

Engineering Diformyl Diaryldipyrromethane into a Molecular Keypad

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1. General Information

Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra were measured on a SPEX-Fluorolog F112X spectrofluorimeter. Photoirradiation of **DA_{KK}** was carried out using an Oriel optical bench with thermostatic cell holders and a 200 W high pressure mercury lamp. To prepare mixture of **DA_{KK}** and **DA_{EE}** (**DA_{KK}**/**DA_{EE}**), 2.14×10^{-5} M solution of **DA_{KK}** in CH₃CN (3 mL) was taken in a 1 cm quartz cuvette and irradiated with 300 nm UV light ($\lambda_{\text{band pass}} = 300 \pm 30$ nm, 0.1 W/cm²) for 40 seconds and further used for sensing studies.

2. Deprotonation Experiments by Using Various Anions

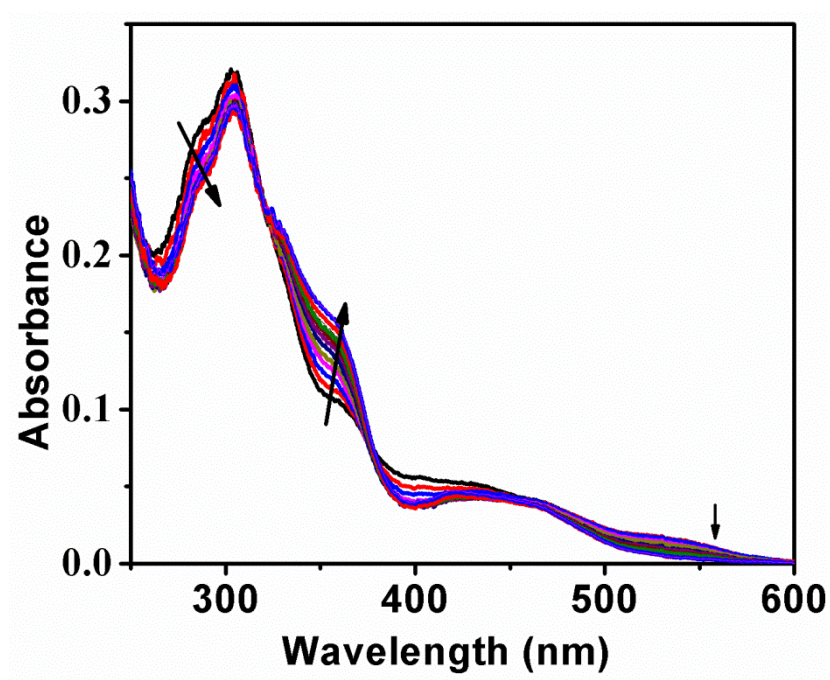


Fig S1. Addition of F^- ions (1 - 2.2 equiv) to DA_{KK}/DA_{EE} mixture ($2.14 \times 10^{-5} M$) in CH_3CN .

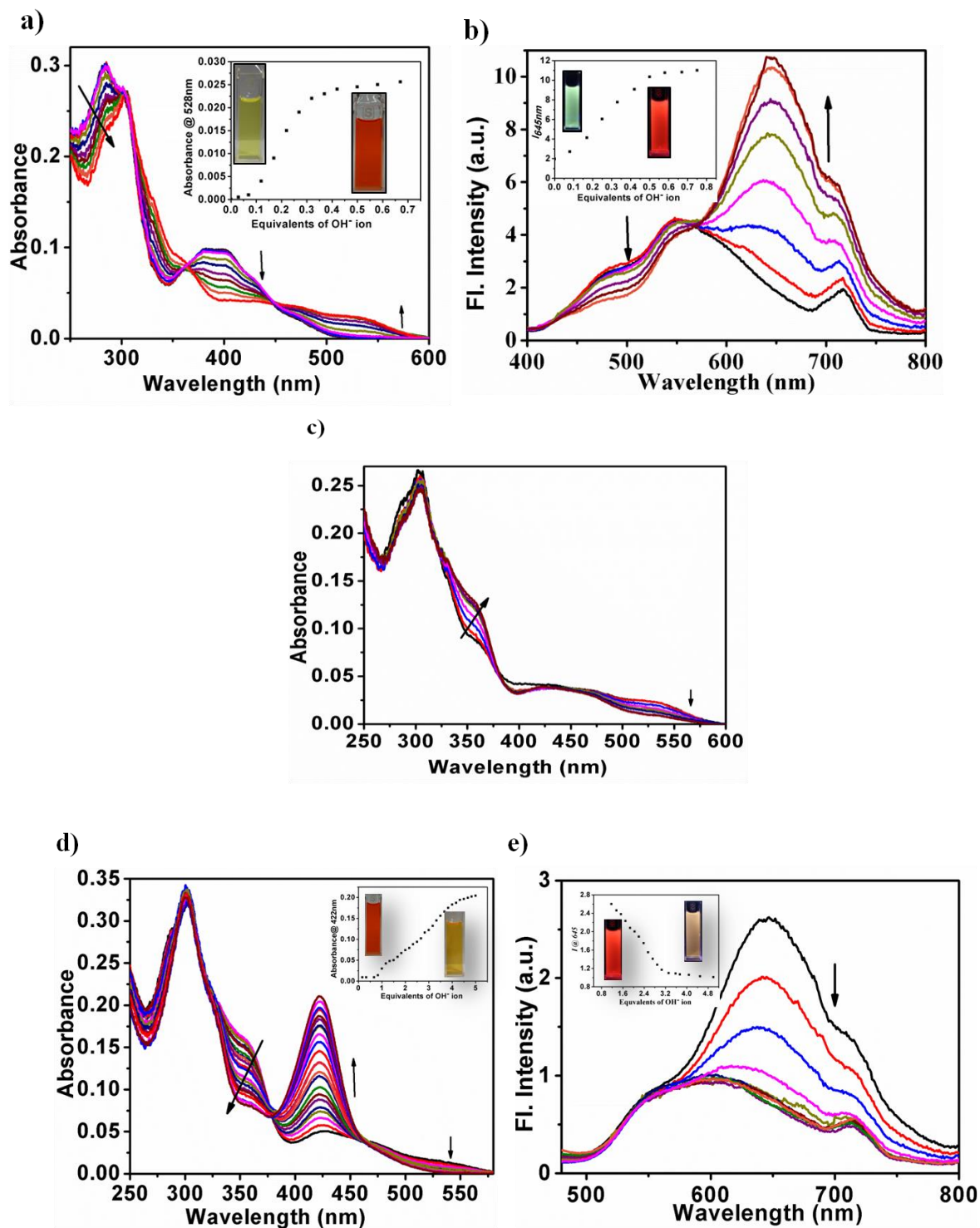


Fig S2 (a) Absorption and (b) emission changes of DA_{KK}/DA_{EE} mixture with 0-0.6 equiv of OH^- ions. (c) Absorption changes with 0.6-1.2 equiv of OH^- ion addition. (d) Absorption and (e) emission changes upon excess addition of OH^- ions.

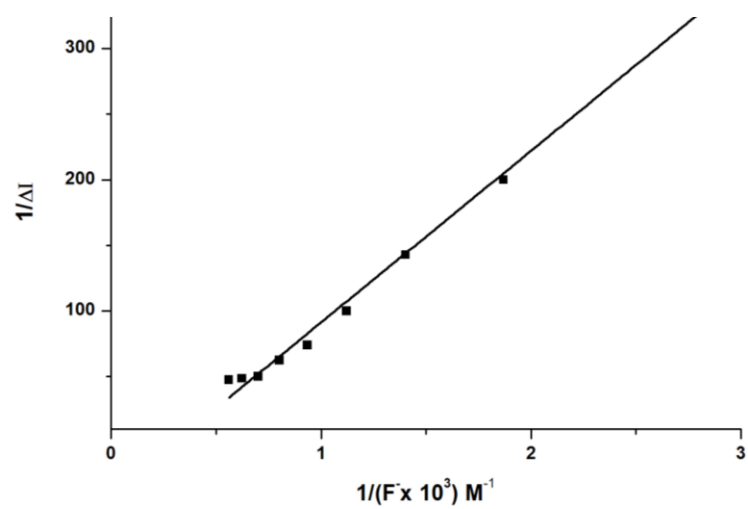


Fig. S3. Benesi-Hildebrand plot for DA_{EE}^-

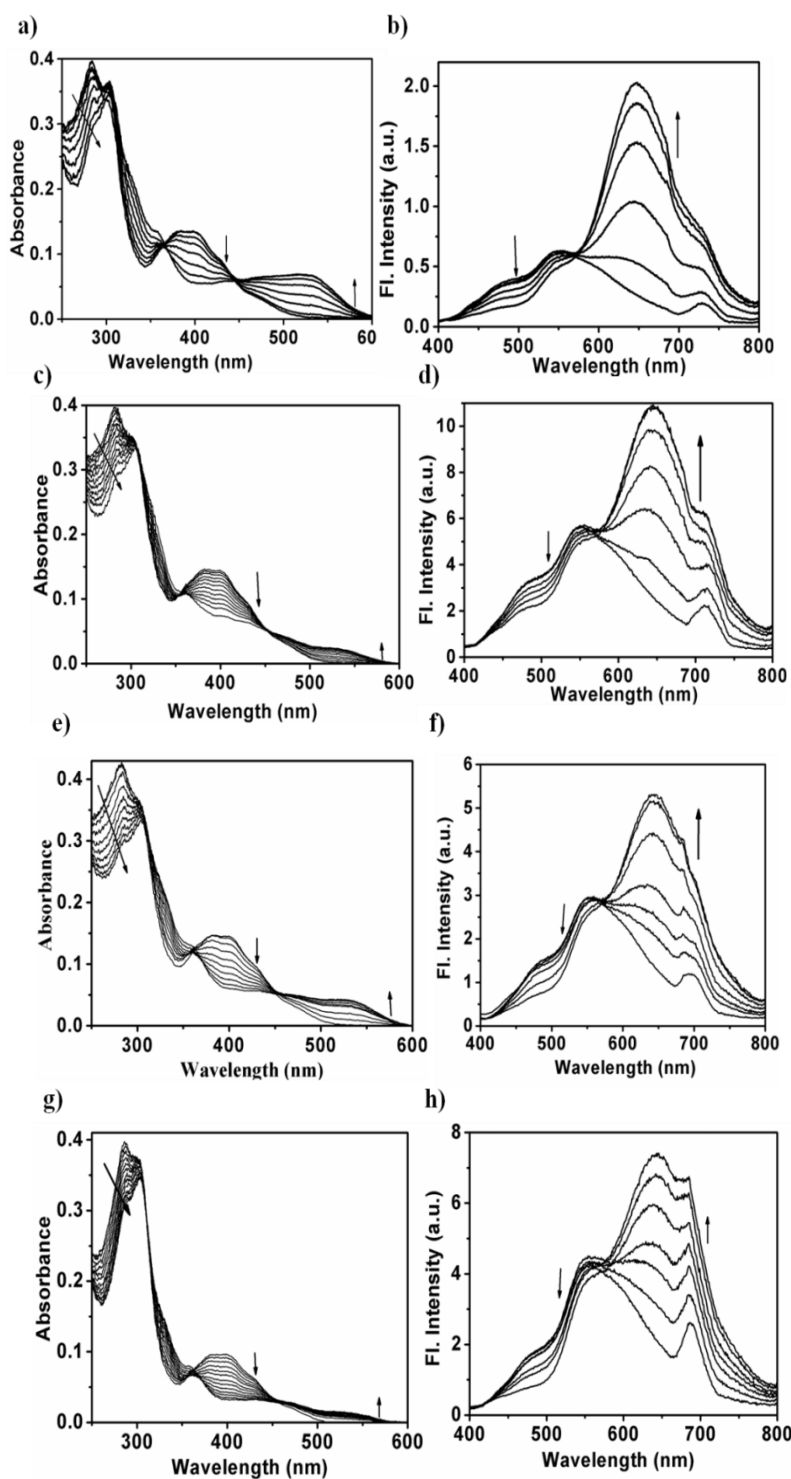


Fig S4: Absorption and emission changes ($\lambda_{ex} = 375$ nm) of DA_{KK}/DA_{EE} (2.14×10^{-5} M) upon addition of 0.5 equiv. of CN^- (a & b), $H_2PO_4^-$ (c & d), $CH_3CO_2^-$ (e & f) and $C_6H_5CO_2^-$ (g & h) in CH_3CN .

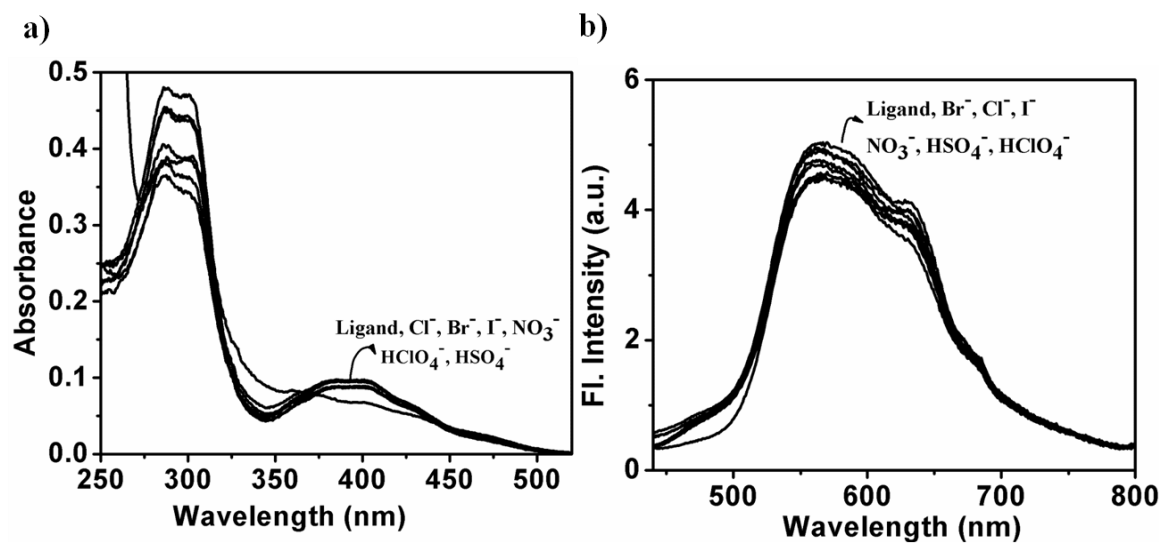
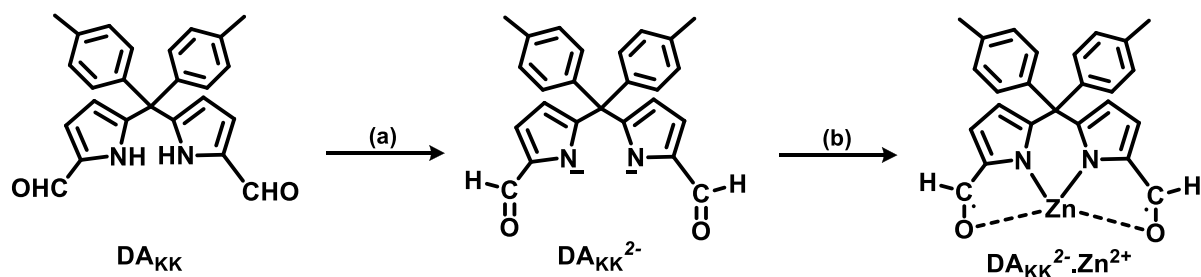


Fig S5. a) Absorption changes of DA_{KK}/DA_{EE} mixture ($2.14 \times 10^{-5} M$) and b) emission changes of DA_{EE} upon addition of 10 equiv of various anions in CH_3CN .

3. Metal ion Binding Studies



Scheme S1. Receptor studies of DA_{KK} . (a) Excess F^- ions; (b) Zn^{2+} ions.

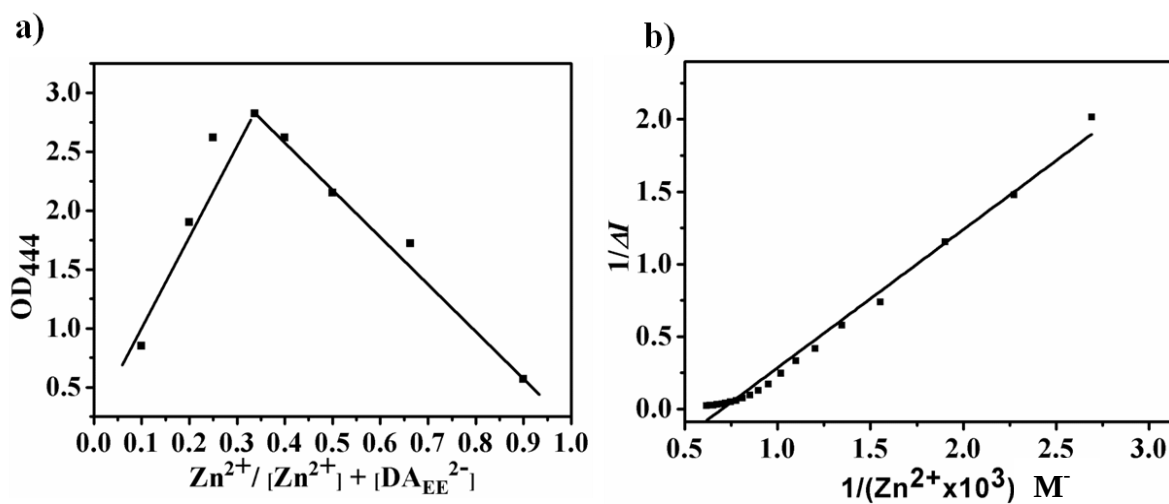


Fig. S6. a) The Job's plot for DA_{EE}^{2-} with Zn^{2+} ions and b) Benesi-Hildebrand plot for $DA_{EE}^{2-} \cdot Zn^{2+}$ system.

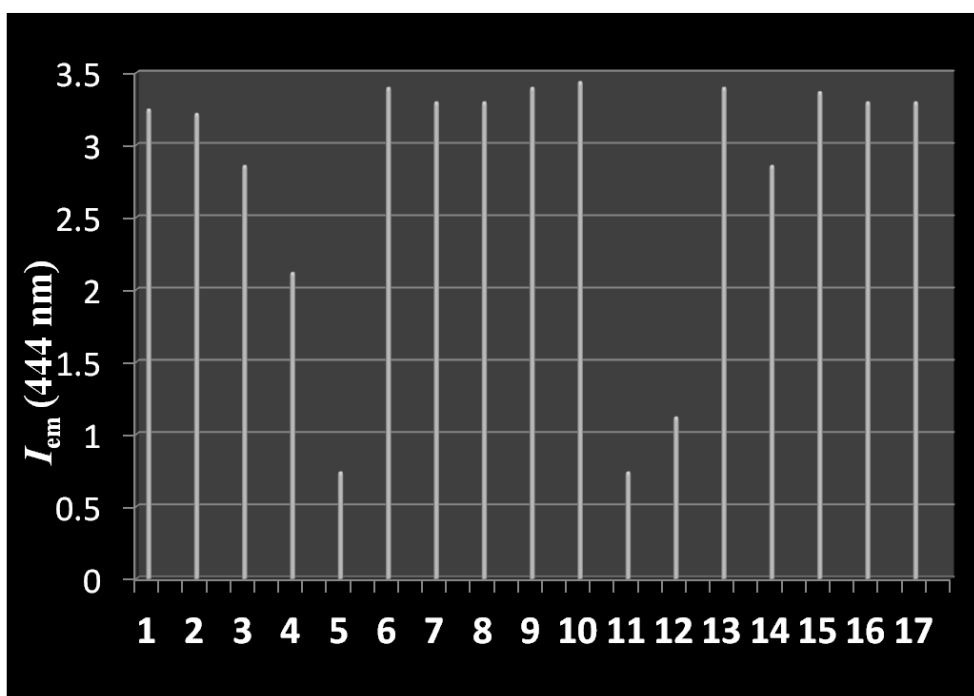


Fig. S7. Plot showing the response of DA_{EE}^{2-} in CH_3CN ($2.14 \times 10^{-5} M$) with 1 equiv of Zn^{2+} in presence of 10 equiv of other cations 1) Pb^{2+} , 2) Cd^{2+} , 3) Gd^{3+} , 4) Eu^{3+} , 5) Cu^{2+} , 6) Fe^{3+} , 7) Li^{+} , 8) Mg^{2+} , 9) Ag^{+} , 10) Zn^{2+} , 11) Cr^{3+} , 12) $Cr^{3+} + Cu^{2+}$ (here 10 equiv of Zn^{2+} were added), 13) K^{+} , 14) Ni^{2+} , 15) Co^{2+} , 16) Mn^{2+} and 17) Na^{+} . The emission intensity was monitored at 444 nm.

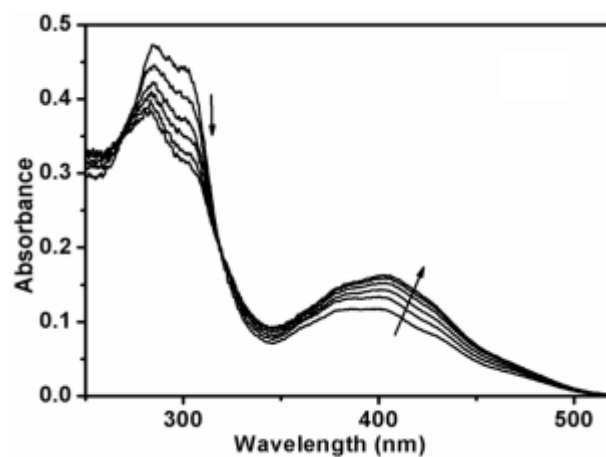


Fig S8. Absorption changes of DA_{KK}/DA_{EE} mixture upon direct addition of Zn^{2+} ions in CH_3CN .