^{-5} M, λ_{ex}= 336 nm) with the addition of 2-nitrotoluene in DMSO. The arrows indicate the changes in the fluorescence intensity by addition of an appropriate aliquot of 2-nitrotoluene.

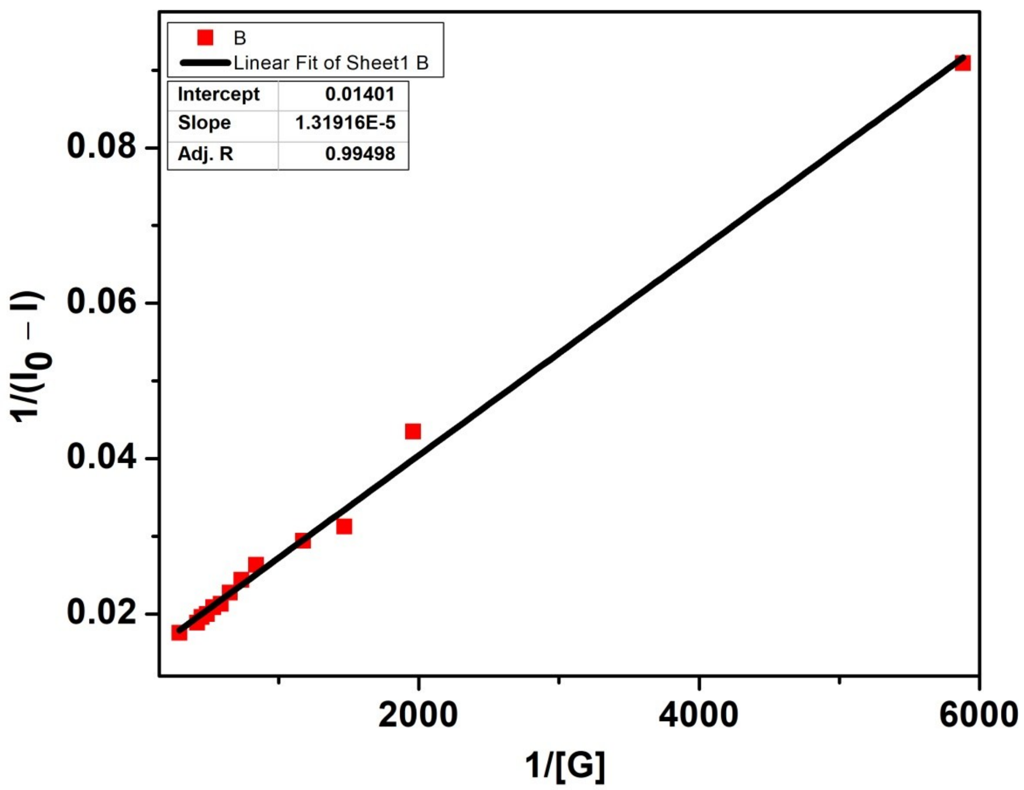

Fig. S25 Benesi-Hildebrand plot for the emission quenching of host **1** (at 371 nm) with an increase in the concentration of 2-nitrotoluene in DMSO.

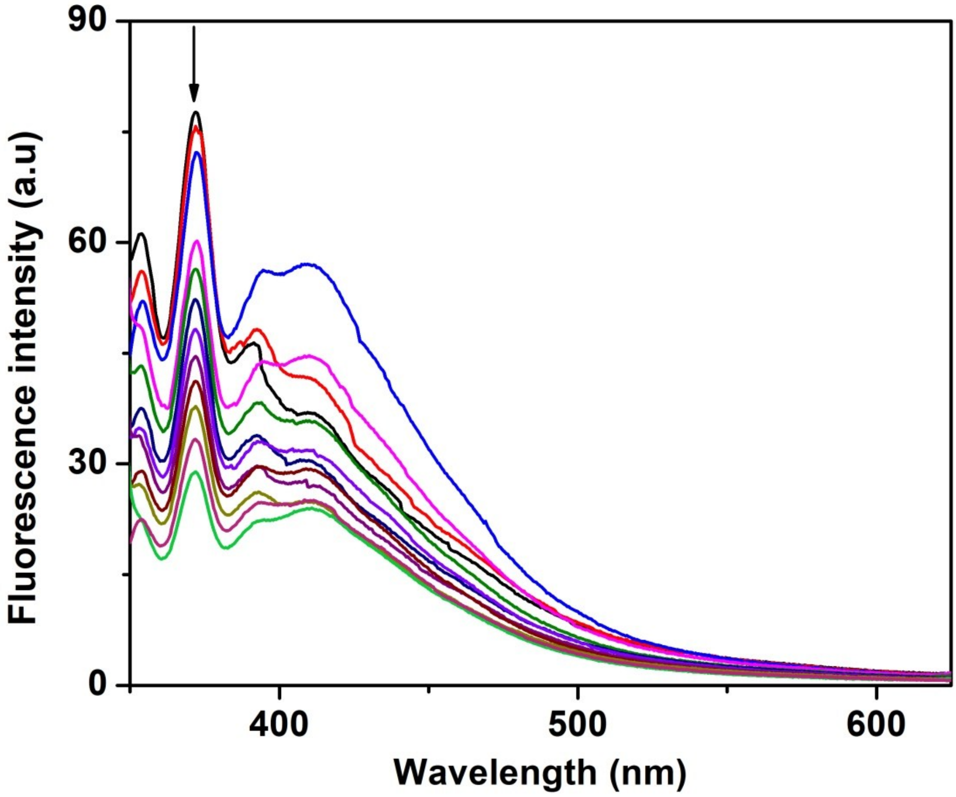

Fig. S26 Changes in the emission spectra of **1** ($3.84{\times}10^{-5}$ M, λ_{ex}= 336 nm) with the addition of 4-nitrotoluene in DMSO. The arrows indicate the changes in the fluorescence intensity by addition of an appropriate aliquot of 4-nitrotoluene.

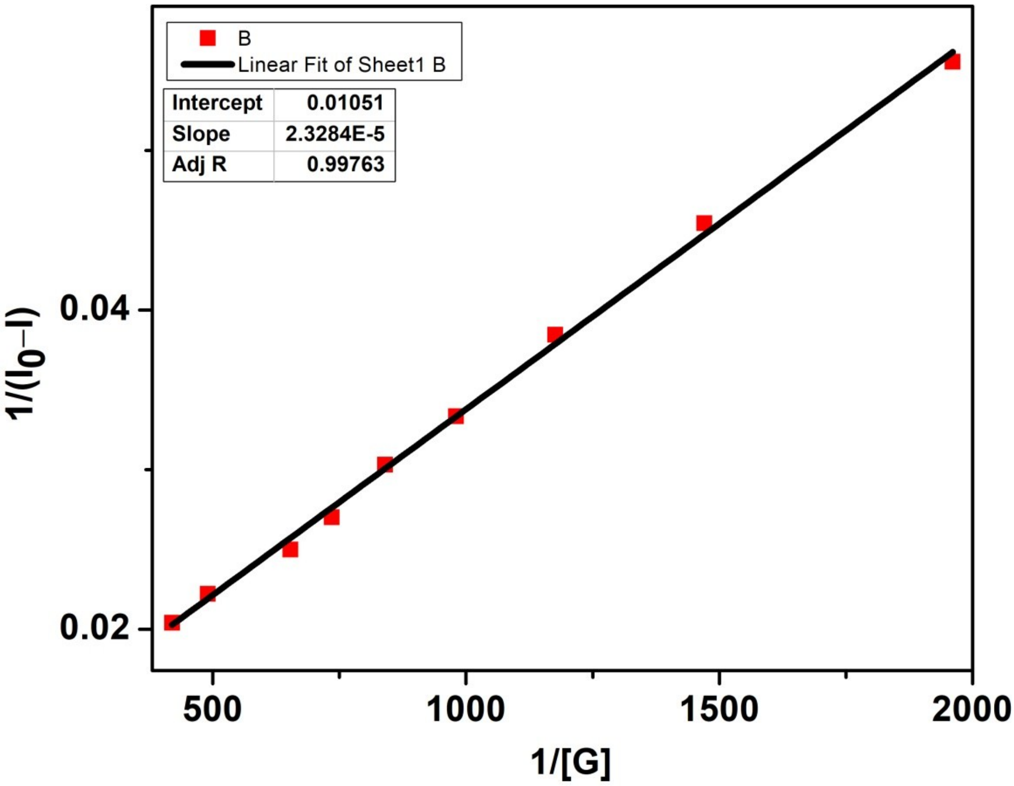

Fig. S27 Benesi-Hildebrand plot for the emission quenching of host **1** (at 372 nm) with an increase in the concentration of 4-nitrotoluene in DMSO.

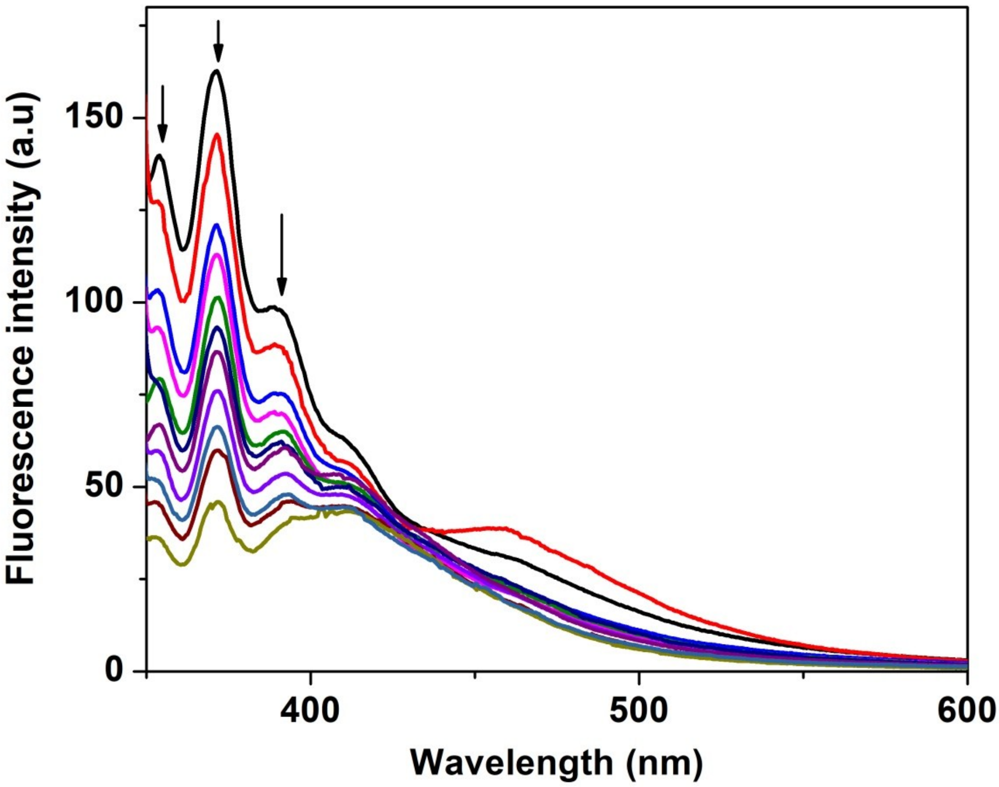

Fig. S28 Changes in the emission spectra of **1** (3.84×10^{-5} M, λ_{ex}= 336 nm) with the addition of 2,4-dinitrotoluene in DMSO. The arrows indicate the changes in the fluorescence intensity by addition of an appropriate aliquot of 2,4-dinitrotoluene.

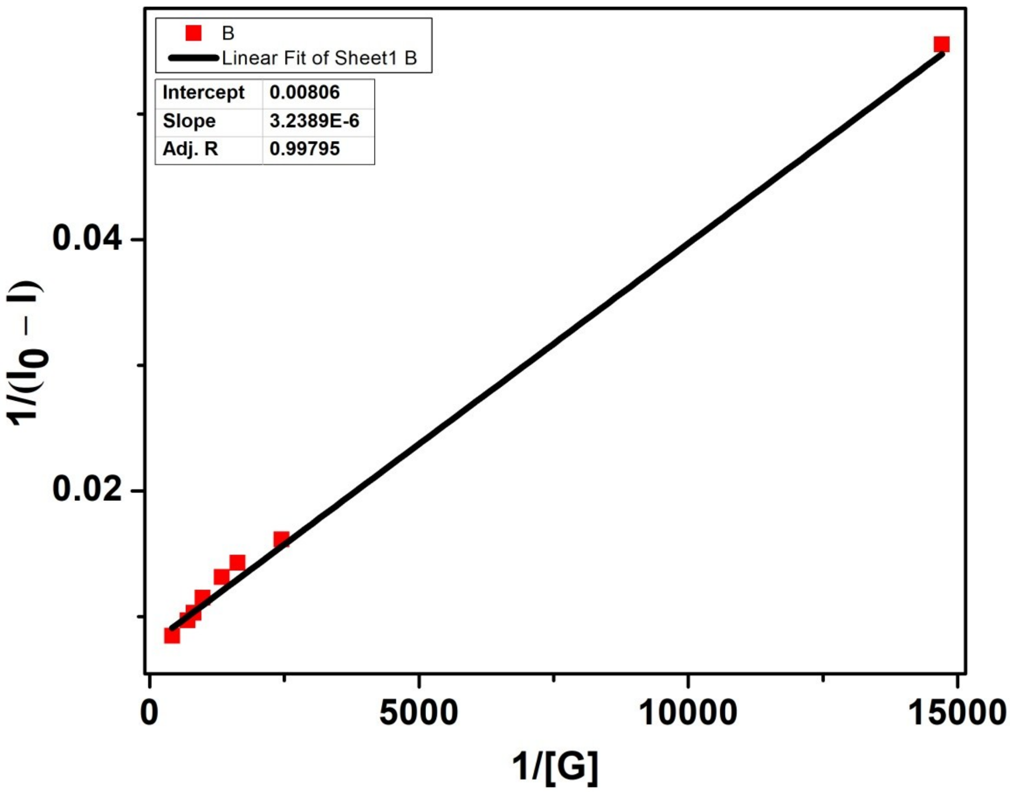

Fig. S29 Benesi-Hildebrand plot for the emission quenching of host **1** (at 371 nm) with an increase in the concentration of 2,4-dinitrotoluene in DMSO.

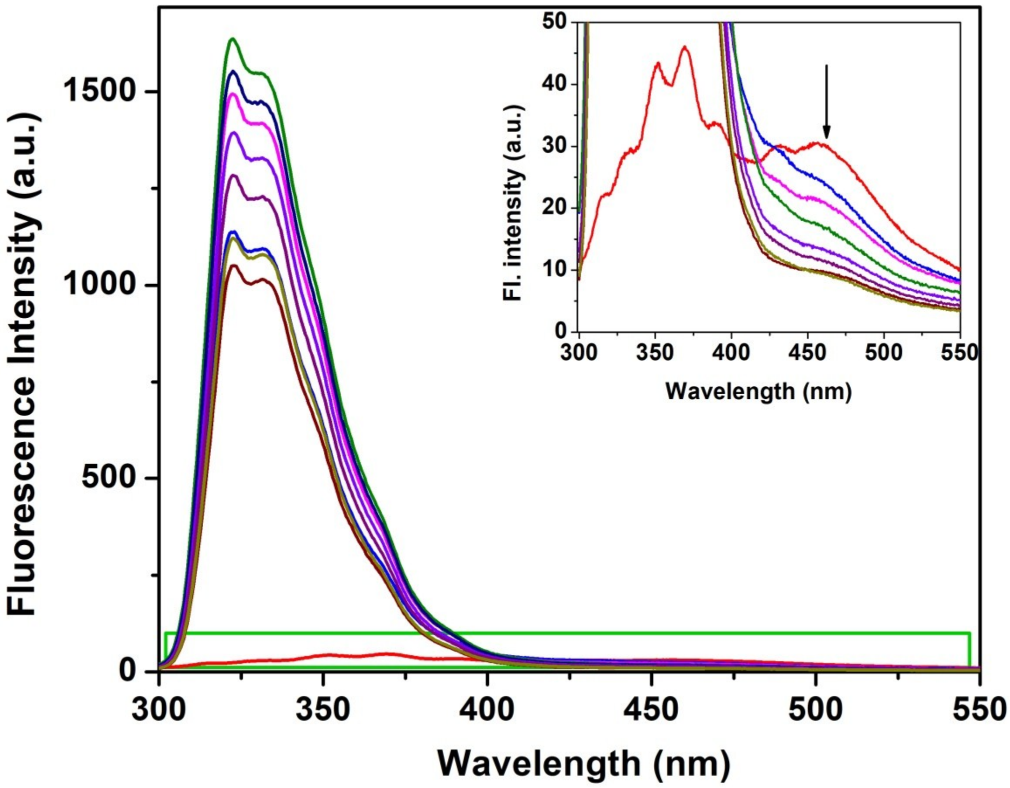

Fig. S30 Changes in the emission spectra of **1** (4.26×10^{-5} M, λ_{ex}= 290 nm) with the addition of naphthalene in DMSO. The arrow indicates the changes in the fluorescence intensity by addition of an appropriate aliquot of naphthalene.

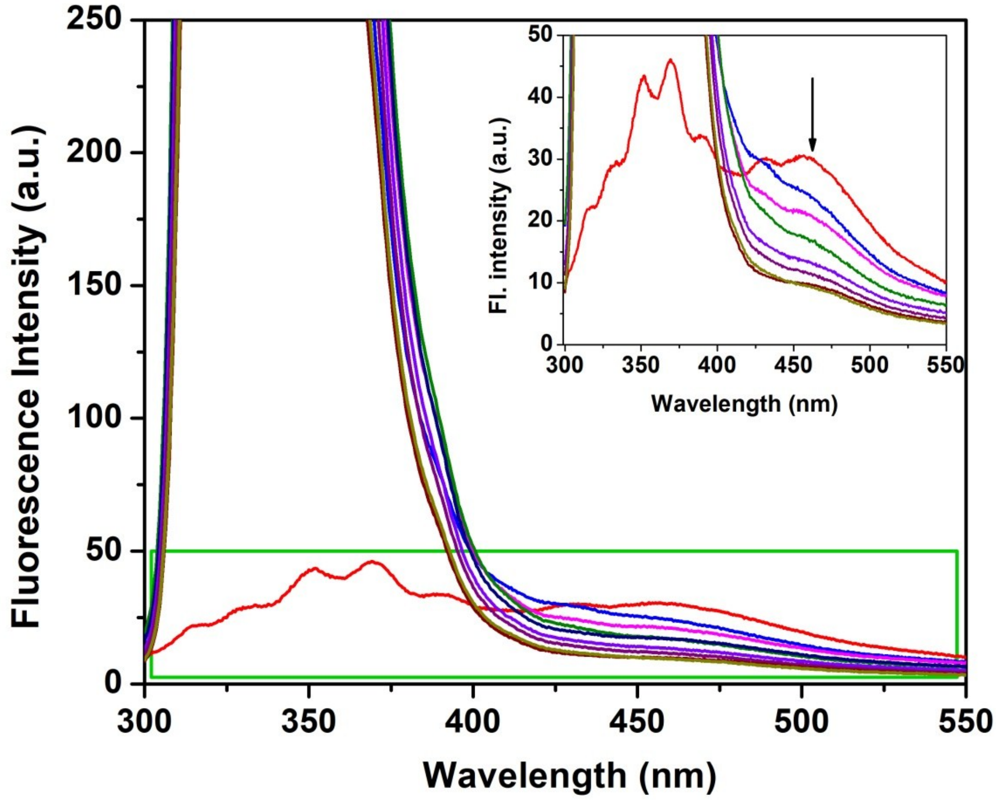

Fig.S30A Changes in the emission spectra of **1** (4.26×10^{-5} M, λ_{ex}=336 nm) with the addition of naphthalene in DMSO. The arrow indicates the changes in the fluorescence intensity by addition of an appropriate aliquot of naphthalene.

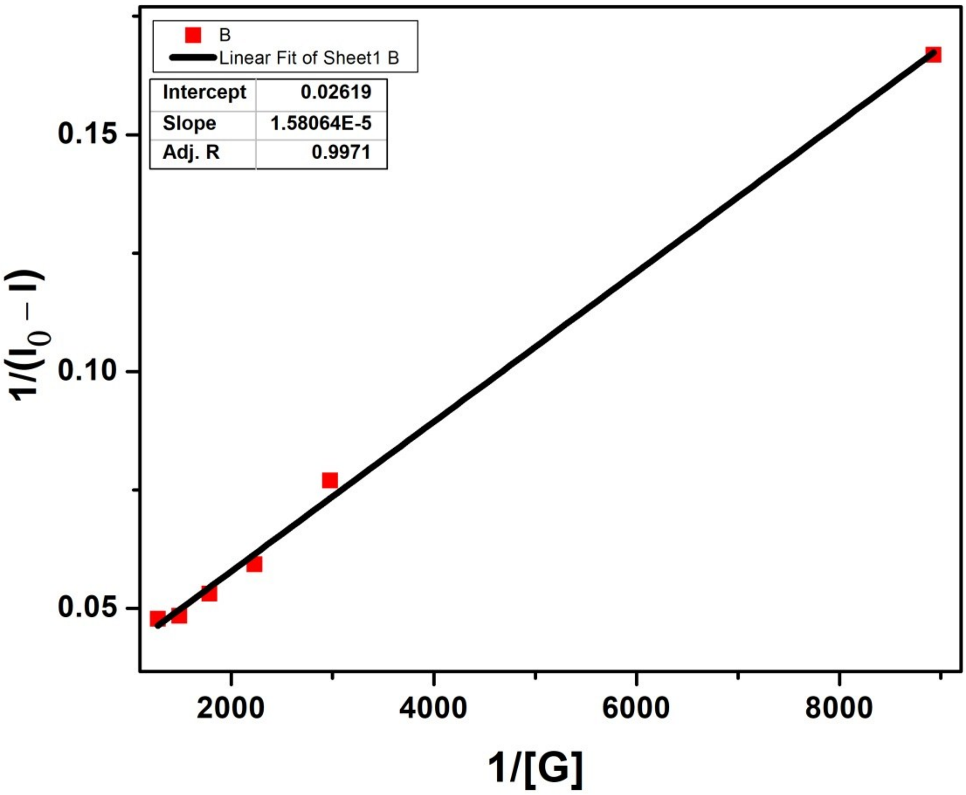

Fig. 31 Benesi-Hildebrand plot for the emission quenching of host **1** (at 457 nm) with an increase in the concentration of naphthalene in DMSO.

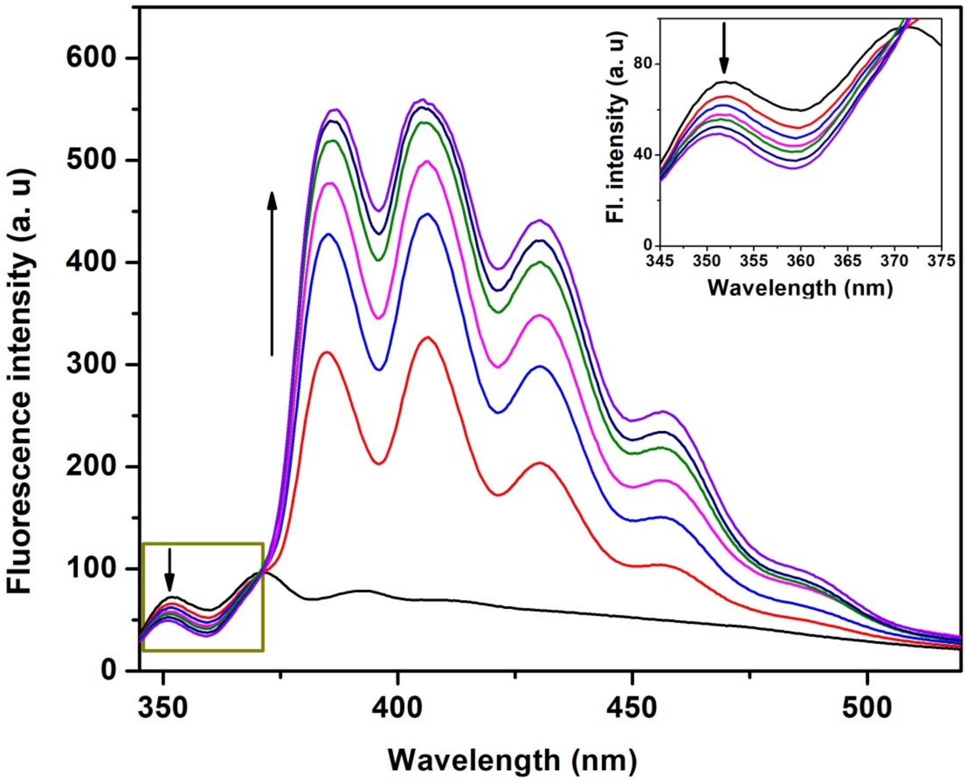

Fig. S32 Changes in the emission spectra of **1** (3.84×10^{-5} M, λ_{ex}=336 nm) with the addition of anthracene in DMSO. The arrows indicate the changes in the fluorescence intensity by addition of an appropriate aliquot of anthracene.

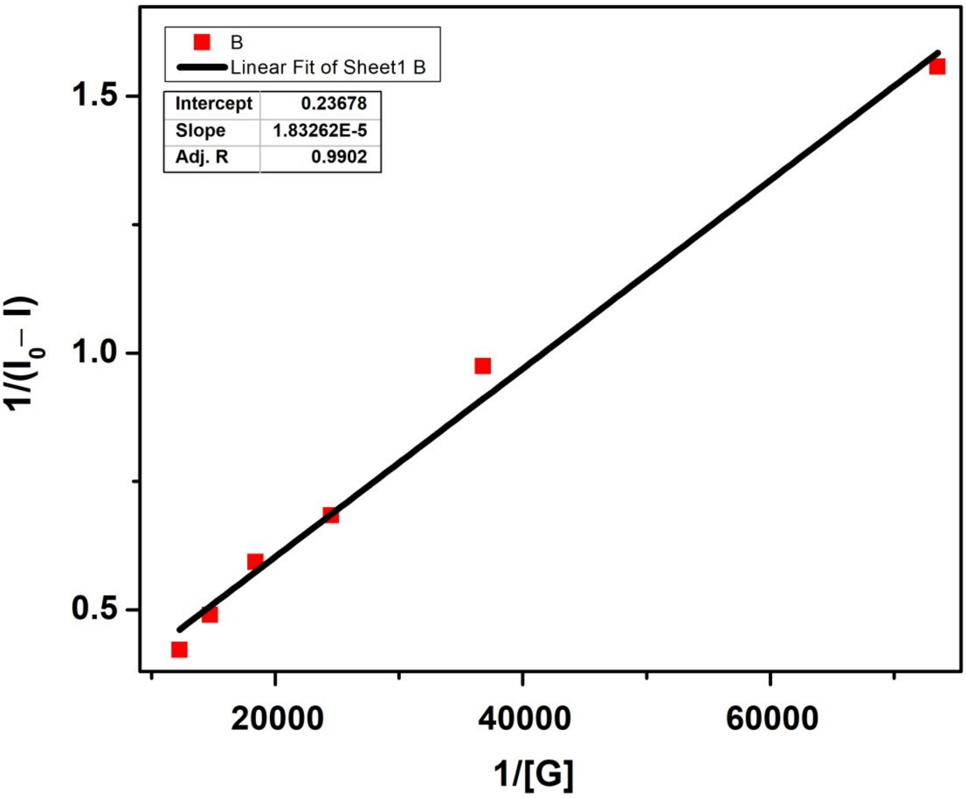

Fig. S33 Benesi-Hildebrand plot for the emission quenching of host **1** (at 352 nm) with an increase in the concentration of anthracene in DMSO.

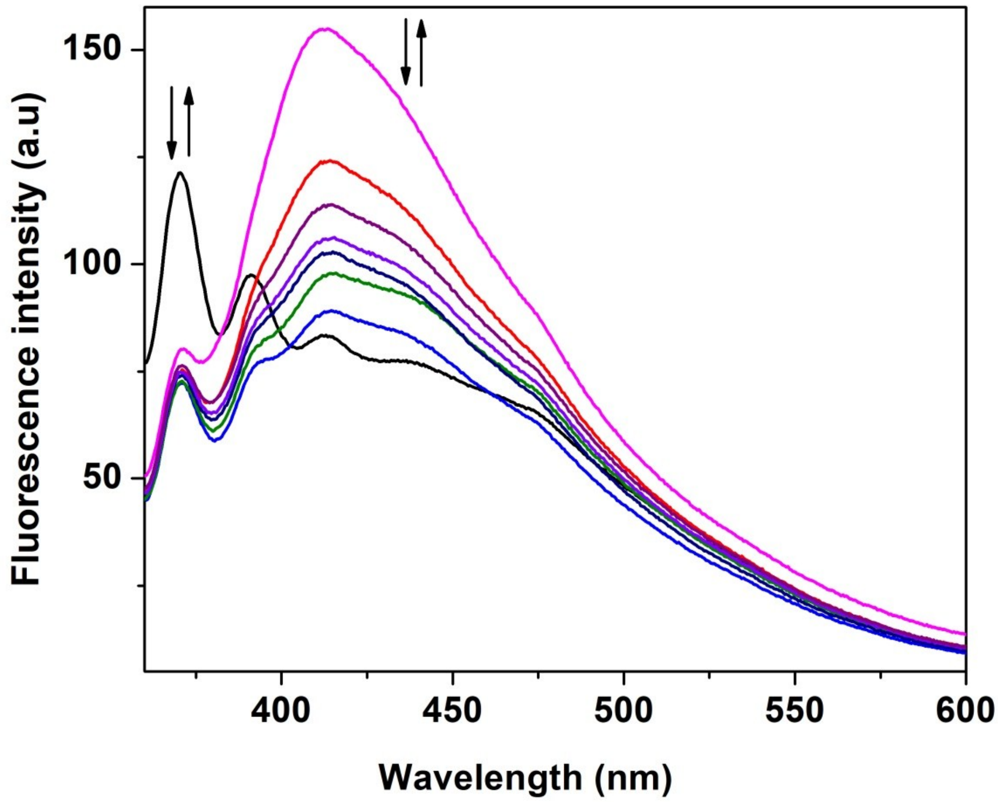

Fig. S34 Changes in the emission spectra of **1** (3.84×10^{-5} M, λ_{ex}= 350 nm).with the addition of benzene in DMSO. The arrows indicate the arbitrary changes in the fluorescence intensity (not detectable) by addition of an appropriate aliquot of benzene.

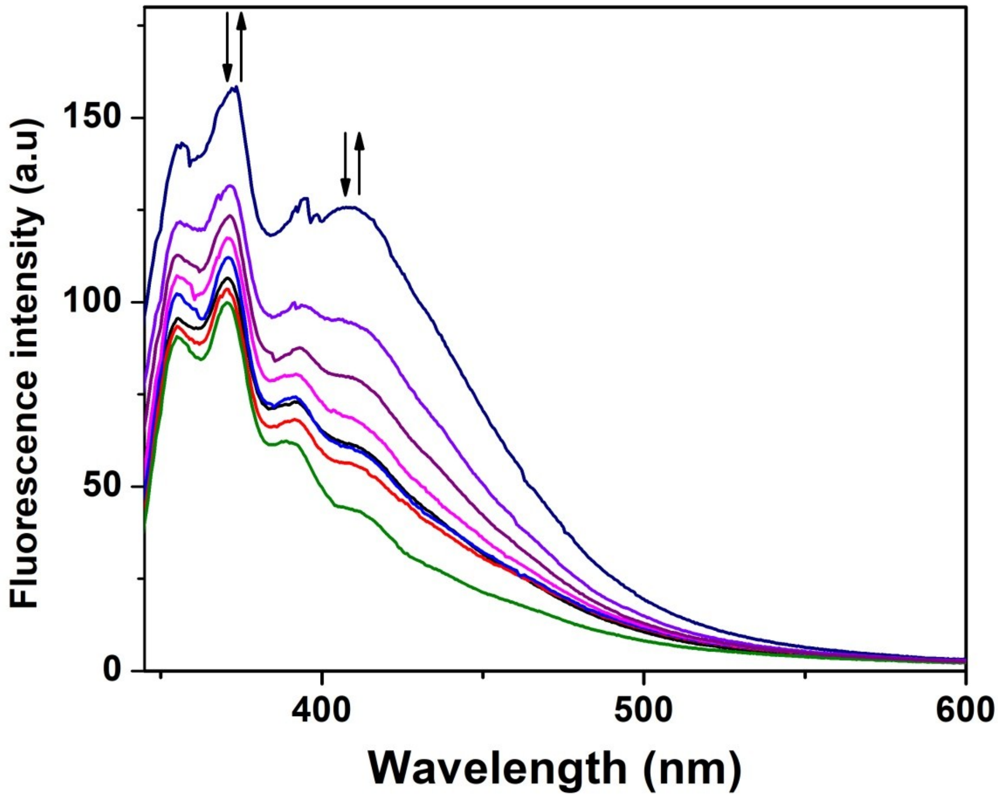

Fig. S35 Changes in the emission spectra of **1** (3.84×10^{-5} M, λ_{ex}= 325 nm) with the addition of mesitylene in DMSO. The arrows indicate the arbitrary changes in the fluorescence intensity (not detectable) by addition of an appropriate aliquot of mesitylene.