

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/260028117>

7-Oxy-3-(3,4,5-trimethoxyphenyl)coumarin substituted phthalonitrile derivatives as fluorescent sensors for detection of Fe³⁺ ions: Experimental and theoretical study

ARTICLE in SENSORS AND ACTUATORS B CHEMICAL · APRIL 2014

Impact Factor: 4.1 · DOI: 10.1016/j.snb.2013.12.044

CITATIONS

5

READS

120

5 AUTHORS, INCLUDING:



Esra Nur Kaya

Gebze Technical University

7 PUBLICATIONS 15 CITATIONS

SEE PROFILE



Fatma Yuksel

Gebze Technical University

62 PUBLICATIONS 304 CITATIONS

SEE PROFILE



Gül Özpinar

Çanakkale Onsekiz Mart Üniversitesi

11 PUBLICATIONS 80 CITATIONS

SEE PROFILE



Mahmut Durmuş

Gebze Technical University

225 PUBLICATIONS 2,325 CITATIONS

SEE PROFILE



7-Oxy-3-(3,4,5-trimethoxyphenyl)coumarin substituted phthalonitrile derivatives as fluorescent sensors for detection of Fe³⁺ ions: Experimental and theoretical study

Esra Nur Kaya^{a,b}, Fatma Yuksel^b, Gül Altınbaş Özpinar^c,
Mustafa Bulut^a, Mahmut Durmuş^{b,*}

^a Marmara University, Faculty of Art and Science, Department of Chemistry, 34722 Kadikoy, Istanbul, Turkey

^b Gebze Institute of Technology, Department of Chemistry, PO Box 141, Gebze 41400, Kocaeli, Turkey

^c Çanakkale Onsekiz Mart University, Biga Vocational School, Department of Chemistry Technology, Biga 17200, Çanakkale, Turkey

ARTICLE INFO

Article history:

Received 3 October 2013

Received in revised form

10 December 2013

Accepted 10 December 2013

Available online 3 January 2014

Keywords:

Coumarin (2H-chromen-2-one)

Phthalonitrile, Fluorescence

Chemosensor

Fe³⁺ ions

ABSTRACT

The novel 7-hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) has been synthesized via Perkin reaction and its phthalonitrile derivatives (**2**, **3**, **4** and **5**) have also been prepared from the reaction of this coumarin (**1**) with 3-nitrophthalonitrile, 4-nitrophthalonitrile or 4,5-dichlorophthalonitrile compounds for the first time in this study. The newly synthesized compounds have been fully characterized by ¹H NMR, MALDI-TOF, FT-IR, UV-vis and fluorescence spectral data as well as elemental analysis. The exact structure of the coumarin substituted phthalonitrile derivatives (**2**, **3** and **5**) have also been determined using X-ray diffraction. The electronic absorption and fluorescence properties of these new compounds have been studied in different solvents. The chemosensor behaviors of these compounds to metal ions have also been examined by fluorescence spectroscopy and these compounds exhibited as fluorescence chemosensor for the determination of Fe³⁺ ions in solution. Fe³⁺ complex structures of mono-coumarin ring substituted derivatives (**1–4**) have been investigated by using density functional theory computations.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Coumarin (2H-chromen-2-one, 2H-1-benzopyran-2-one) derivatives are a very important class of oxygen heterocycles [1]. They have interesting photophysical properties and a wide range of applications in detection of metal ions, laser dyes, photosensitizers, pesticides etc. [2]. The coumarin derivatives are a key species for organic fluorescent chromophores [3]. Fluorescence characteristic of these compounds can be changed with substitution of different groups at the 3- and/or the 7-position of coumarin skeleton [4]. Perkin, Knoevenagel, Pechmann etc. methods have been developed for the synthesis of coumarin derivatives in the literature [5]. Perkin reaction is a very useful method for the synthesis of α,β -unsaturated aromatic carbonyl compounds and this reaction involves the condensation of acetic anhydride with an aromatic aldehyde in the presence of a weak base like sodium or potassium acetate or triethylamine [2].

Chemosensors are used for the determination of the different analytes such as metal cations, different anions or some biological substrates in aqueous or organic media. They are one of the most important probe materials due to in term of portability, simplicity and cheapness of these compounds [6]. Fluorescent chemosensors which is a subunit of chemosensors can be used in the biological environment for investigating of small organic and inorganic analytes [7]. Lately coumarins are used as fluorescent chemosensors by reason of their less toxicity and easy to be modified for sensing of different analytes [8]. Fluorescent sensors have been attracting considerable attention for the determination of ions and neutral analytes in many fields such as biological probes, environmental sensors, molecular devices, detection of nerve gases, etc. [9]. Fe³⁺ which involve important role in human and animal supports the oxygen-carrying capacity of heme and acts as a cofactor in many enzymatic reactions involved in the mitochondrial respiratory chain. On the other hand if the level of Fe³⁺ ions is high it can be toxic for promote oxidation of lipids, proteins and other cellular components [10]. The deficiency of Fe³⁺ ions in the body causes anemia, hemochromatosis, liver damage, diabetes, Parkinson's disease and cancer [11].

In this study, the novel coumarin substituted phthalonitrile derivatives were synthesized and characterized for the first time. Their chemosensor behaviors to metal ions (Li⁺, Na⁺, K⁺, Cs⁺, Mg²⁺,

* Corresponding authors at: Gebze Institute of Technology, Department of Chemistry, PO Box 141, Gebze 41400, Kocaeli, Turkey. Tel.: +90 262 6053075; fax: +90 262 6053101.

E-mail address: durmus@gyte.edu.tr (M. Durmuş).

Ba²⁺, Ca²⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Al³⁺, Ag⁺, Cd²⁺, Hg²⁺ and Pb²⁺) were also investigated by fluorescence spectroscopy in solution. The coumarin substituted phthalonitrile-metal binding ratio values were also determined by the combination of Benesi–Hildebrand analysis and the Continuous Variation (Job's) method. The plausible iron(III) complex structures of mono-coumarin ring substituted derivatives (**1–4**) were investigated by using quantum chemical computations.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried, purified and stored over molecular sieves (4 Å). The purity of the products was tested in each step using thin layer chromatography (TLC) (silica gel). 3,4,5-trimethoxyphenylacetic acid and 2,4-dihydroxybenzaldehyde were purchased from Aldrich Chemical Company. Silica gel which used for purification of the compounds was purchased from Merck. 4-Nitrophthalonitrile [12], 3-nitrophthalonitrile [13] and 4,5-dichlorophthalonitrile [14] were synthesized according to the reported procedures. The used LiCl, NaCl, KCl, CsCl, MgCl₂, BaCl₂, CaCl₂, CrCl₃, MnCl₂, FeCl₃, CoCl₂, NiCl₂, CuCl₂, ZnCl₂, AlCl₃, AgNO₃, CdCl₂, HgCl₂ and PbCl₂ for the determination of sensor properties of phthalonitrile compounds were obtained from commercial suppliers.

2.2. Measurements

FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer. Absorption spectra in the UV–vis region were recorded with a Shimadzu 2101 UV spectrophotometer. Mass spectra were performed on a Bruker Autoflex III MALDI-TOF spectrometer. A 2,5-dihydroxybenzoic acid (DHB) was used as MALDI matrix. ¹H NMR spectra were recorded on a Varian 500 MHz spectrometer in DMSO-*d*₆ and CDCl₃ solutions. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature.

2.3. Synthesis

2.3.1. 7-Hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**)

3,4,5-Trimethoxyphenylacetic acid (2.50 g, 11.1 mmol), 2,4-dihydroxybenzaldehyde (1.53 g, 11.1 mmol), sodium acetate (4.55 g, 55.5 mmol) and anhydrous acetic anhydride (13 mL) were mixed and heated for 9 h at 160 °C. After cooling to room temperature, 100 mL water was added and the mixture was stirred overnight. The resulting solid, 7-acetoxy-3-(3,4,5-trimethoxyphenyl)coumarin, was filtered and washed with water. The crude product was suspended in MeOH. A 10% aq. HCl solution was added to adjust the pH to 3 and this mixture was heated and stirred at 65 °C for 72 h under vacuum. The resulting solid was filtered, washed with water and dried under vacuo. The obtained solid was recrystallized from MeOH. The pure compound was soluble in MeOH, THF, DMSO and DMF. Yield: 2.02 g (57%); m.p.: 234 °C; UV–vis (CHCl₃): λ_{max}, nm (log ε): 345 (2.60); ¹H NMR (500 MHz; DMSO-*d*₆): δ_H, ppm: 8.18 (s, 1H, lactone-H), 7.59 (d, J: 8.5 Hz, 1H, Ar-H), 7.03 (s, 2H, Ar-H), 6.83 (dd, J: 8.5 and 2.3 Hz, 1H, Ar-H), 6.76 (s, 1H, Ar-H), 3.83 (s, 6H, -OCH₃), 3.71 (s, 3H, -OCH₃); IR ν (cm⁻¹): 3206 (Ar-OH), 3035–3007 (Ar-CH), 2943–2829 (aliphatic -CH), 1719 (C=O lactone), 1607–1461 (C=C), 1218–1121 (Ar-O-C); Anal. calc. for C₁₈H₁₆O₆: C, 65.85; H, 4.91%, found: C, 65.79; H, 4.97%, MALDI-TOF (*m/z*) calc. 328.32, found: 329.3 [M+H]⁺, 351.3 [M+Na]⁺, 367.3 [M+K]⁺.

2.3.2. 4-[2-Oxo-3-(3,4,5-trimethoxyphenyl)-2H-chromen-7-yloxy]phthalonitrile (**2**)

7-Hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) (0.50 g, 1.2 mmol) was dissolved in 20 mL of dry DMF and 4-nitrophthalonitrile (0.26 g, 1.52 mmol) was added to this solution. After stirring for 10 min finely ground anhydrous K₂CO₃ (0.31 g, 2.28 mmol) was added and the reaction mixture was stirred at 50 °C for 72 h under vacuum. Then the reaction mixture was poured into 100 mL ice-water. The resulting solid was collected by filtration and washed with water. The crude product was purified on a silica gel column using chloroform as eluent. Yield: 0.57 g (83%); m.p.: 207 °C; UV–vis (CHCl₃): λ_{max}, nm (log ε): 348 (4.22); ¹H NMR (500 MHz; CDCl₃): δ_H, ppm: 7.82 (s, 1H, lactone-H), 7.81 (d, J: 1.6 Hz, 1H, Ar-H), 7.65 (dd, J: 8.4 Hz and 1.5 Hz, 1H, Ar-H), 7.40 (brd, 1H, Ar-H), 7.37 (dd, J: 8.1 and 2.1 Hz, 1H, Ar-H), 7.09 (brd s, 1H, Ar-H), 7.03 (d, J: 8.49 Hz, 1H, Ar-H), 6.95 (s, 2H, Ar-H), 3.94 (s, 6H, -OCH₃), 3.91 (s, 3H, -OCH₃); IR ν (cm⁻¹): 3092–3039 (Ar-CH), 2972–2826 (aliphatic -CH), 2227 (C≡N) 1716, (C=O lactone), 1587–1453 (C=C), 1258 (Ar-O-Ar), 1238–1126 (Ar-O-C); Anal. calc. for C₂₆H₁₈O₆N₂: C, 68.72; H, 3.99; N, 6.16%, found: C, 68.62; H, 4.02; N, 6.04%, MALDI-TOF (*m/z*) calc. 454.4, found: 455.8 [M+H]⁺, 477.6 [M+Na]⁺.

2.3.3. 3-[2-Oxo-3-(3,4,5-trimethoxyphenyl)-2H-chromen-7-yloxy]phthalonitrile (**3**)

7-Hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) (0.50 g, 1.52 mmol) was dissolved in 20 mL of dry DMF and 3-nitrophthalonitrile (0.26 g, 1.52 mmol) was added to this solution. After stirring for 10 min finely ground anhydrous K₂CO₃ (0.31 g, 2.28 mmol) was added and the reaction mixture was stirred at 50 °C for 48 h under vacuum. Then the reaction mixture was poured into 100 mL ice-water. The resulting solid was collected by filtration and washed with water. The crude product was purified on a silica gel column using chloroform as eluent. Yield: 0.60 g (88%); m.p.: 219 °C; UV–vis (CHCl₃): λ_{max}, nm (log ε): 343 (4.29); ¹H NMR (500 MHz; CDCl₃): δ_H, ppm: 7.81 (s, 1H, lactone 4-H), 7.70 (dd, J: 8.40 and 8.53 Hz, 1H, Ar-H), 7.64 (dd, J: 7.7 and 2.5 Hz, 1H, Ar-H), 7.29 (dd, J: 7.6 and 2.5 Hz, 1H, Ar-H), 7.30 (dd, J: 8.53 and 2.58 Hz, 1H, Ar-H), 7.08–7.06 (m, 1H, Ar-H), 7.05 (brd, 1H, Ar-H), 6.93 (s, 2H, Ar-H), 3.93 (s, 6H, -OCH₃), 3.90 (s, 3H, -OCH₃); IR ν (cm⁻¹): 3086 (Ar-CH), 2960–2837 (aliphatic -CH), 2229 (C≡N) 1724 (C=O lactone), 1578–1465 (C=C), 1284 (Ar-O-Ar), 1236–1126 (Ar-O-C); Anal. calc. for C₂₆H₁₈O₆N₂: C, 68.72; H, 3.99; N, 6.16%, found: C, 68.65; H, 4.03; N, 6.09%, MALDI-TOF (*m/z*) calc. 454.4, found: 455.0 [M+H]⁺, 477.6 [M+Na]⁺, 493.6 [M+K]⁺.

2.3.4. 4-Chloro-5-[2-oxo-3-(3,4,5-trimethoxyphenyl)-2H-chromen-7-yloxy]phthalonitrile (**4**)

7-Hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) (0.50 g, 1.52 mmol) was dissolved in 20 mL of dry DMF and 4,5-dichlorophthalonitrile (0.29 g, 1.52 mmol) was added to this solution. After stirring for 10 min finely ground anhydrous K₂CO₃ (0.31 g, 2.28 mmol) was added and the reaction mixture was stirred at 50 °C for 48 h under vacuum. Then the reaction mixture was poured into 100 mL ice-water. The resulting solid was collected by filtration and washed with water. The crude product was purified on a silica gel column using 100:1 CH₂Cl₂:MeOH as eluent. Yield: 0.51 g (70%); m.p.: 290 °C; UV–vis (CHCl₃): λ_{max}, nm (log ε): 346 (4.26); ¹H NMR (500 MHz; DMSO-*d*₆): δ_H, ppm: 8.62 (brd s, 1H, Ar-H), 8.35 (s, 1H, lactone 4-H), 8.03 (brd s, 1H, Ar-H), 7.87 (d, J: 8.6 Hz 1H, Ar-H), 7.32 (d, J: 2.39 Hz, 1H, Ar-H), 7.22 (dd, J: 8.64 and 2.46 Hz, 1H, Ar-H), 7.07 (s, 2H, Ar-H); 3.84

(s, 6H, $-\text{OCH}_3$), 3.73 (s, 3H, $-\text{OCH}_3$); IR ν (cm^{-1}): 3084–3004 (Ar–H), 2946–2839 (aliphatic CH), 2236 ($\text{C}\equiv\text{N}$) 1713 ($\text{C}=\text{O}$ lactone), 1585–1488 ($\text{C}=\text{C}$), 1280 (Ar–O–Ar), 1231–1120 (Ar–O–C). Anal. calc. for $\text{C}_{26}\text{H}_{17}\text{Cl}_1\text{O}_6\text{N}_2$: C, 63.88; H, 3.50; N, 5.73%, found: C, 63.81; H, 3.57; N, 5.85%, MALDI-TOF (m/z) calc. 488.8, found: 488.2 $[\text{M}]^+$.

2.3.5. 4,5-Bis[2-oxo-3-(3,4,5-trimethoxyphenyl)-2H-chromen-7-yloxy]phthalonitrile (5)

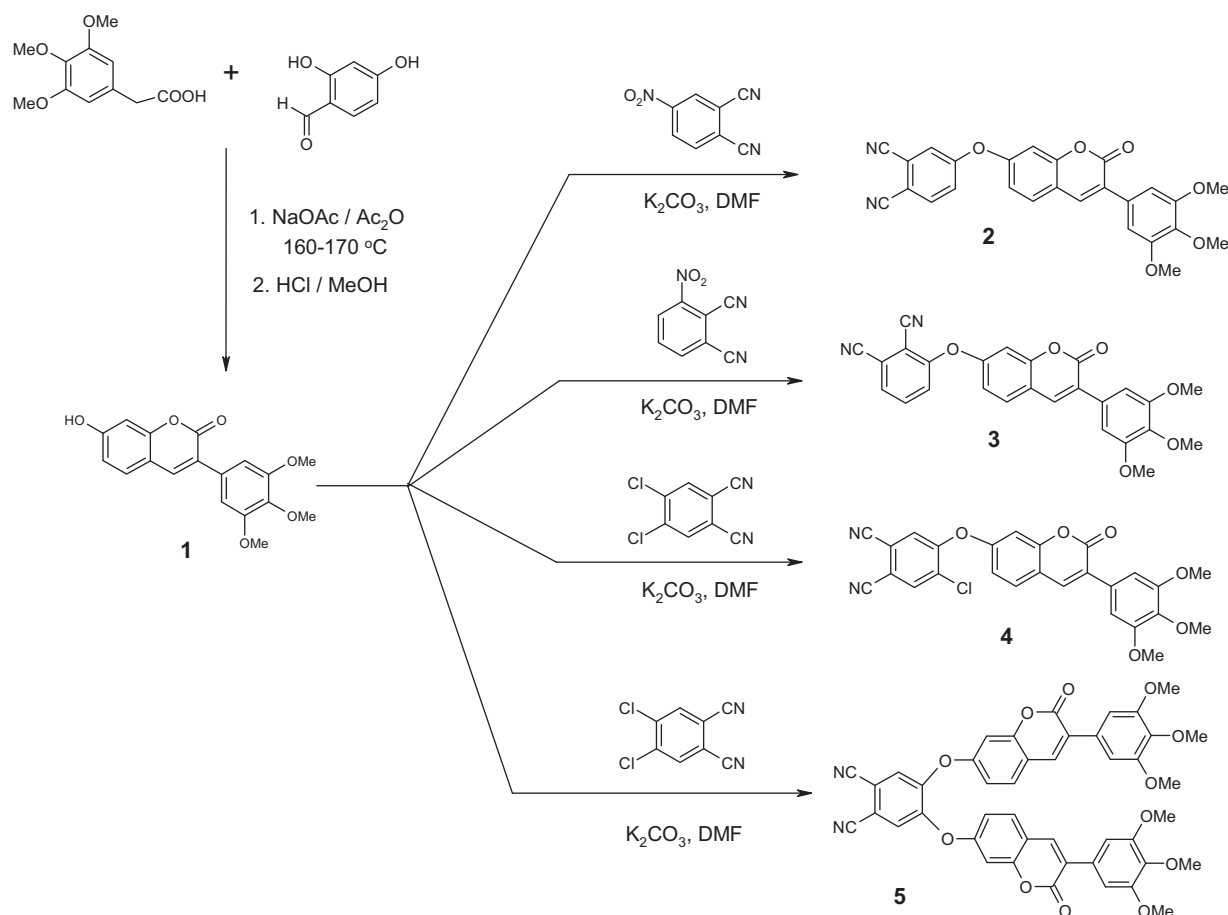
7-Hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) (0.50 g, 1.52 mmol) was dissolved in 20 mL of dry DMF and 4,5-dichlorophthalonitrile (0.15 g, 0.76 mmol) was added to this solution. After stirring for 10 min finely ground anhydrous K_2CO_3 (0.42 g, 3.04 mmol) was added and the reaction mixture was stirred at 50°C for 72 h under vacuum. Then the reaction mixture was poured into 100 mL ice-water. The resulting solid was collected by filtration and washed with water. The crude product was purified on a silica gel column using 100:1 CH_2Cl_2 :MeOH as eluent. Yield: 0.34 g (58%); m.p.: 181°C ; UV–vis (CHCl_3): λ_{max} , nm ($\log \epsilon$): 345 (4.70); ^1H NMR (500 MHz; CDCl_3): δ_{H} , ppm 7.80 (s, 2H, lactone H), 7.62 (dd, J : 8.92 and 1.29 Hz, 2H, Ar–H), 7.48 (s, 2H, Ar–H), 6.99–6.95 (m, 2H, Ar–H), 6.96 (brd s, 2H, Ar–H), 6.92 (s, 4H, Ar–H), 3.92 (s, 12H, $-\text{OCH}_3$), 3.82 (s, 6H, $-\text{OCH}_3$); IR ν (cm^{-1}): 3060–3003 (Ar–H), 2969–2837 (aliphatic $-\text{CH}$), 2232 ($\text{C}\equiv\text{N}$) 1716 ($\text{C}=\text{O}$ lactone), 1583–1463 ($\text{C}=\text{C}$), 1292, 1267 (Ar–O–Ar), 1233–1118 (Ar–O–C). Anal. calc. for $\text{C}_{44}\text{H}_{32}\text{O}_{12}\text{N}_2$: C, 67.69; H, 4.13; N, 3.59%, found: C, 67.73; H, 4.18; N, 3.66%, MALDI-TOF (m/z) calc. 780.7, found: 780.2 $[\text{M}]^+$, 803.3 $[\text{M} + \text{Na}]$.

2.4. X-ray crystallography

Intensity data were recorded on a Bruker APEX II QUAZAR diffractometer. Absorption correction by multi-scan has been applied [15] and space groups were determined using XPREP implemented in APEX2 [16]. Structures were determined using the direct methods procedure in SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97 [17]. All non-hydrogen atoms were refined with anisotropic displacement factors and C–H hydrogen atoms were placed in calculated positions and allowed to ride on the parent atom. There are some electron peaks due to disordered solvent molecules with very larger displacement parameters which were difficult to model in unit cell of compound **5**. Therefore, the rest molecules were refined without the effect of the solvent molecules by using SQUEEZE command of PLATON [18]. There are four cavities per unit cell; two cavities 63 \AA^3 of volume with 19 void electron counts and other two cavities 266 \AA^3 of volume with 70 void electron counts. The final geometrical calculations and molecular drawings were carried out using PLATON [18], and MERCURY [19] programs and the molecular drawings were done with DIAMOND [20] programs. Structure determinations have been deposited with the Cambridge Crystallographic Data Centre with references CCDC 918135, 918136 and 952926 for compounds **2**, **3**, and **5**, respectively.

2.5. Chemosensor studies

Spectroscopic changes upon addition of metal salts to the ligands were recorded using a fluorescence spectrophotometer. All fluorescence emission spectral studies were performed in 1,



Scheme 1. The synthesis route of 7-hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) and its phthalonitrile derivatives (**2**, **3**, **4** and **5**).

4-dioxane solutions ($C = 1.0 \times 10^{-6}$ M) of the coumarin substituted phthalonitrile compounds (**2**, **3**, **4** and **5**) at room temperature, while the water solutions ($C = 0.1$ M) of the corresponding metal chlorides (nitrate derivative for Ag ion) were used as the source of metal ions. Spectra were routinely acquired at 25°C in a 1 cm path length quartz cuvette with a volume of 4 mL by the addition of different metal (Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ba^{2+} , Ca^{2+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} , Ag^+ , Cd^{2+} , Hg^{2+} and Pb^{2+}) solutions. The titration experiments of ligands in presence of Fe^{3+} were carried out with the freshly prepared stock solutions of ligand in 1,4-dioxane and metal salts in water using by fluorescence spectrophotometer.

2.6. Computational details

All computations were done using Gaussian 09 software package [21]. Each possible iron(III) complex structure was fully optimized using UB3LYP/6-31G(d) computational level. Normal mode analysis was carried out to characterize each stationary point (no imaginary frequency). Zero point corrected electronic energies of the optimized geometries were used to calculate relative energies of the structures. Among the synthesized compounds, only iron(III) complex structure of compound **5** was not modeled since existence of two coumarin ring in this compound increases the number of possible iron(III) complex structures. Optimized Cartesian coordinates and absolute energies of the model complex structures are given in Supporting information.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic procedures of the 7-hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) and its phthalonitrile derivatives (**2**, **3**, **4** and **5**) are given in Scheme 1. 7-hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) was synthesized by the reaction of 3,4,5-trimethoxyphenylacetic acid with 2,4-dihydroxybenzaldehyde via Perkin reaction [22,23]. The novel 7-oxy-3-(3,4,5-trimethoxyphenyl)coumarin substituted phthalonitriles (**2**, **3**, **4** and **5**) were synthesized with 7-hydroxy-3-(3,4,5-trimethoxyphenyl)coumarin (**1**) and 4-nitrophthalonitrile, 3-nitrophthalonitrile or 4,5-dichlorophthalonitrile in the presence of K_2CO_3 in DMF under a N_2 atmosphere through base catalyzed nucleophilic aromatic displacement reaction. The newly synthesized products were characterized by general spectroscopic methods including FT-IR, ^1H NMR, UV–vis and MALDI-TOF and elemental analysis as well. The single crystals of compounds **2**, **3** and **5** were obtained and the exact structures of these compounds were determined by X-ray diffraction method. The analyses are consistent with the predicted structures as shown in Section 2.

Comparison of the FT-IR spectral data clearly indicated the formation of compound **1** by the appearance of new vibration bands at 3206 cm^{-1} for OH stretching, $3035\text{--}3007\text{ cm}^{-1}$ for aromatic–CH stretching, 1719 cm^{-1} for C=O stretching on the lactone ring. After conversion of the compound **1** corresponding phthalonitrile derivatives (**2**, **3**, **4** and **5**) the broad peak for the –OH band disappeared and the characteristic vibrations of the $\text{--C}\equiv\text{N}$ stretching was observed.

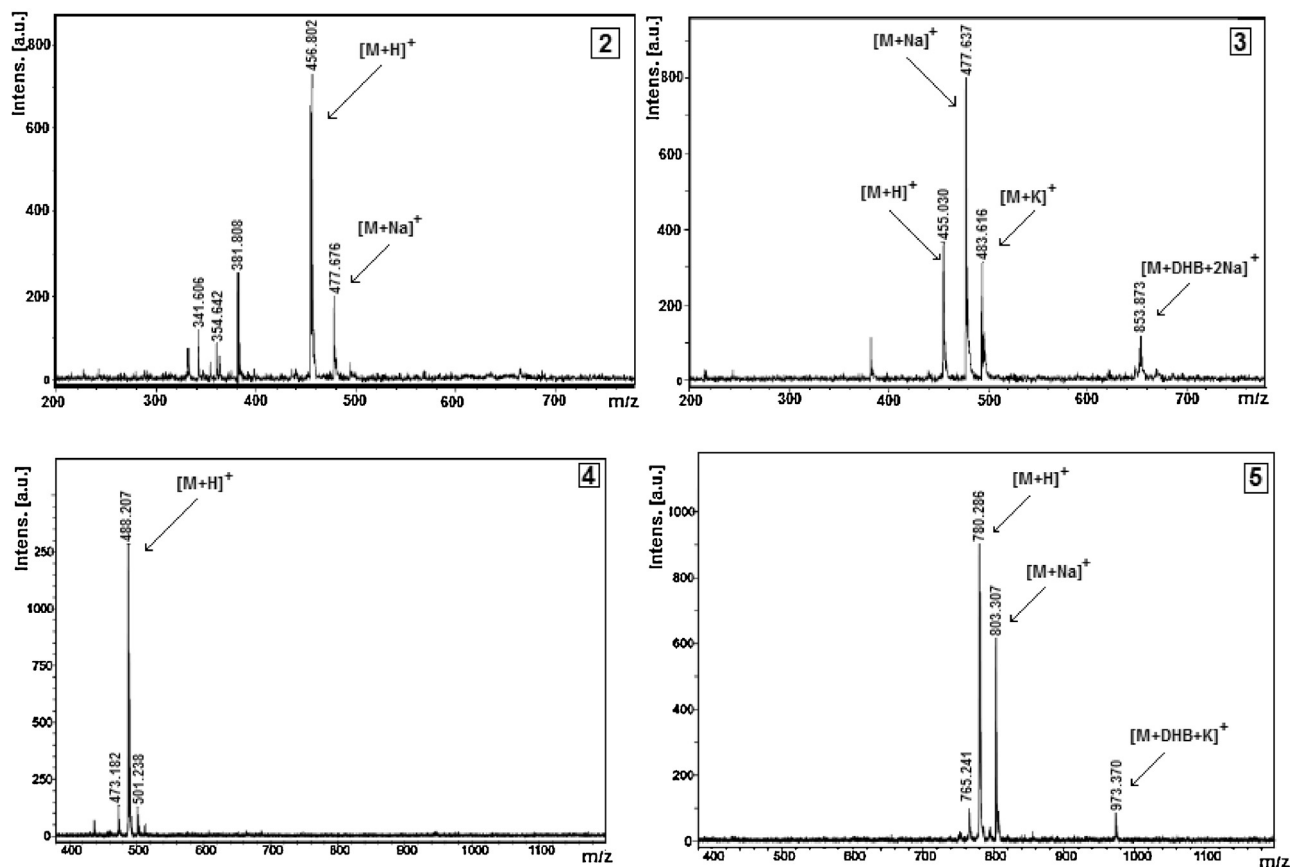


Fig. 1. MALDI-TOF spectra of compounds **2**, **3**, **4** and **5**.

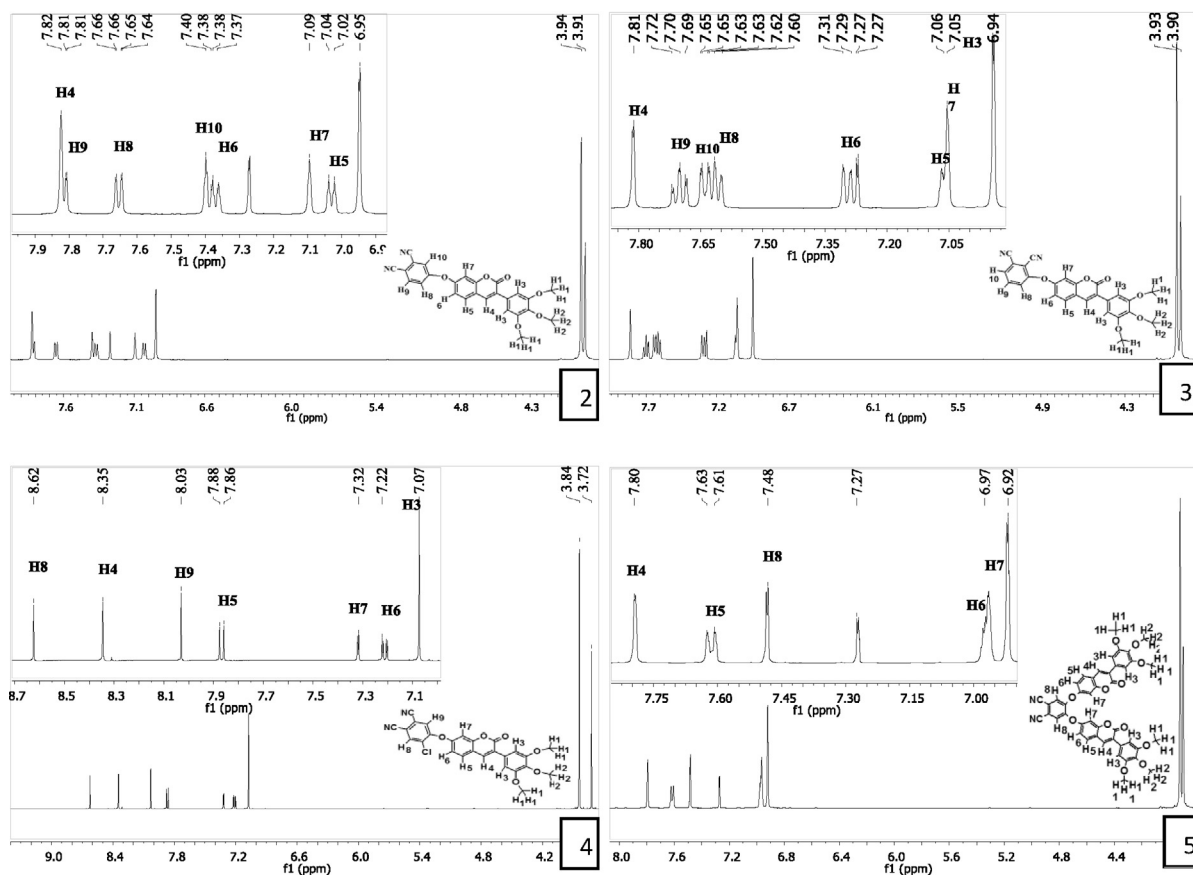


Fig. 2. ^1H -NMR spectra of compounds **2**, **3** and **5** in CDCl_3 and compound **4** in $\text{DMSO}-d_6$.

The FT-IR spectra of the all phthalonitrile compounds showed a sharp peak at around $2227\text{--}2236\text{ cm}^{-1}$ for $\text{C}\equiv\text{N}$ stretching.

The MALDI-TOF mass spectra of newly synthesized compounds confirmed the proposed structures; molecular ion peaks were easily identified at m/z : 329.3 $[\text{M} + \text{H}]^+$ for compound **1**, 455.8 $[\text{M} + \text{H}]^+$ for compound **2**, 455.0 $[\text{M} + \text{H}]^+$ for compound **3**, 488.2 $[\text{M}]^+$ for compound **4** and 780.2 $[\text{M}]^+$ for compound **5** (Fig. 1).

The ^1H -NMR spectra of 7-hydroxy-3-(3,4,5-trimethoxyphenyl) coumarin (**1**) and its phthalonitrile derivatives (**2**, **3**, **4** and **5**) were recorded in CDCl_3 or $\text{DMSO}-d_6$ solutions. The ^1H NMR spectra of phthalonitrile derivatives (**2**, **3**, **4** and **5**) were almost similar except for small shift (Fig. 2). The aromatic protons were observed at between δ 6.95–7.81 ppm for compound **2**, δ 6.93–7.70 ppm for compound **3**, δ 7.22–8.62 ppm for compound **4** and δ 6.92–7.62 ppm for compound **5**. The methoxy protons were observed at δ 3.94 ppm and δ 3.91 ppm for compound **2**, 3.93 ppm and δ 3.90 ppm for compound **3**, 3.84 ppm and δ 3.73 ppm for compound **4** and δ 3.92 ppm and δ 3.82 ppm for compound **5** as singlet peaks. The protons for coumarin lactone ring at four positions were observed at δ 7.82 ppm for compound **2**, 7.81 ppm for compound **3**, δ 8.35 ppm for compound **4** and δ 7.80 ppm for compound **5** as singlet peaks. The CH proton on the coumarin lacton ring for compound **4** was seen at down field compared to other counterparts due to the effect of electronegative chlorine atom on the phthalonitrile benzene group.

3.2. Crystal structure analysis

The molecular structures of compounds **2**, **3** and **5** were established by single-crystal X-ray structural analysis and data collection and refinement details are presented in Table 1. The X-ray molecular structures of compounds **2**, **3** and **5** confirmed the

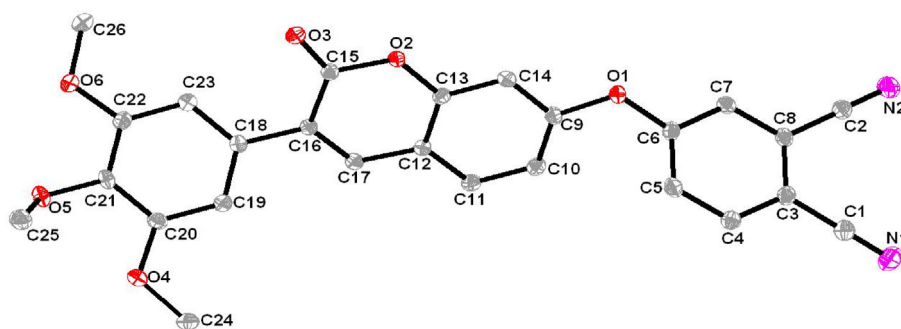
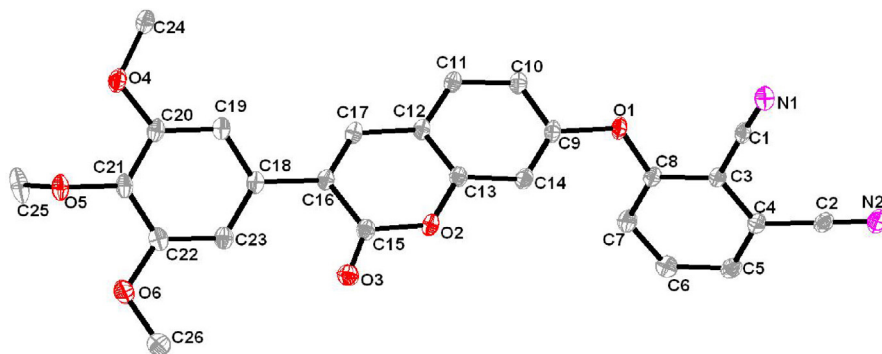
assignments of their structure from spectroscopic data; all three structures are 7-oxy-3-(3,4,5-trimethoxyphenyl)coumarin substituted phthalonitrile derivatives as shown in Figs. 3–5, respectively. Compounds **2** and **3** are structural isomers, they contain one 7-oxy-3-(3,4,5-trimethoxyphenyl)coumarin moiety which are linked to different position of phthalonitrile ring, whilst compound **5** is disubstituted with two 7-oxy-3-(3,4,5-trimethoxyphenyl)coumarin moieties.

The bond lengths of compounds **2**, **3** and **5** are found in the normal range for those similar phthalonitrile and coumarin derivatives [24–27]. The selected bond parameters are given in Table 2. In every molecule, the double $\text{C}=\text{O}$ bond length of coumarin moieties is in the range of 1.272–1.214 Å. The single $\text{C}_{\text{ar}}\text{--O}$ bond lengths [1.363–1.386 Å] are found slightly smaller than $\text{CH}_3\text{--O}$ bond lengths [1.411–1.443 Å] as expected (Table 2).

The phthalonitrile and coumarin moieties are not coplanar in all structures. Although the C--O--C bond angle between phthalonitrile and coumarin moieties is found similar in all structures [$121.83(9)^\circ$ (for **2**) and $119.40(17)^\circ$ (for **3**) and $118.6(3)^\circ$ and $119(2)^\circ$ (for **5**)], the orientation of coumarin with respect to phthalonitrile is different in all three structures; the angle between the main planes of phthalonitrile and coumarin moieties is 49.01° in compound **2**, and 65.80° in compound **3** (Fig. S1) while it is 74.63° and 71.04° in compound **5** (Fig. S2). The related C--O--C--C dihedral angles are also different in every structures as shown in Table 2. The coumarin and trimethoxyphenyl-moieties of all structures are also not coplanar. However, the orientation of trimethoxyphenyl-moiety with respect to coumarin is similar in all structures. The angle between the main planes of coumarin and trimethoxyphenyl-moieties is 31.19° in compound **2**, 28.71° in compound **3** (Fig. S3) and 35.70° and 30.10° in compound **5** (Fig. S4). The C--C--C dihedral angle between these two moieties is approximately 30° in every structure (Table 2).

Table 1X-ray crystallographic data and refinement parameters for compounds **2**, **3** and **5**.

Compound	2	3	5
Empirical formula	C ₂₆ H ₁₈ N ₂ O ₆	C ₂₆ H ₁₈ N ₂ O ₆	C ₄₄ H ₃₂ N ₂ O ₁₂
Formula weight	454.42	454.42	780.72
Temperature (K)	120 (2)	120 (2)	150 (2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	8.2809(5)	14.9344(10)	16.8625(4)
<i>b</i> (Å)	10.8659(6)	7.7642(6)	7.4668(2)
<i>c</i> (Å)	12.6882(7)	19.0759(13)	32.9409(9)
α (°)	80.013(3)		
β (°)	78.087(3)	99.823(4)	93.017(2)
γ (°)	72.406(3)		
Volume (Å ³)	1057.26(10)	2179.5(3)	4141.80(19)
<i>Z</i>	2	4	4
Density (calc, Mg/m ³)	1.427	1.385	1.252
Absorption coeff. (mm ⁻¹)	0.103	0.100	0.092
<i>F</i> (000)	472	944	1624
Crystal size (mm ³)	0.22 × 0.29 × 0.42	0.11 × 0.12 × 0.16	0.11 × 0.14 × 0.22
θ_{\max} (°)	28.32	28.27	24.99
Reflections collected	18,738	19,874	7186
Independent reflections	5216	5391	4810
<i>R</i> _{int} (merging <i>R</i> value)	0.0394	0.0367	0.000
Data/restraints/parameters	5216/0/310	5391/0/310	7186/2/549
<i>R</i> (<i>F</i> ² > 2σ <i>F</i> ²)	0.0413	0.0571	0.0705
<i>wR</i> (all data)	0.1151	0.1692	0.1930
Goodness-of-fit on <i>F</i> ²	1.043	1.055	1.056

**Fig. 3.** (A) DIAMOND [20] drawing of compound **2** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.**Fig. 4.** (A) DIAMOND [20] drawing of compound **3** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

A close investigation of the crystal structures of compounds **2**, **3** and **5** shows that there is no usual hydrogen bonding in all structures, but there are weak CHAN and CHAO inter-molecular interactions in which may be effective in the stabilization of their unit cell.

3.3. Electronic absorption and fluorescence behavior

All absorption and emission spectral studies were performed in freshly distilled 1,4-dioxane solutions at room temperature (Fig.

S5 as an example for compound **2**). Mainly absorption bands were observed at approximately 345 nm in the UV region of electronic spectra for studied phthalonitrile derivatives (**2–5**). The fluorescence emission bands for all studied phthalonitrile compounds were observed at approximately 480 nm (Fig. S6). These compounds showed approximately 135 nm Stokes shift which is very high compared to other chromophores [28]. When the compare of emission intensities of studied phthalonitrile derivatives, the compound **5** exhibited the most intense fluorescence emission among the studied phthalonitrile derivatives due to presence of

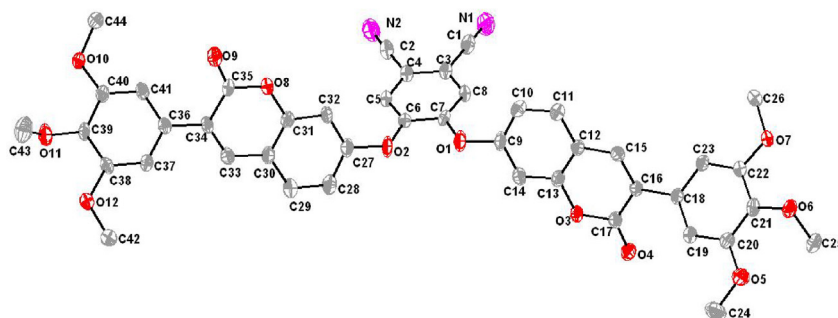


Fig. 5. (A) DIAMOND [20] drawing of compound **5** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

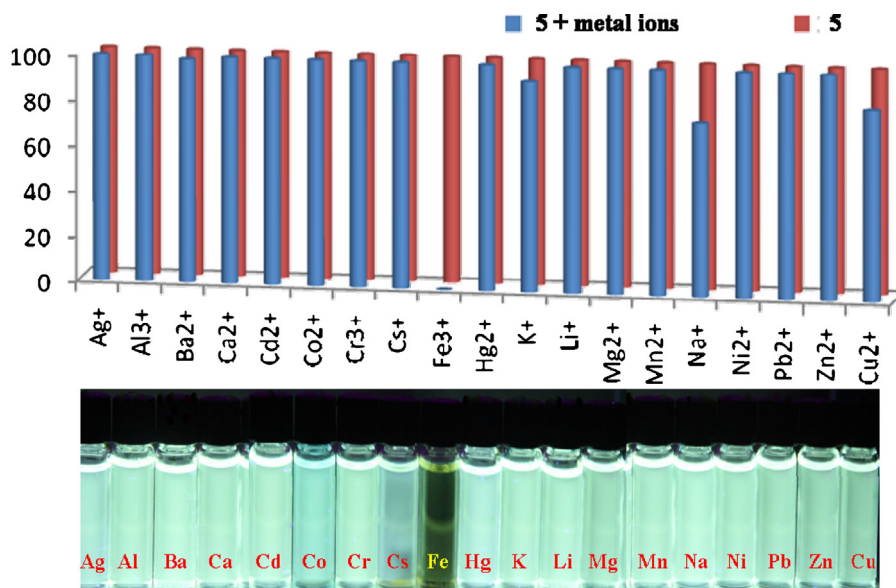


Fig. 6. The fluorescence emission responses of the compound **5** to different metal ions.

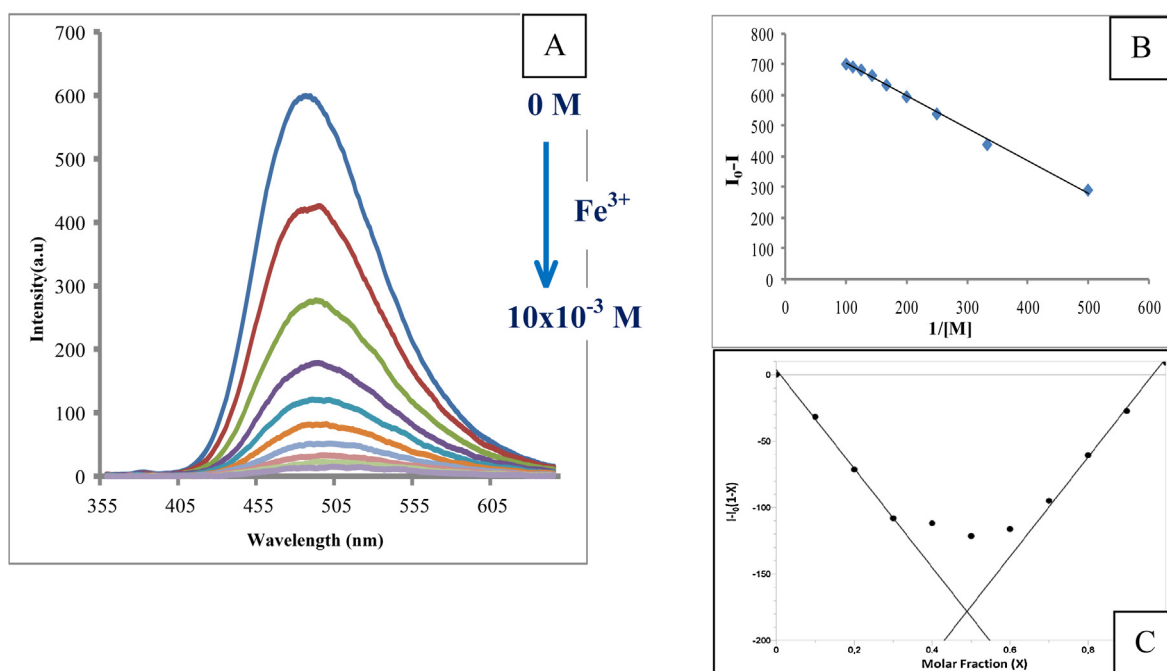
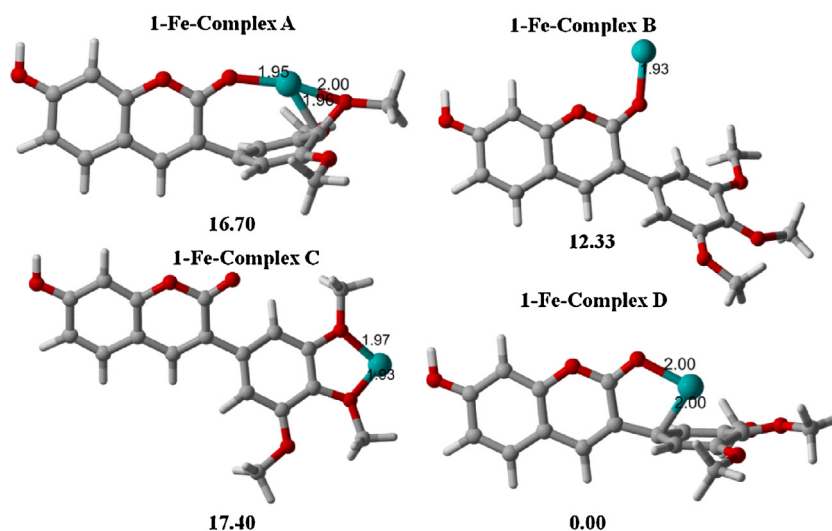


Fig. 7. (A) Fluorescence response of chemosensor **5** to various equivalents of Fe³⁺. (B) The Benesi-Hildebrand graph and (C) Job's plot of **5**-Fe³⁺ complexes in 1,4-dioxane solutions. The total concentration of **5** and Fe³⁺ was 1 × 10⁻⁶ M. The excitation wavelength was 345 nm. The monitored wavelength was 480 nm.

Table 2
Selected bond parameters for compounds **2**, **3** and **5**.

2		3		5	
Bond lengths (Å)					
C1–N1	1.1485(17)	C1–N1	1.153(3)	C1–N1	1.140(5)
C2–N2	1.1439(17)	C2–N2	1.144(3)	C2–N2	1.140(5)
O1–C6	1.3721(13)	O1–C8	1.371(3)	O1–C7	1.376(4)
O1–C9	1.3864(14)	O1–C9	1.402(2)	O1–C9	1.405(4)
O2–C13	1.3742(13)	O2–C13	1.374(3)	O2–C6	1.372(4)
O2–C15	1.3852(13)	O2–C15	1.378(2)	O2–C27	1.400(4)
O3–C15	1.2072(14)	O3–C15	1.202(3)	O3–C17	1.369(4)
O4–C20	1.3632(14)	O4–C20	1.368(3)	O3–C13	1.378(4)
O4–C24	1.4311(14)	O4–C24	1.428(3)	O8–C35	1.373(4)
O5–C21	1.3835(13)	O5–C21	1.381(2)	O8–C31	1.381(4)
O5–C25	1.4369(15)	O5–C25	1.421(3)	O4–C17	1.214(4)
O6–C22	1.3645(13)	O6–C22	1.370(3)	O9–C35	1.210(4)
O6–C26	1.4267(16)	O6–C26	1.424(3)	O5–C20	1.369(4)
				O5–C24	1.411(5)
				O6A–C21	1.404(5)
				O6A–C25A	1.432(6)
				O7–C22	1.369(4)
				O7–C26	1.425(4)
				O10–C40	1.368(4)
				O10–C44	1.437(4)
				O11–C43	1.338(5)
				O11–C39	1.367(4)
				O12–C38	1.374(4)
				O12–C42	1.443(5)
Bond angles (°)					
C6–O1–C9	121.83(9)	C8–O1–C9	119.40(17)	C7–O1–C9	118.6(3)
C13–O2–C15	122.75(9)	C13–O2–C15	122.79(17)	C6–O2–C27	119.2(3)
C20–O4–C24	116.62(9)	C20–O4–C24	118.05(16)	C17–O3–C13	122.6(2)
C21–O5–C25	113.36(9)	C21–O5–C25	113.38(19)	C35–O8–C31	122.7(3)
				C20–O5–C24	117.7(3)
				C21–O6A–C25A	117.7(4)
				C22–O7–C26	117.5(2)
				C40–O10–C44	118.0(2)
				C43–O11–C39	116.0(4)
				C38–O12–C42	117.6(2)
Dihedral angles (°)					
C9–O1–C6–C5	–35.60(17)	C9–O1–C8–C7	24.0(4)	C9–O1–C7–C8	–0.7(5)
C9–O1–C6–C7	148.82(11)	C9–O1–C8–C3	–160.3(2)	C9–O1–C7–C6	178.1(3)
C17–C16–C18–C19	29.17(17)	C17–C16–C18–C23	152.7(2)	C27–O2–C6–C5	–10.4(6)
C15–C16–C18–C19	–148.73(11)	C15–C16–C18–C23	–28.9(3)	C27–O2–C6–C7	172.1(3)
				C15–C16–C18–C23	–34.1(4)
				C17–C16–C18–C19	–37.8(4)
				C33–C34–C36–C37	30.4(5)
				C35–C34–C36–C41	32.4(5)

**Fig. 8.** Four different plausible iron(III) complex structures of the compound **1** optimized using UB3LYP/6-31G(d) and their relative zero-point corrected electronic energies (kcal/mol).

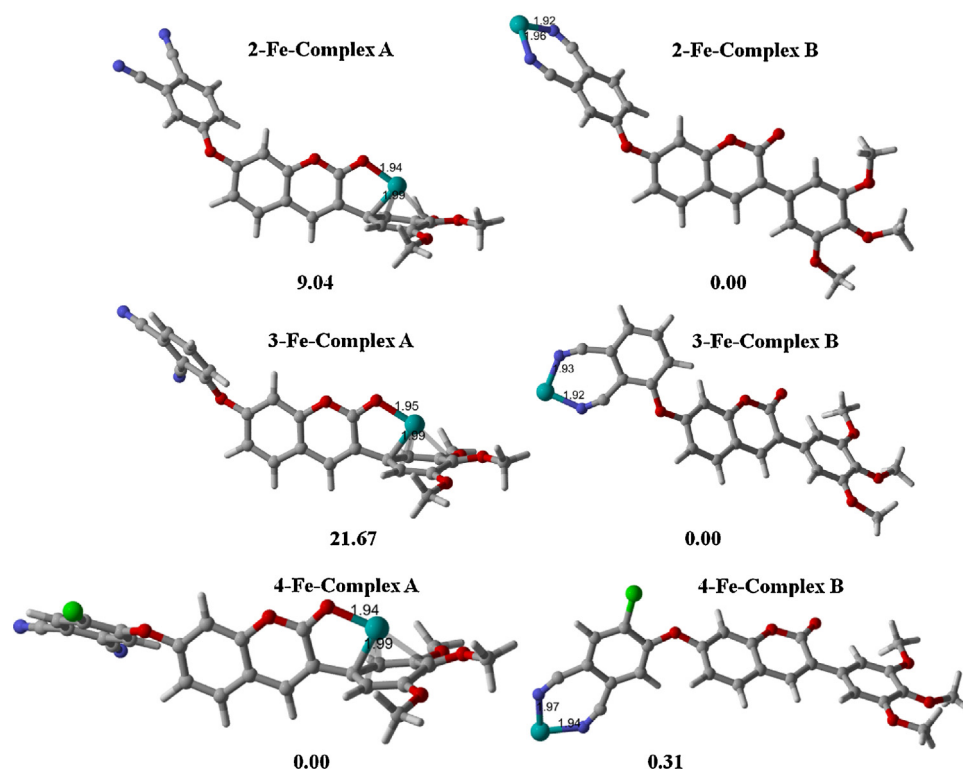


Fig. 9. Plausible iron(III) complex structures of the compounds 2–4 optimized using UB3LYP/6-31G(d) and their relative zero-point corrected electronic energies (kcal/mol).

two coumarin moieties in the structure. Compound **3** display more fluorescence intensity than compound **2** because the electronegative $C\equiv N$ groups on the compound **3** are closer to fluorescence coumarin system than compound **2**. The fluorescence quantum yields (Φ_F) of the studied compounds (**2–5**) were determined in 1,4-dioxane by the comparative method using Eq. (1) in the Supporting information. 2-Aminopyridine was used as standard. The compound **5** showed highest fluorescence quantum yield value ($\Phi_F=0.65$) among the studied phthalonitrile compounds because this compound contains two chromophore coumarin groups on the molecule. However, the compound **4** showed lowest fluorescence quantum yield value ($\Phi_F=0.38$). It could be attributed to the more quenching of this compound due to the electronegative chlorine atom on the molecule. The compounds **2** and **3** which are contain only one chromophore coumarin group on the molecules showed almost the same fluorescence quantum yield values ($\Phi_F=0.53$ for compound **2** and $\Phi_F=0.47$ for compound **3**). The compound **3** showed slightly lower Φ_F value than compound **2** could be due to the electronegative nitrile groups are close to coumarin group for compound **2**.

3.4. Chemosensor properties to metal ions

As mentioned earlier, the metal binding properties of coumarin molecules [29] may allow the use of these molecules as metal sensors. The effects of a variety of metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ba^{2+} , Ca^{2+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} , Ag^+ , Cd^{2+} , Hg^{2+} and Pb^{2+}) on the fluorescence properties of the newly synthesized coumarin substituted phthalonitrile compounds have been investigated using fluorescence spectroscopy. All fluorescence emission spectral studies were performed in 1,4-dioxane solutions of the phthalonitrile compounds at room temperature, while the water solutions of the corresponding metal chlorides (nitrate derivative for Ag ion) were used as the source of metal ions. The fluorescence spectra of the novel phthalonitrile compounds

exhibited little enhancement by the addition of the 30 μL of 0.1 M metal solutions except for Fe^{3+} . In sharp contrast, there was an enormous decrease of its fluorescence intensity upon the addition of Fe^{3+} , while no or minimal change was observed with the other metal ions (Fig. 6 as an example for compound **5** and Figs. S7–S9 for other compounds). All novel coumarin substituted phthalonitrile derivatives exhibited ‘turn-off’ chemosensor properties against the Fe^{3+} ions in the solution.

The titration of the coumarin substituted phthalonitrile chemosensor compounds with Fe^{3+} cations showed a decrease in the fluorescence intensities by the increasing concentrations of this cation (Fig. 7A for chemosensor **5** and Figs. S10A–S12A for other compounds). The graphs from a Benesi–Hildebrand analysis showed linear behavior for all studied coumarin substituted phthalonitrile chemosensor compounds interactions with Fe^{3+} ions (Fig. 7B for chemosensor **5** and Figs. S10B–S12B for other compounds) indicated that the stoichiometry of the complexes between phthalonitrile chemosensors and Fe^{3+} cations is 1:1 as mentioned by Garcia-Beltran et al. [30]. The Continuous Variation method was also used for the determination of the stoichiometry between the novel phthalonitrile chemosensors and detected metal cation (Fe^{3+}). Consistent with the Benesi–Hildebrand graphs, application of the Method of Continuous Variation resulted in a Job’s with a maximum at a mole fraction of Fe^{3+} close to 0.55, (Fig. 7C for chemosensor **5** and Figs. S10C–S12C for other compounds) indicating a preferred 1:1 stoichiometry for the formation of interactions between the phthalonitrile chemosensors and Fe^{3+} cations. The binding constant (K_b) values between the phthalonitrile compounds (**2–5**) and Fe^{3+} ions were determined in 1,4-dioxane. The intercepts of the plots of $\log [(F_0 - F) / (F - F_\infty)]$ against $\log [Fe^{3+}]$ (Fig. S13 in Supporting information) would provide the K_b values of the studied phthalonitrile chemosensors. These values were found of the order of $10^{-3} M^{-1}$ for all studied phthalonitrile compounds ($K_b = 2.45 \times 10^{-3}$ for **2**, 2.25×10^{-3} for **3**, 2.48×10^{-3} for **4** and 2.37×10^{-3} for **5**).

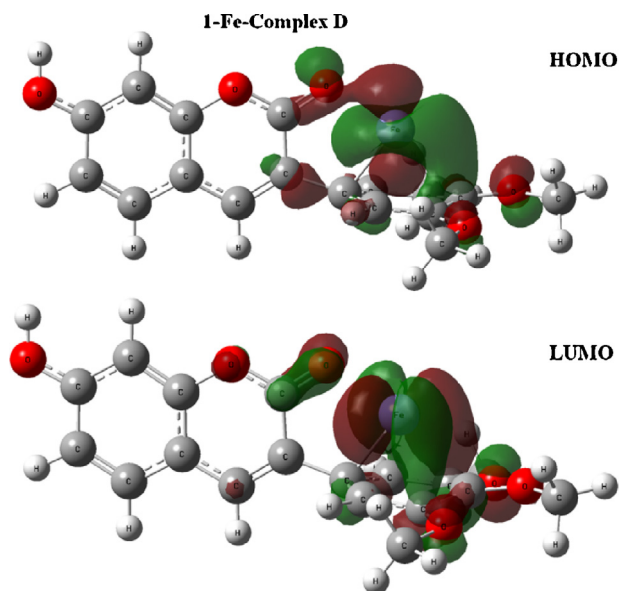


Fig. 10. HOMO and LUMO of the 1-Fe-Complex-D structure calculated with UB3LYP/6-31G(d).

3.5. Computational studies

Although it is found that the iron(III) complex formation ends up with a 1:1 ratio, it is still unclear how to bind Fe^{3+} cation to the compounds since the synthesized structures have different binding sites such as methoxy groups, cyano groups, oxygens from coumarin lactone ring which are able to interact with Fe^{3+} cation. With this purpose, we proposed different plausible iron(III) complex structures of mono-coumarin substituted derivatives (**1–4**) (Figs. 8 and 9) and fully optimized using UB3LYP/6-31G(d)

computational level. Highest occupied and lowest unoccupied molecular orbitals of the most stable complex structures are also shown in Figs. 10 and 11.

For the compound **1**, four different iron(III) complexes were proposed and their optimized geometries and relative energies are presented in Fig. 8. Fe^{3+} cation is positioned between carbonyl oxygen atom and methoxy group in the 1-Fe-Complex-A structure while it is situated at the site of methoxy groups for the 1-Fe-Complex-C structure. Energies of both complexes are close to each other. On the other hand, 1-Fe-Complex-B is more stable than complexes A and C by 4–5 kcal/mol even though Fe^{3+} cation interacts with only carbonyl oxygen (1.93 Å). The reason of this can be steric effects in the 1-Fe-Complex-A and 1-Fe-Complex-C structures. Among proposed complexes for the compound **1**, the most stable one is the 1-Fe-Complex-D. In this complex structure, Fe^{3+} cation placed above the horizontal benzene ring and interacts with carbonyl oxygen. The distance between Fe^{3+} cation and carbonyl oxygen is 2.00 Å. The stability of this complex can be attributed to the fact that half-filled 3d orbitals of Fe^{3+} cation strongly interacts with the π orbitals of benzene ring. HOMO and LUMO orbitals of the 1-Fe-Complex-D (Fig. 10) support this notion.

The plausible complex structures of the compounds **2**, **3**, and **4** are shown in Fig. 9. For each compound, two possible complex structures were proposed. Since the compounds **2**, **3**, and **4** involves 3-(3,4,5-trimethoxy)coumarin moiety similarly to the compound **1** and the 1-Fe-Complex-D is found to be the most plausible complex structure, the possible complex structures resembling 1-Fe-complexes A, B and C were rule out. Additionally, the existence of phthalonitrile ring in the compounds **2–4** causes formation of another plausible iron(III) complex structures in which Fe^{3+} cation interacts with cyano groups. Molecular orbitals of the most energetically stable complex structures are depicted in Fig. 11. For both the compounds **2** and **3**, the iron(III) complex involving Fe–NC interactions (in the range of 1.92–1.96 Å) (2-Fe-complex-B and 3-Fe-complex-B) are more stable than the other complex structure

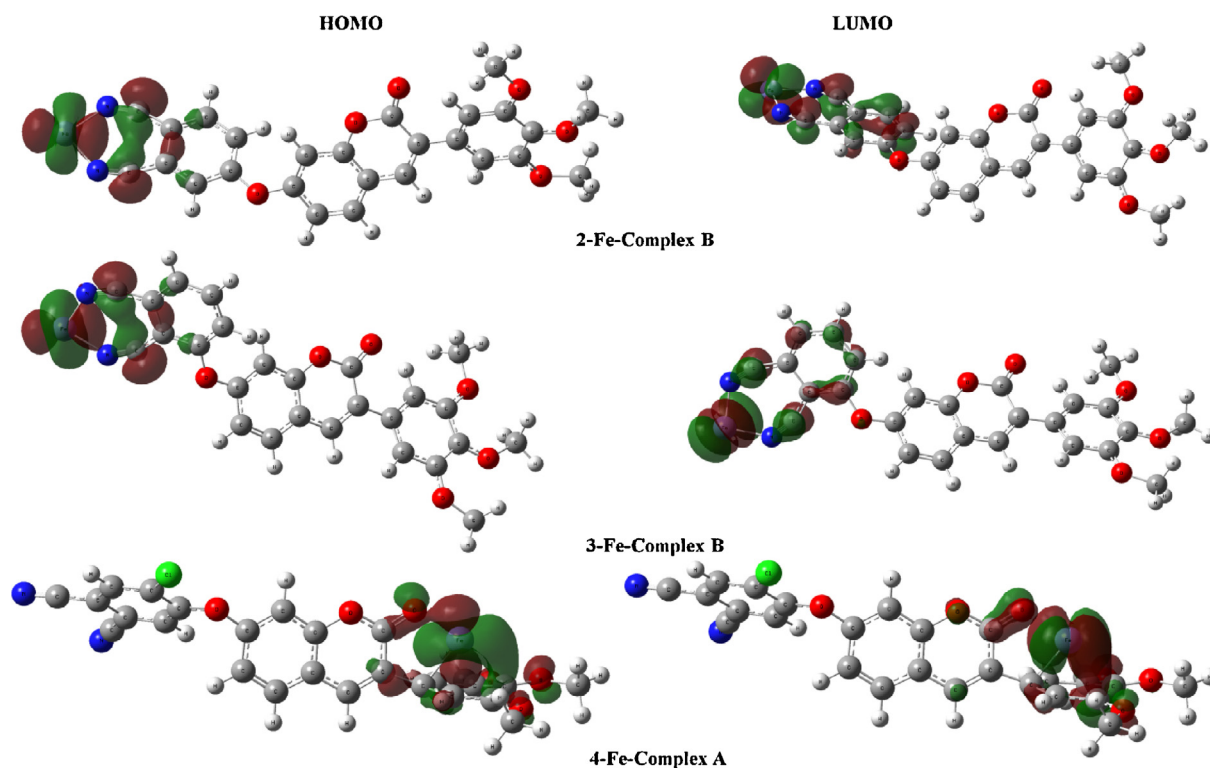


Fig. 11. HOMO and LUMO of the most plausible iron(III) complex structures of the compounds **2–4** calculated with UB3LYP/6-31G(d).

(by 9.04 and 21.67 kcal/mol, respectively). On the contrary, for the compound **4**, it is found to be that the 4-Fe-complex A structure including Fe– π orbitals (1.99 Å) and Fe–O=C (1.94 Å) interactions is slightly more stable than one involving Fe–NC interactions (1.94 and 1.97 Å) (4-Fe-complex-B) by only 0.31 kcal/mol. This can be due to effect of electronegative chlorine atom on the phthalonitril benzene moiety in the structure.

4. Conclusions

In conclusion, the new 7-oxy-3-(3,4,5-trimethoxyphenyl) coumarin substituted phthalonitrile derivatives (**2**, **3**, **4** and **5**) were designed and synthesized for the first time. The newly synthesized compounds (**2**, **3**, **4** and **5**) were characterized by different spectroscopic methods including mass, UV–vis, FT-IR, $^1\text{H-NMR}$ and elemental analysis as well. The fluorescence behaviors of the synthesized compounds have been investigated and intense emission bands were observed at approximately 480 nm. A significant decrease in the fluorescence emission by the addition of the Fe^{3+} cation solution has been observed. The newly synthesized coumarin substituted phthalonitrile derivatives showed highly selectivity toward Fe^{3+} ions and these compounds have the potential to use as chemosensors for this metal ions in solution. Iron(III) complex structures of the synthesized compounds were enlightened using UB3LYP/6-31G(d) computations and it was seen that Fe^{3+} ion prefers binding π orbitals of trimethoxy-substituted benzene ring in the compounds **1** and **4** while it prefers binding CN groups for the compounds **2** and **3**. We anticipate that the experimental results of this study should find utility in the future design of metal-ion sensors for a variety of chemical and biological applications.

Acknowledgments

We thank TUBITAK ULAKBIM, High Performance and Grid Computing Center (TR-Grid e-Infrastructure) for the calculations reported in the theoretical part of this paper.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.12.044>.

References

- [1] A.A. Esenpinar, H. Çakıcı, M. Bulut, Synthesis and characterization of novel phthalocyanines bearing quaternizable coumarin, *Polyhedron* 27 (2008) 3625–3630.
- [2] M. Çamur, A.A. Esenpinar, A.R. Özkaya, M. Bulut, Synthesis, characterization, spectroscopic and electrochemical properties of phthalocyanines substituted with four 3-ferrocenyl-7-oxycoumarin moieties, *J. Organomet. Chem.* 696 (2011) 1868–1873.
- [3] A.A. Esenpinar, M. Bulut, Synthesis and characterization of novel α - or β -tetra[6,7-dihexyloxy-3-(4-oxophenyl)coumarin]-substituted metal-free and metallo phthalocyanines, *Polyhedron* 28 (2009) 3129–3137.
- [4] A.R. Jagtap, V.S. Satam, R.N. Rajule, V.R. Kanetkar, Synthesis of highly fluorescent coumarinyl chalcones derived from 8-acetyl-1,4-diethyl 1,2,3,4-tetrahydro-7H-pyrano[2,3-g]quinoxalin-7-one and their spectral characteristics, *Dyes Pigm.* 91 (2011) 20–25.
- [5] A. Parvez, J. Meshram, V. Tiwari, J. Sheik, R. Dongre, M.H. Youssoufi, T. Ben Hadda, Pharmacophores modeling in terms of prediction of theoretical physico-chemical properties and verification by experimental correlations of novel coumarin derivatives produced via Betti's protocol, *Eur. J. Med. Chem.* 45 (2010) 4370–4378.
- [6] H. Ikeda, A. Ueno, Fluorescent α -cyclodextrin as a chemosensor for halomethanes, *Chem. Commun.* 28 (2009) 4281–4283.
- [7] C.J. Chang, E.M. Nolan, J. Jaworski, S.C. Burdette, M. Sheng, S.J. Lippard, Bright Fluorescent chemosensor platforms for imaging endogenous pools of neuronal zinc, *Chem. Biol.* 11 (2004) 203–210.

- [8] L. Wang, H. Li, D. Cao, A new photoresponsive coumarin-derived Schiff base: chemosensor selectively for Al^{3+} and Fe^{3+} and fluorescence turn-on under room light, *Sens. Actuators, B* 181 (2013) 749–755.
- [9] H. Kim, M. Lee, H.J. Kim, J.S. Kim, J. Yoon, A new trend in rhodamine-based chemosensors: application of spirolactam ring-opening to sensing ions, *Chem. Soc. Rev.* 37 (2008) 1465–1472.
- [10] X. Chen, H. Hong, R. Han, D. Zhang, Y. Ye, Y. Zhao, A new bis(rhodamine) based fluorescent chemosensor for Fe^{3+} , *J. Fluoresc.* 22 (2012) 789–794.
- [11] S. Devaraj, Y. Tsui, C. Chiang, Y. Yen, A new dual functional sensor: highly selective colorimetric chemosensor for Fe^{3+} and fluorescent sensor for Mg^{2+} , *Spectrochim. Acta, Part A* 96 (2012) 594–599.
- [12] J.G. Young, W. Onyebuagu, Synthesis and characterization of di-disubstituted phthalocyanines, *J. Org. Chem.* 55 (1990) 2155–2159.
- [13] R.D. George, A.W. Snow, Synthesis of 3-nitrophthalonitrile and tetra- α -substituted phthalocyanines, *J. Heterocycl. Chem.* 32 (1995) 495–498.
- [14] D. Wöhrle, M. Eskes, K. Shigehara, A. Yamada, A simple synthesis of 4,5-disubstituted 1,2-dicyanobenzenes and 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines, *Synthesis* 2 (1993) 194–196.
- [15] Bruker, SADABS, Bruker AXS Inc., Madison, WI, 2005.
- [16] Bruker, APEX2, Bruker AXS Inc., Madison, WI, 2008.
- [17] G.M. Sheldrick, A short history of SHELX, *Acta Crystallogr. A* 64 (2008) 112–122.
- [18] A.L. Spek, Structure validation in chemical crystallography, *Acta Crystallogr. D* 65 (2009) 148–155.
- [19] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, Mercury CSD 2.0—new features for the visualization and investigation of crystal structures, *J. Appl. Crystallogr.* 41 (2008) 466–470.
- [20] K. Brandenburg, DIAMOND 3.1 for Windows, Crystal Impact GbR, Bonn, Germany, 2006.
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [22] M. Çamur, M. Bulut, The synthesis and characterization of novel soluble phthalocyanines substituted with 7-octyloxy-3-(4-oxophenyl)coumarin moieties, *Dyes Pigm.* 77 (2008) 165–170.
- [23] Y. Jiang, W. Chen, W. Lu, Synthesis of 3-arylcoumarins through N-heterocyclic carbene catalyzed condensation and annulation of 2-chloro-2-arylacetaldehydes with salicylaldehydes, *Tetrahedron* 69 (2013) 3669–3676.
- [24] F. Yuksel, S. Tuncel, A.G. Gürek, V. Ahsen, E. Jeanneau, D. Luneau, Bis[(-45-dicyano-N,N'-bis(p-tolylsulfonfyl)-o-phenylenediaminato]bis-[diamminecopper(II)] dihydrate, *Acta Crystallogr. E* 63 (2007) m1380–m1382.
- [25] U. Kumru, F. Dumoulin, E. Jeanneau, F. Yuksel, Y. Cabezas, Y. Zorlu, V. Ahsen, 4,5-, 3,6-, and 3,4,5,6-tert-butylsulfanylphtalonitriles: synthesis and comparative structural and spectroscopic analyses, *Struct. Chem.* 23 (2012) 175–183.
- [26] C.-F. Chang, L.-Y. Yang, S.-W. Chang, Y.-T. Fang, Y.-J. Lee, Total synthesis of demethylweddelolactone and weddelolactone by Cu-mediated/Pd(0)-catalysis and oxidative-cyclization, *Tetrahedron* 64 (2008) 3661–3666.
- [27] H. Jiang, P. Xia, Q. Zhang, 4-(7-Acetoxy-6-methoxy-4-methyl-2-oxo-2H-chromen-3-yl)phenyl acetate, *Acta Crystallogr. E* 64 (2008) o1230.
- [28] B.A. Kamino, Y. Chang, Z. Lu, T.P. Bender, Phthalonitrile based fluorophores as fluorescent dopant emitters in deep-blue OLEDs: approaching the NTSC standard for blue, *Org. Electron.* 13 (2012) 1479–1485.
- [29] B.N. Ahmed, P. Ghosh, Selective colorimetric and fluorometric sensing of Cu(II) by iminocoumarin derivative in aqueous buffer, *Dalton Trans.* 40 (2011) 6411–6419.
- [30] O. Garcia-Beltran, N. Mena, L.C. Friedrich, J.C. Netto-Ferrera, V. Vargasa, F.H. Quina, M.T. Nunez, B.K. Cassels, Design and synthesis of a new coumarin-based 'turn-on' fluorescent probe selective for Cu^{2+} , *Tetrahedron Lett.* 53 (2012) 5280–5283.

Biographies

Esra Nur Kaya received the BSc and MSc degree from Department of Chemistry of Marmara University, Turkey. Her research interests are the synthesis and characterization of coumarin, phthalocyanines and the investigation of their photophysical and photochemical properties.

Fatma Yuksel BSc, MSc, PhD is an Associated Professor at Chemistry Department, Gebze Institute of Technology, Turkey. Her research interests are the synthesis, characterization, and single crystal structure determination of novel compounds for the purpose of investigation of sensor, liquid crystal, photophysical and magnetic properties. Especially the phthalocyanines, Schiff bases, vic-dioximes, and their metal complexes are in the focus of her interest.

Gül Altınbaş Özpınar BSc, MSc, PhD is an assistant professor at Department of Chemistry Technology of Biga Vocational school at Çanakkale Onsekiz Mart University, Turkey. Her research interests are computational chemistry, modeling of organic reaction mechanisms and inorganic complex structures, investigation of structural, electronic, energetic and spectroscopic properties of organic and inorganic compounds.

Mustafa Bulut BSc and MSc (at the Chemistry Department of Cologne University, Germany), PhD (at the Physiologische Chemie, University of Bonn, Germany) is a Professor at the Chemistry Department of Science and Letters faculty of Marmara

University, Istanbul/Turkey. His research interest lies in the synthesis of flavonoids-crown ethers and phthalocyanines with coumarin functional groups.

Mahmut Durmuş BSc, MSc, PhD is an Associated Professor at Gebze Institute of Technology, Department of Chemistry in Turkey. His research interests are the design, synthesis and characterization of advanced materials such as phthalocyanines, borondipyrromethenes (BODIPY), coumarins and phosphazenes for different applications including photodynamic therapy (PDT) of cancer, liquid crystals, energy transfer dyes, chemosensorsetc.