Photoluminescent Ester Oligomers Containing Curcumin Dye Units: A Selective Fluorescent "Turn off" Chemosensor for Ferric Ions†

Hoay-Ching Ong and Chuan-Wei Oo*

School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.
*Corresponding author (e-mail: oocw@usm.my)

New curcumin-based ester oligomers were synthesized via polycondensation of curcumin diol with aromatic diacid. The oligomers were characterized by elemental analysis, ^{1}H-NMR, ^{13}C-NMR, FT-IR and TGA. The onset of thermal degradation was at 280°C and ester oligomers with longer alkyl chains showed lower thermal stability. Photoluminescence properties of the ester oligomers were examined by using UV-Vis and fluorescence spectroscopies. The ester oligomers exhibited green emission under UV irradiation. Selective fluorescence quenching was observed upon the addition of ferric (Fe^{3+}) ions over other heavy metal cations. The result suggested the new curcumin-based ester oligomers can be potential chemosensors for Fe^{3+} ions.

Key words: Chemosensor; oligomers; photoluminescence; thermal stability

Photoluminescence is a process in which electrons are excited by absorbing photon and then returned to lower energy ground state via emitting light [1]. Photoluminescence polymer sensors are being developed recently for chemical and biochemical detection as well as bioimaging by observing the fluorescence intensity changes [2]. Selectivity and sensitivity of the polymer sensors are tunable by incorporating specific functionalities such as aza-crown ethers, benzothiazole, and cyclodextrin along the polymer chains either to the backbone or the side-chain [3]. Besides, fluorescein, diketopyrrolopyrrole, and terpyridine were the fluorophores that had been introduced into different conjugated polymers which enhanced the photoluminescence property of the polymers [4-6]. Curcumin is also known as fluorophore which possesses 1,3-diketone moiety that can exist in keto–enol tautomeric forms. These tautomers could act as chelating agents for metal ions [7]. Although most of the studies on curcumin-based polymers had been developed for drug carriers but there are very few curcumin-based polymer sensors [8-10].

Aromatic polyester is less processable due to its limitation in solubility. High planarity of polyester backbone limits the conformational disorder along the conjugated backbone. This enhances π-π stacking interaction, and hence resulting in poor solubility [11]. In a previous study, flexible alkyl side chains were bridged by triazole ring to improve the solubility of material owing to the rigid structure of conjugated backbones [12]. In addition, the triazole ring had been proven to enhance the thermal stability of the studied material and it showed excellent cations binding motifs [13,14].

The objectives of this study were to synthesize and characterize new conjugated ester oligomers containing curcumin in the backbone with enhanced solubility by incorporating alkyl groups with different lengths in the side-chains. The thermal behavior of the synthesized ester oligomers and their potential as chemosensors toward heavy metal ions were investigated.

EXPERIMENTAL

Materials

Curcumin, 5-hydroxyisopthalic acid, 1-bromodecane, 1-bromododecane, 1-bromotetradecane, copper(II) sulfate pentahydrate, thionyl chloride, and sodium azide were purchased from Merck (Darmstadt, Germany). Potassium hydroxide and potassium iodide were purchased from Q-rec Chemicals (New Zealand). Propargyl bromide and 1-bromohexadecane were purchased from Tokyo Chemical Industry (Tokyo, Japan). Potassium carbonate and sodium ascorbate were obtained from Sigma-Aldrich (St. Louis, MO, USA). Triethylamine was obtained from R&M Chemicals (Alberta, Canada). All the chemicals were used as received without further purification.

Physicochemical Characterization

The synthesized monomers and ester oligomers were analyzed by Perkin Elmer ATR-FTIR at the frequency range of 4000-500 cm^{-1}. Bruker Avance 500 MHz ultrashield spectrometer equipped with ultrashield magnets was used to record the ^{1}H and ^{13}C-NMR spectra of the monomers and ester oligomers. Mettler 851e thermogravimetric analyser was used for TGA

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analysis on the synthesized ester oligomers in nitrogen atmosphere with the heating rate of $10^{\circ}C$ min^{-1}. The number of averaged molecular weight, weight-molecular weight and dispersity index were obtained via gel permeation chromatography (GPC) equipped with Waters 1515 isocratic HPLC pump and Waters 2414 refractive index detector. The calibration was done using polystyrene as the standard and GPC grade THF was used as the eluent. UV-Vis and fluorescence spectra were recorded on Shimadzu UV-2600 UV-Vis spectrophotometer and LS-55 fluorescence spectrophotometer, respectively, with quartz cell (1 cm × 1cm).

Synthesis of Monomers and Ester Oligomers

All the monomers and ester oligomers were synthesized according to the synthesis route as shown in Scheme 1. 5-Hydroxyisophtalic acid (6.00 g, 32.91 mmol) was refluxed in 12 mL absolute ethanol with a catalytic amount of H_2SO_4 for 8 h. The resultant mixture was extracted with diethyl ether to yield **S1**. Then, propargyl bromide (2.55 g, 21.41 mmol) was mixed with **S1** (4.00 g, 17.84 mmol) in acetone. 2 molar equivalent of potassium carbonate and a catalytic amount of potassium iodide were added into the mixture. The reaction mixture was refluxed for 12 h and the precipitate formed was recrystallized using ethanol to yield **S3**. Sodium azide (1.95 g, 30 mmol) was added into N,N'-dimethylformamide solution containing the corresponding 1-bromoalkane (15 mmol), then refluxed for 8 h. The resultant mixture was filtered, and the filtrate was extracted with dichloromethane. **S2**, a yellow oily liquid was obtained after evaporation. **S3** was added into N,N'-dimethylformamide solution containing equimolar of the corresponding **S2** (15 mmol), 20 mol % of $CuSO_4.5H_2O$ and 20 mol % sodium ascorbate. The reaction mixture was left stirred at ambient temperature for 24 h. The obtained precipitate after pouring into cold water was recrystallized from ethanol to yield **S4**. **S4** was subsequently refluxed with 2 molar equivalent of potassium hydroxide in ethanol for 5 h. The resulted mixture was neutralized to yield the corresponding monomers.

MS10-MS16.

Monomer (**MS10**): 81% yield. ATR-FTIR (cm^{-1}): 3081, 3167-2549, 2915, 2847, 1695, 1595 and 1280. ^{1}H-NMR (DMSO-d_6) δ/ppm: 8.21 (1H, s, H2), 8.09 (1H, t, J=1.8, 1.3 Hz, H4), 7.75 (2H, d, J=1.4 Hz, H1/H1'), 5.28 (2H, s, H3), 4.34-4.37 (2H, t, J=7.0 Hz, H5), 1.77-1.82 (2H, quint, J=7.1 Hz, H6), 1.15-1.27 (14H, m, H7-H13), 0.83-0.86 (3H, t, J=6.9 Hz, H14). ^{13}C-NMR (DMSO-d_6) δ/ppm: 166.8, 158.6, 142.7, 133.1, 124.9, 123.0, 120.0, 62.3, 49.9, 31.7-26.2, 22.5, 14.4.

Monomer (**MS12**): 84% yield. ATR-FTIR (cm^{-1}): 3084, 3211-2571, 2912, 2853, 1698, 1594 and 1273. ^{1}H-NMR (DMSO-d_6) δ/ppm: 8.21 (1H, s, H2), 8.09 (1H, t, J=1.8, 1.3 Hz, H4), 7.75 (2H, d, J=1.4 Hz,

H1/H1'), 5.28 (2H, s, H3), 4.33-4.36 (2H, t, J=7.0 Hz, H5), 1.76-1.82 (2H, quint, J=7.1 Hz, H6), 1.20-1.25 (18H, m, H7-H15), 0.84-0.86 (3H, t, J=6.9 Hz, H16). ^{13}C-NMR (DMSO-d_6) δ/ppm: 166.8, 158.6, 142.7, 133.1, 124.9, 123.1, 120.0, 62.2, 49.9, 31.7-26.1, 22.5, 14.3.

Monomer (**MS14**): 82% yield. ATR-FTIR (cm^{-1}): 3099, 3371-2579, 2912, 2846, 1699, 1594 and 1273. ^{1}H-NMR (DMSO-d_6) δ/ppm: 8.21 (1H, s, H2), 8.09 (1H, t, J=1.8, 1.3 Hz, H4), 7.75 (2H, d, J=1.4 Hz, H1/H1'), 5.28 (2H, s, H3), 4.33-4.36 (2H, t, J=7.0 Hz, H5), 1.77-1.80 (2H, quint, J=7.1 Hz, H6), 1.21-1.25 (22H, m, H7-H17), 0.83-0.85 (3H, t, J=6.9 Hz, H18). ^{13}C-NMR (DMSO-d_6) δ/ppm: 166.8, 158.6, 142.7, 133.1, 124.9, 123.1, 120.0, 62.2, 49.9, 31.8-26.2, 22.5, 14.3.

Monomer (**MS16**): 81% yield. ATR-FTIR (cm^{-1}): 3099, 3371-2579, 2912, 2846, 1695, 1594 and 1270. ^{1}H-NMR (DMSO-d_6) δ/ppm: 8.21 (1H, s, H2), 8.09 (1H, t, J=1.8, 1.3 Hz, H4), 7.75 (2H, d, J=1.4 Hz, H1/H1'), 5.27 (2H, s, H3), 4.33-4.36 (2H, t, J=7.0 Hz, H5), 1.76-1.81 (2H, quint, J=7.1 Hz, H6), 1.27-1.18 (26H, m, H7-H19), 0.83-0.85 (3H, t, J=6.9 Hz, H20). ^{13}C-NMR (DMSO-d_6) δ/ppm: 166.8, 158.6, 142.7, 133.1, 124.9, 123.1, 120.0, 62.2, 49.9, 31.7-26.2, 22.5, 14.4.

The ester oligomers were synthesized using the acylated monomers. **MS10-MS16** were refluxed with thionyl chloride and a catalytic amount of N,N'-dimethylformamide in benzene for 3 h to yield **MT10-MT16**, which were then directly mixed with THF/triethylamine. The resultant mixture was stirred overnight and poured into methanol to form the desired ester oligomers, **CM10-CM16**.

Oligomer (**CM10**): 49% yield. ATR-FTIR (cm^{-1}): 3344-3555, 3084, 2925, 2853, 1742, 1627, 1593, 1192 and 1162. ^{1}H-NMR (CDCl$_3$) δ/ppm: 15.96 (OH, s, br), 8.66 (1H, s, H8), 8.08 (2H, s, H9/H9'), 7.63-7.71 (5H, m, H1/H1', H5/H5', H11), 7.29-7.17 (4H, s, H4/H4', H6/H6'), 6.59, (2H, d, H2/H2'), 5.89 (1H, s, H3), 5.36 (2H, s, H10), 4.39 (2H, s, H12), 3.88 (6H, s, H7/H7'), 1.93 (2H, s, H13), 1.26-1.40 (14H, m, H14-H20), 0.88 (3H, t, H21). ^{13}C-NMR (CDCl$_3$) δ/ppm: 183.1, 163.4, 158.6, 151.5, 142.9, 141.3, 139.9, 134.3, 131.2, 129.3, 124.5, 123.3, 122.9, 122.12, 121.1, 111.7, 101.9, 62.5, 56.0, 50.7, 31.8, 26.5-31.8, 22.6, 14.1.

Oligomer (**CM12**): 48% yield. ATR-FTIR (cm^{-1}): 3621-3251, 3081, 2924, 2854, 1742, 1627, 1594, 1189 and 1156. ^{1}H-NMR (CDCl$_3$) δ/ppm: 15.96 (OH, s, br), 8.66 (1H, s, H8), 8.07 (2H, s, H9/H9'), 7.65-7.70 (5H, m, H1/H1', H5/H5', H11), 7.28-7.19 (4H, s, H4/H4', H6/H6'), 6.59, (2H, d, H2/H2'), 5.90 (1H, s, H3), 5.34 (2H, s, H10), 4.38 (2H, s, H12), 3.89 (6H, s, H7/H7'), 1.93 (2H, s, H13), 1.26-1.34 (18H, m, H14-H22), 0.88 (3H, t, H23). ^{13}C-NMR (CDCl$_3$) δ/ppm: 183.1, 163.4, 158.6, 151.5, 142.9, 141.3, 139.9, 134.3, 131.2, 129.3, 124.5, 123.3, 122.9, 122.1, 121.1, 111.7, 101.9, 62.5, 56.0, 50.7, 31.8, 26.5-31.8, 22.6, 14.1.

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Scheme 1. Reagents and reaction conditions: (i) $H_2SO_{4,conc}$ (dropwise), reflux, ethanol, 24 h.; (ii) propargyl bromide (1.2 equiv.), K_2CO_3 (2 equiv.), relux, acetone, 12 h.; (iii) sodium azide (2 equiv.), DMF, 80 °C, 8 h.; (iv) 20 mol% of sodium ascorbate, 20 mol% of $CuSO_4.5H_2O$, DMF, r. t., 24 h.; (v) KOH (2 equiv.), reflux, ethanol, 7 h.; (vi) $SOCl_2$ (8 equiv.), DMF (dropwise), reflux, benzene.; (vii) triethylamine (2 equiv.), THF, r.t., overnight.
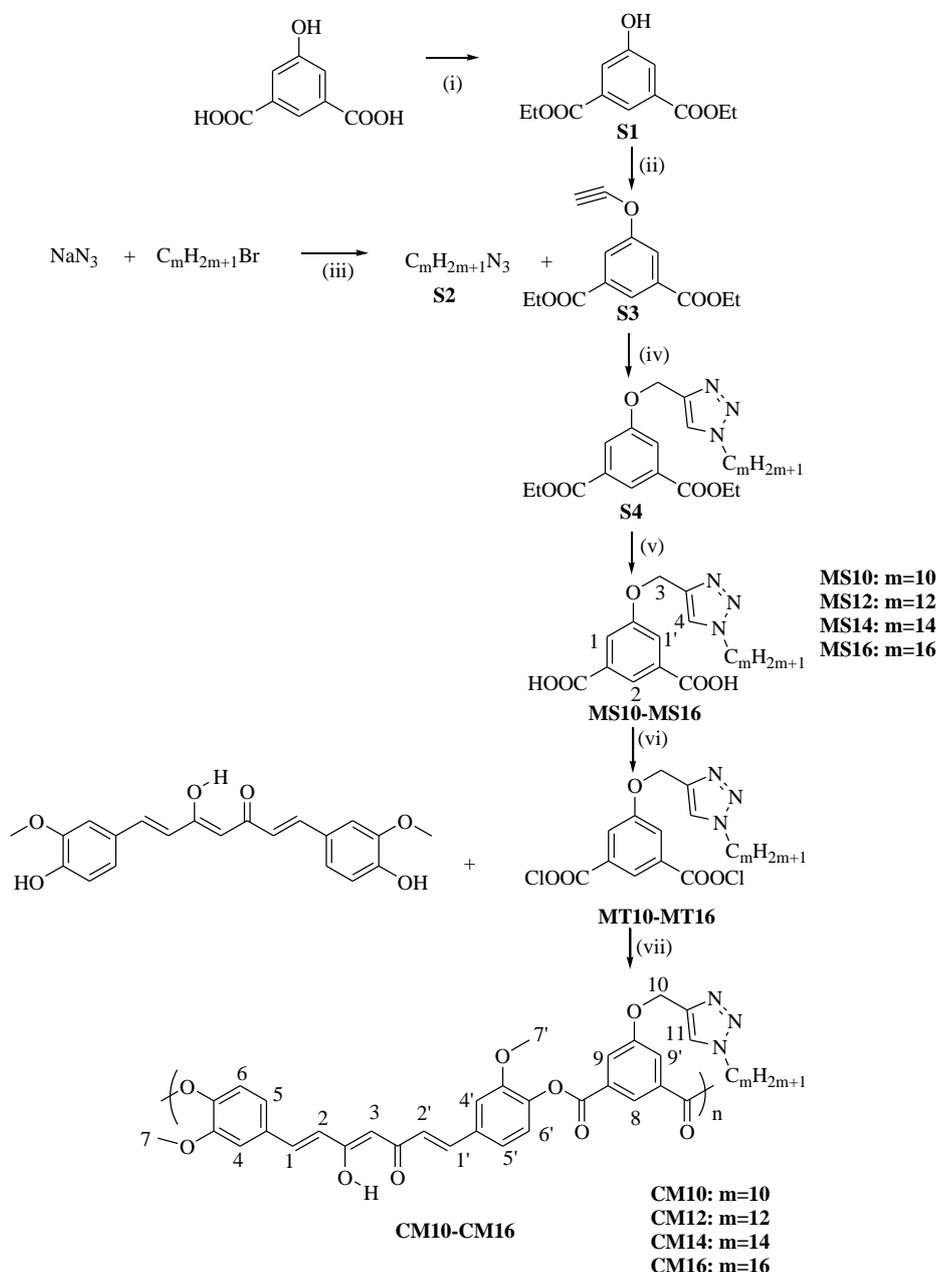
Oligomer (**CM14**): 51% yield. ATR-FTIR (cm^{-1}): 3622-3292, 3080, 2924, 2853, 1742, 1628, 1593, 1190 and 1160. ^{1}H-NMR (CDCl$_3$) δ/ppm: 15.87 (OH, s, br), 8.59 (1H, s, H8), 8.00 (2H, s, H9/H9'), 7.61-7.52 (5H, m, H1/H1', H5/H5', H11), 7.19-7.10 (4H, s, H4/H4', H6/H6'), 6.51, (2H, d, H2/H2'), 5.79 (1H, s, H3), 5.29 (2H, s, H10), 4.30 (2H, s, H12), 3.80 (6H, s, H7/H7'), 1.85 (2H, s, H13), 1.17-1.20 (22H, m, H14-H24), 0.80 (3H, t, H25). ^{13}C-NMR (CDCl$_3$) δ/ppm: 183.1, 163.4, 158.6, 151.5, 142.8, 141.2, 139.9, 134.3, 131.2, 129.3, 124.4, 123.3, 122.9, 122.2, 121.1, 111.7, 102.0, 62.5, 56.0, 50.7, 31.9, 26.5-30.3, 22.7, 14.1.

Oligomer (**CM16**): 51% yield. ATR-FTIR (cm^{-1}): 3680-3266, 3088, 2923, 2853, 1742, 1629, 1594, 1190 and 1159. ^{1}H-NMR (CDCl$_3$) δ/ppm: 15.96 (OH, s, br), 8.59 (1H, s, H8), 8.00 (2H, s, H9/H9'), 7.60-7.52 (5H, m, H1/H1', H5/H5', H11), 7.19-7.10 (4H, s, H4/H4', H6/H6'), 6.52, (2H, d, H2/H2'), 5.80 (1H, s, H3), 5.28 (2H, s, H10), 4.30 (2H, s, H12), 3.80 (6H, s, H7/H7'), 1.85 (2H, s, H13), 1.17-1.26 (26H, m, H14-H26), 0.80 (3H, t, H27). ^{13}C-NMR (CDCl$_3$) δ/ppm: 183.1, 163.4, 158.6, 151.5, 143.0, 141.3, 139.9, 134.3, 131.2, 129.3, 124.5, 123.3, 122.8, 122.2, 121.1, 111.7, 101.9, 62.6, 56.0, 50.6, 31.9, 26.5-30.3, 22.7, 14.1.

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UV-Vis Absorption and Photoluminescence Measurements

Series of **CM10-CM16** solutions with the concentration of 8.0×10^{-4} mg mL^{-1} were prepared in THF solution. 30 µM of Cu^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+}, Zn^{2+}, and Pb^{2+} solutions were prepared using deionized water. Metal sensing tests were carried out by titrating 30 µM of metal ions into 3 mL of **CM10-CM16** in the 1 cm quartz cell. **CM10** was titrated with different concentrations of Fe^{3+} solution in the range of 0-30 µM for sensitivity test. The UV-Vis absorption and photoluminescence spectra for these solutions were recorded.

RESULTS AND DISCUSSION

Structures of the synthesized ester oligomers were elucidated using FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopies. Since all the synthesized ester oligomers, **CM10-CM16** exhibited similar characteristics in their FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectra, homologous **CM10** was selected for further discussion. The presence of C=O ester gave rise to an absorption band at 1742 cm^1 which confirmed the completeness of esterification reaction that formed the desired ester oligomers [15]. The presence of ester functionality was further substantiated by the appearance of strong absorption band at 1192 cm^{-1} which could be ascribed to the stretching of C-O-C ester [16]. ^{1}H-NMR of **CM10** illustrated broad signals with increased complexity which suggested the occurrence of polymerization [17]. A broad signal which resonated at δ= 15.96 ppm could be assigned to hydroxyl proton on the oxygen atom in the enol. Carbon signals at δ= 183.11 and 101.93 ppm could be attributed to the carbonyl carbon of curcumin and methine carbon attached to H3, respectively. These indicated the presence of keto-enol tautomer of curcumin moiety in **CM10** [18].

The GPC results showed the number-average

molecular weight (Mn) and weight average molecular weight (Mw) which were found to be in the range of 1284-2294 gmol^{-1} and 1971-6239 gmol^{-1}, respectively. Polydispersity index (PDI) was obtained in the range of 1.78-2.72. Degree of polymerization of **CM10**, **CM12**, **CM14**, and **CM16** were 3, 8, 2, and 3, respectively.

CM10-CM16 were found to be insoluble in polar protic solvents such as water, methanol, and ethanol, as well as n-hexane and benzene which are non-polar solvents. However, the synthesized ester oligomers were soluble in common polar aprotic solvents such as chloroform, tetrahydrofuran and dichloromethane, and partially soluble in acetone as well as N,N'-dimethylformamide due to the tetrahedral nature of the alkyl chains arranged at different planes compared to the conjugated backbone. As such, these alkyl chains prevented molecular chain packing to a certain extent and increased the solubility of the oligomers [12]. The unreported curcumin-based ester oligomer with a shorter alkyl chain of two carbon atoms was found to be partially soluble even in hot organic solvents. The longer alkyl chains increased the steric hindrance and caused the ester oligomer chains to become less packed, hence, increased the free volume of the ester oligomers. This improved the diffusion of solvent molecules within the oligomer network causing it to swell and eventually dissolve.

Thermal Properties of CM10-CM16

The thermal properties of ester oligomers **CM10-CM16** were examined via thermogravimetric analysis under nitrogen atmosphere with the heating rate of $10°C$ min^{-1} from $30°C$ to $700°C$. The onset thermal degradation temperature of the ester oligomers was recorded at $280°C$. The temperature for 50% weight loss ($T_{d50\%}$) of **CM10-CM16** and their percentage char yield decreased with the increase in the length of the alkyl chains (m=10 to 16).
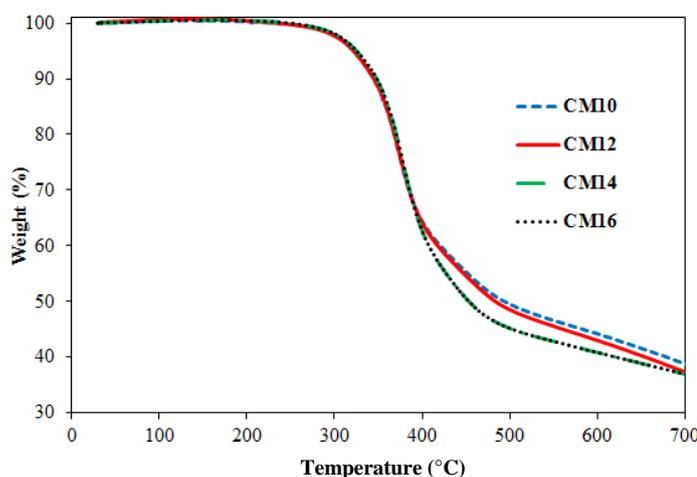

Figure 1. TGA thermograms of **CM10-CM16**

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Table 1. Thermal decomposition values of **CM10-CM16**

Ester oligomer	$T_{d50\%}$ (°C)	Char yield at 700°C (%)
CM10	494	39
CM12	483	37
CM14	458	36
CM16	453	32

$T_{d50\%}$ for **CM10-CM16** were recorded at 494, 483, 458, and 453°C, respectively. The percentage of char yield at 700°C for the ester oligomers were 39%, 37%, 36%, and 32 %, respectively. Hence, the thermal stability of the ester oligomers was found to be affected by the length of the alkyl chains. The longer the alkyl chains, the lower the thermal stability of the ester oligomers. This could be attributed to the increase of steric hindrance upon increasing the length of alkyl chains which disrupted the packing of the oligomer chains, and thus reduced the intermolecular interaction. However, the shorter alkyl chain led to less steric hindrance and lower flexibility to the oligomer chain. This created a more rigid oligomer network as oligomer packing became denser which enhanced the intermolecular interaction with higher thermal stability [19]. Data from the thermogravimetric analysis of **CM10-CM16** are illustrated in Table 1.

Selectivity of CM10-CM16 on Metal Ions

The response of the ester oligomers towards different metal ions namely Zn^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, and Pb^{2+} was investigated and changes on their fluorescence intensity were recorded using UV-Vis and fluorescence spectrophotometers. Since the spectra for all the homologous oligomers showed similar characteristics, only **CM10** is discussed in detail. As shown in Figure 2a, λ_{max} of free **CM10** recorded at 403 nm was assigned to $\pi\rightarrow\pi^*$ for the enol structure of curcumin moiety, whereas absorption at 284 nm was due to $\pi\rightarrow\pi^*$ for the keto structure [20]. When **CM10** was excited at 403 nm, green emission

was recorded with emission maxima at 505 nm (Figure 2b).

As **CM10-CM16** showed similar metal sensing abilities which were not affected by the length of the alkyl chains, therefore, only **CM10** is discussed in detail. UV-Vis absorption of **CM10** showed significant changes upon addition of Fe^{3+} compared to other metal ions in which λ_{max} at 403 nm was blue shifted to 370 nm with decreased molar absorptivity. A new low intense absorption band was recorded in the range of $\lambda=$ 418 to 650 nm (Figure 3a). All metal ions reduced the fluorescence intensity of **CM10**, especially Fe^{3+} by 3.1-fold as shown in Figure 3b.

Selectivity of **CM10** was further investigated by adding various metal ions to **CM10** in the presence of Fe^{3+} (red bar). I_o/I was the relative fluorescence intensity in which I_o and I represented initial and final fluorescence intensity, respectively. Hence, the more the quenching, the higher the value of I_o/I. The values of relative fluorescence intensity, I_o/I as indicated by red bars were almost similar with the bar caused by Fe^{3+} alone (Figure 4). This observation illustrated that detection of Fe^{3+} was not interfered by other 30 μM equivalent competitive metal ions [21]. The responsible quencher is unlikely to be differentiated when lower concentration of Fe^{3+} (<10 μM) and higher concentration of other metal ions coexisted. However, the presence of Fe^{3+} could be identified via UV-Vis spectroscopy as only Fe^{3+} will cause the blue shifting at $\lambda=$ 403 nm and with increased absorption band in the range of $\lambda=$ 418 to 650 nm (Figure 3a).

(a)

(b)
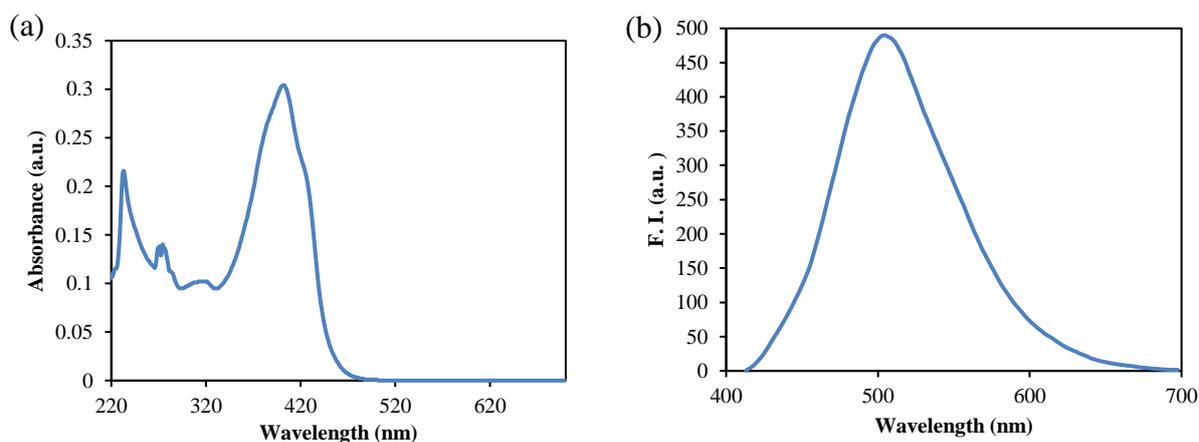
Figure 2. (**a**) UV-Vis spectrum; (**b**) Fluorescence spectrum of 8.0×10^{-4} mg mL^{-1} **CM10** in tetrahydrofuran with $\lambda_{ex}=$ 403 nm
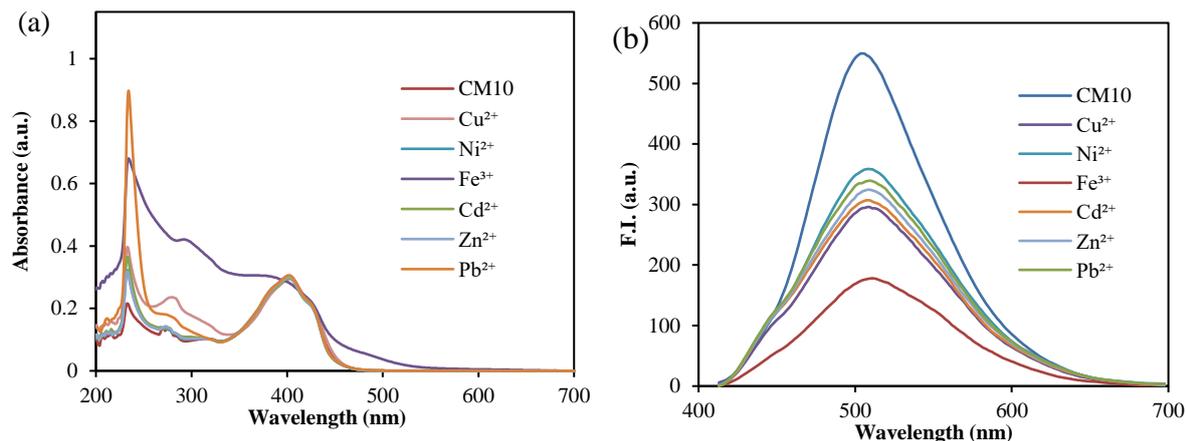
Figure 3. (**a**) UV-Vis spectra; (**b**) Fluorescence spectra of **CM10** in tetrahydrofuran after addition of various metal ions (30µM)
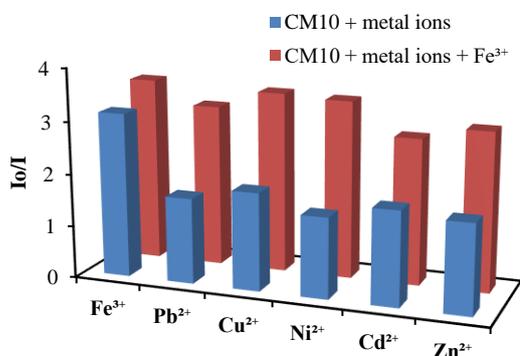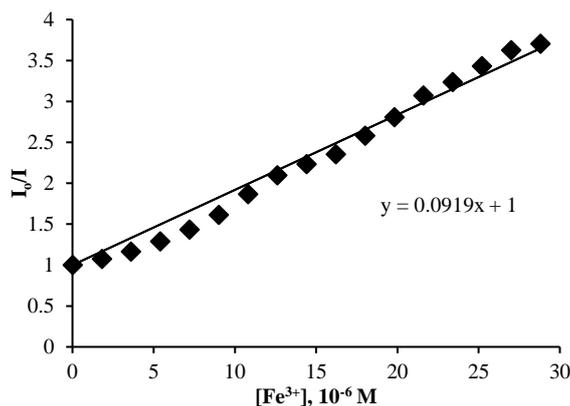

Figure 4. Relative fluorescence intensity of **CM10** with various metal ions at 30 µM (blue bar) and with the presence of additional 30 µM of Fe^{3+} (red bar). The emission wavelength observed was 505 nm.

Besides, two isosbestic points at λ=369, 433 nm were recorded based on the UV-Vis spectra obtained with different concentrations of Fe^{3+} (Figure 5a). The presence of isosbestic points indicated the formation of a new ground-state species which was in equilibrium with the free **CM10** [22]. The formation of this nonfluorescent new ground-state species was responsible to the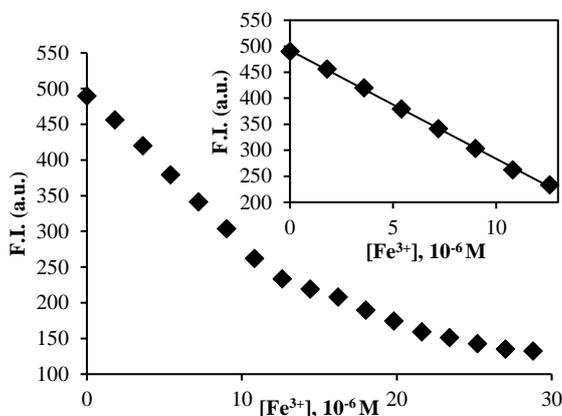 observed fluorescence quenching effect because the nonfluorescent fluorophore-quencher species absorbed light and immediately returned to the ground sate without emission of photon. The fluorescence intensity of **CM10** decreased gradually with increasing Fe^{3+} concentration without any significant spectral shape changes (Figure 5b) which suggested the negligible formation of excited charge-transfer complex (exciplex) that happened during the excited state lifetime [23].
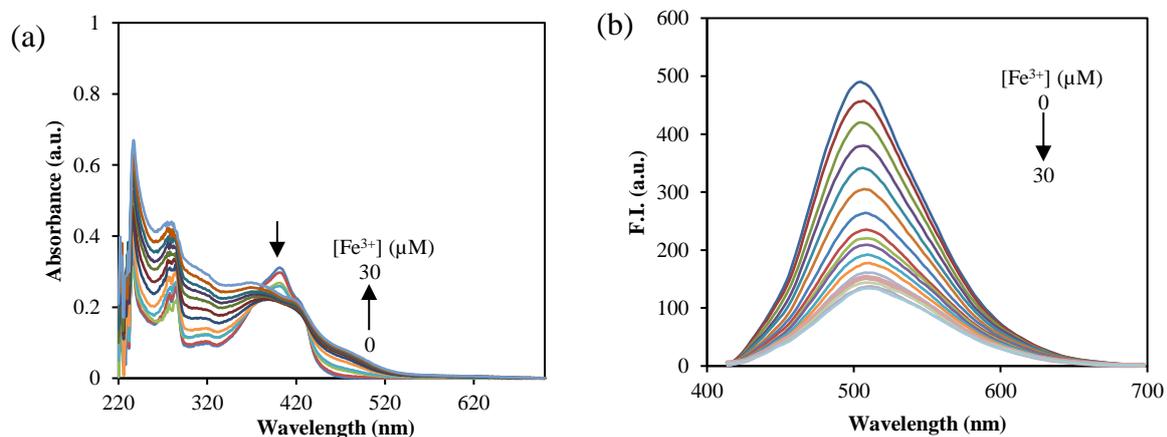
Figure 5. (**a**) UV-Vis absorbance; (**b**) Photoluminescence of **CM10** with various concentration of Fe^{3+}

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Figure 6. Stern-Volmer plot for the quenching fluorescence of **CM10** by Fe^{3+}

Figure 7. CM10 versus increasing concentration of Fe^{3+}; inset shows the plot of linear range of fluorescence intensity **CM10** versus concentration of Fe^{3+}

Table 2. Limit of detection of **CM10** and other reported chemosensors towards Fe^{3+}

Chemosensor	Limit of detection, μM	Reference
Quinoline derivatives	0.12	[27]
Poly(fluorine) derivatives	0.22	[27]
Propane-1,3-dione based polymer	0.4	[27]
Rhodiamine derivatives	0.4	[27]
Anthracene Schiff base derivatives	0.59	[28]
Spiroosazine derivatives	0.88	[27]
Benzimidazole derivatives	1.21	[27]
Julolidinie derivatives	6.8	[27]
CM10 ester oligomers	7.90	Present work
Coumarin based polymer	10.6	[30]
Diethylenetriamine Schiff base derivative	60.49	[31]

A linear Stern-Volmer relationship between **CM10** and Fe^{3+} was obtained as shown in Figure 6, in which I_o and I represented initial and final fluorescence intensity, respectively. This indicated the dominance of fluorescence quenching process by the formation of a new ground-state species, which was proved by UV-Vis experiment (Figure 5a). According to equation: $I_o/I = K_{SV}[Fe^{3+}] + 1$, the Stern-Volmer quenching constant, K_{SV} was $9.19 \times 10^3 \, M^{-1}$ [24].

The linear detection range for Fe^{3+} determination was from 0 to 12.6×10^{-6} M by plotting the fluorescence intensity against concentration of Fe^{3+} as shown in Figure 7. Linear equation thus

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obtained, I_o/I=-20.841[Fe^{3+}] + 492.05, R^2=0.999. The detection limit was calculated by using the equation: detection limit=3S/ρ, where S is the standard deviation of blank measurement and ρ is the slope of fluorescence intensity plotted against analyte concentration [25]. The calculated detection limit for Fe^{3+} (7.90 µM) was lower than the maximum limit of Fe^{3+} that is allowed by the Malaysian standards for water quality (EQA, 1974) (18 µM) and WHO for drinking water quality (WHO, 1993) (18 µM), and the irrigation water quality standards (Fipps, 2003) (90 µM) [26]. Table 2 shows the comparison between the ester oligomer chemosensor **CM10** with other reported chemosensors for Fe^{3+}.

CONCLUSION

Curcumin-based ester oligomers with different lengths of alkyl side chains were successfully synthesized and characterized. The synthesized ester oligomers were soluble in most of the common organic solvents. Thermal stability of the synthesized oligomers was affected by the length of the alkyl side chains. The longer the alkyl side chains, the lower the ester oligomer thermal stability. The synthesized curcumin-based ester oligomers showed selectivity towards Fe^{3+} in which their fluorescence intensity decreased with increasing Fe^{3+} concentration. The detection limit of Fe^{3+} was 7.90 µM.

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