#### **ORIGINAL PAPER**



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Received: 1 November 2019 / Accepted: 2 April 2020 © Springer Science+Business Media, LLC, part of Springer Nature 2020

#### Abstract

Title compound (PTPO) was synthesized by the reaction of 2-acetyl pyridine with 3,4,5-trimethoxy benzaldehyde. The structure of the compound has been confirmed by spectroscopic techniques. Interaction of chalcone with different metal cations was analyzed based on the fluorescence behavior. Results show that chalcone act as on-off switching fluorescent chemosensor for selective and sensitive detection iron metal ion. Mechanism of quenching and complexation were resolute by Benesi-Hildebrand, Stern-Volmer plot and Job-plot.

Keywords Pyridine: chalcone · Metal ion · Sensor · Quenching

# Introduction

Push-pull chromophores consisting electron push group and electron pull group connected through conjugated  $\pi$ -bridge. Organic compounds containing with push and pull group, generally accountable for the fluorescence because of intaramolecular charge transfer form pull to pull through the  $\pi$ -bond conjugations [1]. Organic compound having the fluorescence properties are utilizing in the different field of the optoelectronic devices such as third-order nonlinear optical properties, organic light emitting diodes [2], organic photovoltaies etc. [3], one of the most important application of these type of molecules are use as fluorescent chemosensor for the identification of various toxic metal ions by the fluorescence quenching or enhancement mechanism [4]. Chalcone has the  $\alpha$ ,  $\beta$ - unsaturated ketone framework its push group joint with the  $\alpha$ ,  $\beta$ - unsaturated ketone so, carbonyl group work as pull, so hole molecule can be used as pushpull chromophore [5]. In the past one decade, great

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manuscript we synthesized chalcone 1-(pyridin-2-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one by the reaction of 2-acetyl pyridine with 3,4, 5-trimethoxy benzaldehyde for the detection of iron metal ion.

# Experimental

All the chemical 2-acetyl pyridine, 3,4, 5-trimethoxy benzaldehyde, sodium hydroxide, and all the solvents were parched from the Sigma-Aldrich and used as received without further purification. The stock solution of the hydroxyl chalcone (DHPO) was prepared in DMF and ten different metal salts were prepared in double distilled water. All the conduct experiment was executed at  $25^{\circ}$  temperature.

#### Apparatus

A FT-IR spectrum was recorded on a Nicolet Magna 520 FT-IR spectrometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR experiments were performed in CDCl<sub>3</sub> on a Brucker DPX 600 MHz spectrometer using tetramethylsilane (TMS) as internal standard, at room temperature. Melting points was recorded on a Thomas Hoover capillary melting apparatus without correction. UV–Vis electronic absorption spectra were acquired on a Shimadzu UV-1650 PC spectrophotometer. Absorption spectra were collected using a 1 cm quartz cell. Steady state fluorescence spectra were measured using Shimadzu RF 5301 PC spectrofluorometer with a rectangular quartz cell.

### Synthesis of 1-(pyridin-2-yl)-3-(3,4,5-trimethoxyphenyl) prop-2-en-1-one (PTPO)

A solution of 2-acetyl pyridine (1.14 ml, 0.01 mol) and 3,4,5trimethoxybenzaldehyde (2 g, 0.01 mol) in an ethanolic solution of NaOH (3 g in 20 ml ethanol) was stirred for 5 h at room temperature and allowed to stand overnight. Then the reaction mixture was poured into crushed ice water, the precipitated solid was filtered off and recrystallized from ethanol. Yellow solid; % yield: 94.4%; m.p. 159-159.6; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3083 (= CH), 2997 (C-H), 1667 (C = O), 1607 (C = C), 1576 (C = C aromatic), 1311 (Aromatic C-N), 1120 (C-O), 982 (alkene bending disubstituted). <sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>)  $\delta$ : 8.77 (1H1, d, *J* = 4.8), 7.53 (1H2, td, *J* = 4.8, 7.2), 7.93 (1H3, dd, J = 1.2, 7.8), 8.22 (1H4, d, J = 7.2), 7.88 (1H7, d, J = 16.2), 8.20 (1H8, d, J = 15.6), 6.98 (2H10, 14, s), 3.95 (6H15-17, s), 3.92 (3H16). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) δ: 148.5, 126.9, 137.3, 123.1, 154.0 (Pyridine moiety), 188.9 (C = O), 130.6, 140.8 (alkene moiety), 119.9, 106.1, 153.4, 145.2, 56.2, 61.0 (benzene moiety).

## **Result and Discussion**

### Chemistry

The chalcone (PTPO) has been synthesized via reaction of 2acetyl pyridine with 3,4,5-trimethoxy benzaldehyde under normal condition [18]. The purified of PTPO was characterized by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. The FT-IR spectrum of the PTPO showed two sharp peaks at 1667 and 1607  $\text{cm}^{-1}$ due to the polar C = O and non-polar C = C group and and absent of two peaks that represent the aldehyde hydrogen at  $\sim$ 2720 and 2820 indicated formation of  $\alpha$ ,  $\beta$ -unsaturated ketone by the reaction of aldehyde and ketone. The structure of PTPO was further conformed by the <sup>1</sup>H-NMR spectra, the spectrum of PTPO showed two doublets signal at  $\delta$  7.88 and 8.20 with the J value 16.2 and 15.6 Hz indicated the formation of chalcone, J value indicating the CH = CH part of the  $\alpha$ ,  $\beta$ unsaturated ketone is the trans conformation. The <sup>13</sup>C-NMR spectrum of the chalcone was measured at 125 MHz in CDCl<sub>3</sub>. The spectrum peaks are in good conformity of the structure of PTPO, details of the peaks were given in the experimental section.

## Sensitive Fluorescent Chemosensor of PTPO for Metal lon

In order to examined the selective and sensitive chemosensor behavior of chalcone (PTPO) for ten different metal cations by the fluorescence spectra. The effect of the ten different metal ions namely  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$  on the photophysical properties of the hydroxy chalcone PTPO in the DMF/ Water (9:1, V/V) as shown in Fig. 1. Emission spectra of PTPO displayed extremely good peak when excited at 350 nm wavelength and no more



Fig. 1 Emission spectra of  $1.0 \times 10^{-5}$  moldm<sup>-5</sup> of PTPO upon addition of  $5.0 \times 10^{-5}$  M Co<sup>2+</sup>, Hg<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>, Cd<sup>2+</sup>, Sr<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup> and Mn<sup>2+</sup> in DMF/ water (9:1, v/v)



Fig. 2 Emission of PTPO in presence of different metal ions

significant effect on the fluorescence intensity after addition of 9 eqiv of metal ion  $Co^{2+}$ ,  $Hg^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Al^{3+}$ ,  $Cd^{2+}$ ,  $Sr^{2+}$ ,  $Ni^{2+}$ ,  $Cr^{3+}$  and  $Mn^{2+}$  as shown in Fig. 2. On the other hand upon addition of equivalent amount of  $Fe^{3+}$  metal ion to the PTPO, the fluorescence intensity shifted red shift from 496 to 521 nm with decreased the fluorescence intensity 10-fold and the fluorescence color also changing from yellow to brown color like an on-off fluorescence response. The fluorescence quantum yield of PTPO in the absence of  $Fe^{3+}$  metal ion was calculated to be 0.37 with respect to quinine sulfate (0.54) by the Eq. 1 [19].

$$\Phi_f = \Phi_r \frac{I \times A_r \times n^2}{Ir \times A \times n_r^2} \tag{1}$$

Scheme 1 Synthetic diagram indicating the synthesis of PTPO and interaction with the  $Fe^{3+}$  ion



**Fig. 3** Competitive experiments in the PTPO + Fe<sup>3+</sup> system with interfering metal ion [PTPO] =  $1 \times 10^{-5}$ M, [Fe<sup>3+]</sup> =  $5 \times 10^{-5}$ M, and [M<sup>n+</sup>] =  $5 \times 10^{-5}$ M, excited at 350 nm

Where  $\phi_f$  is the calculated fluorescence quantum yields of the PTPO absence and presence of Fe<sup>3+</sup> in DMF,  $\phi$ r is the fluorescence quantum yield of the quinine sulfate as reference dye, I is the integrated fluorescence intensity, A and Ar are the absorbance of the PTPO and reference and n is the refractive index of the DMF.

Fluorescence quantum yield of PTPO was calculated to be 0.012 in the presence of  $Fe^{3+}$  metal ion, which is greatly lower than the absence of  $Fe^{3+}$  metal ion. This fluorescence quenching performance was examined due to chelation-enhanced quenching sensing mechanism (Scheme 1).

The fluorescence intensity of  $Fe^{3+}$  ion was almost unaffected by the addition of competing metal ion (Co<sup>2+</sup>, Hg<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>,





Fig. 4 Emission spectra of PTPO  $(1 \times 10^{-5} \text{M})$  exposed to various concentration of Fe<sup>3+</sup> in DMF: water (9:1, v/v)

 $Cd^{2+}$ ,  $Sr^{2+}$ ,  $Ni^{2+}$ ,  $Cr^{3+}$  and  $Mn^2$ ) as shown Fig. 3, the ionic strength range of all metals are  $1.5 \times 10^{-4}$  to  $7.5 \times 10^{-4}$  M. These results suggested that molecules PTPO could be used as Fe<sup>3+</sup> selective fluorescent chemosensor.

The fluorescence quenching activities of the Fe<sup>3+</sup> was explored during emission spectrum of PTPO upon Fe<sup>3+</sup> ion was gradually titrated (Fig. 4). The fluorescence intensity of the PTPO gradually decreased with increased the concentration of the Fe<sup>3+</sup> metal ion and when the mount of Fe<sup>3+</sup> added was about  $9 \times 10^{-5}$  M, the fluoresce intensity of the PTPO almost reached a minimum due to utilized of PTPO for the complexation with Fe<sup>3+</sup> metal ion. Initially the fluorescence intensity of PTPO was quickly reduced after addition of low concentration of ranges of Fe<sup>3+</sup> as presented in Fig. 5 and in the range 3 to  $9 \times 10^{-5}$  M its showed good linear response (R = 0.98), which was capable to quantitatively analyzed the coordination of the Fe<sup>3+</sup> metal ion with PTPO molecule. The pH of the PTPO and



Fig. 5 Inset: Fluorescence titrations cure of PTPO  $(1 \times 10^{-5} \text{M})$  with Fe<sup>3+</sup> in aqueous solution



Fig. 6 Benesi-Hildebrand plot for PTPO  $(1 \times 10^{-5} M)$  at various concentration of Fe<sup>3+</sup> ion

PTPO with different concentration of the  $Fe^{3+}$  ion were found between 8.03 and 4.73.

To explore the association constant and binding stoichimerty between the PTPO with  $Fe^{3+}$  metal ion, which is fundamental in relation to the fluorescence chemosensor properties, we have created the benesi-Hildebrand plot from the Eq. 2 [20].

The plot between 1/ (F-F<sub>o</sub>) vs. 1/ Fe<sup>3+</sup> as presented in Fig. 3, exhibited the linearity of Benesi-Hildebrand, indicated complexation between PTPO with Fe<sup>3+</sup> metal having 1 : 1 stoichiometric ratio.

$$\frac{1}{F - F^0} = \frac{1}{F - F^o} + \frac{1}{K_{app}} X \frac{1}{(F - F^o) [F_e^{3+}]}$$
(2)

Where F is the emission intensity of the PTPO molecule absence of Fe3 + metal ion, Fo is the emission intensity of PTPO in the presence of  $Fe^{3+}$  metal ion and  $K_{app}$  is the evident association constant. The Benesi-Hildebrand plot between 1/F-



Fig. 7 Stren-Volmer plot for PTPO  $(1 \times 10^{-5} \text{M})$  at various concentration of Fe<sup>3+</sup> ion



Fig. 8 Job's plot, Fluorescence Intensity vs. mole fraction of  $Fe^{3+}$  Job's plot

Fo vs. 1/ Fe<sup>3+</sup> showed linearity as showed in Fig. 6 indicate complexation between the PTPO and Fe<sup>3+</sup> metal ion having 1: 1 stoichiometric ratio. The K<sub>app</sub> association constant for the complexation between PTPO molecule and Fe<sup>3+</sup> metal ion was predictable from this nonlinear curve fitting process of the fluorescence titration data was found to be  $7.02 \times 10^{-8}$  M<sup>-1</sup>.

The fluorescence quenching behavior of the PTPO with  $Fe^{3+}$  metal ion was further understood by the Stern-Volmer plot and the coverage of fluorescence quenching has been quantitatively investigated by the Sterm-Volmer Eq. 3:

$$\frac{Io}{I} = 1 + K_{sv} \left[ F_e^{3+} \right] \tag{3}$$

where, I and Io are the fluorescence intensity of the PTPO in the absence and presence of  $Fe^{3+}$  metal ion and  $K_{sv}$  is the Stern-Volmer constant. The Stern-Volmer constant ( $K_{sv}$ ) was designed by the plot of Stern-Volmer and originate 1.54 M<sup>-1</sup> with correlation coefficient ( $R^2$ ) equal to 0.96 as shown Fig. 7. The elevated value of the Stern-Volmer constant indicates the effectual interaction involving the PTPO with Fe<sup>3+</sup> metal ion [21].

Binding stoichiometry of  $Fe^{3+}$  with POPT also determined by the Job plot method [22], we calculated that the binding stoichiometry of POPT and  $Fe^{3+}$  was 1: 1 by Job's plot, and the fluorescence intensity would reach the maximum value when the mole fraction was 0.5 as mentaion in Fig. 8.

# Conclusions

The title donor- $\pi$ -acceptor chromophore (PPTO) has been synthesized by the reaction of 2-acetyl pyridine with 3,4, 5-

trimethoxy benzaldehyde undernormal condition. In this cram, it was focused on the effect of ten different metal ions on the physicochemical properties of the chalcone (PTPO) as fluorescent chemosensor for the detraction of metal ions by using fluorescence spectra. The fluorescence spectra of PTPO did not affected by the presence of any metal ions among the ten metal ions exemption  $Fe^{3+}$  metal ion.  $F^{3+}$  metal ion decreased the emission intensity of PTPO spectacularly when the concentration of  $Fe^{3+}$  metal ion increased. The bonding or interaction of the  $Fe^{3+}$  with PTPO has been found by Job plot methods and its showed 1:1 stoichiometry. The complexation reaction of PTPO with respect to  $Fe^{3+}$  has explained by the Benesi-Hildebrand, Stern-volmer and Job plot proposed that 1: 1 ratio complex formation and the non linearity of the Stern-volmer plot designated that decreased the emission intensity through the dynamic and static system.

Acknowledgements This project was funded by the Deanship of Scientific Research (DSR) at King Abdulaziz University, Jeddah, Saudi Arabia under grant no. KEP-PhD-19-130-41. The authors, therefore, acknowledge with thanks DSR for technical and financial support.

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