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Novel coumarin fluorescent dyes: Synthesis, structural characterization and recognition behavior towards Cu(II) and Ni(II)

Hongqi Li*, Li Cai, Jinxing Li, Yixin Hu, Pingping Zhou, Jiming Zhang

Key Laboratory of Science & Technology of Eco-Textile, Ministry of Education, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China

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ABSTRACT

A series of novel coumarin dyes (**3**–**12**) were designed and synthesized. The structures of the dyes were characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, MS and single crystal X-ray diffraction. 3-(2-Benzoylhydrazonotrifluoroethyl)-7-(*N*,*N*-diethylamino)coumarin (**11**) could recognize Cu^{2+} and Ni^{2+} selectively in aqueous solution. Upon addition of Cu^{2+} or Ni^{2+} to **11** a blue shift or a bathochromatic shift of the absorption band was observed while the emission band blue-shifted with decrease in the fluorescence intensity. Upon addition of Cu^{2+} the color of the solution of **11** changed from orange to red. The results showed that **11** could be used as an optical chemosensor of Cu^{2+} and Ni^{2+}.

1. Introduction

Coumarins have been widely used in the fields of biology, medicine, perfumes, cosmetics, and fluorescent dyes [1–3]. The structure of benzopyrone has many advantages including high fluorescence quantum yield, large Stokes shift, excellent light stability, and low toxicity [4–6]. Coumarin derivatives have been used as fluorescent probes of pH [7,8], for detection of nitric oxide [9], nitroxide [10], and hydrogen peroxide [11,12]. Moreover, coumarin derivatives have served as good chemosensors of anions including cyanide [13–16], fluoride [17], pyrophosphate [18], acetate, benzoate, and dihydrogenphosphate [19] as well as various metal ions comprised of Cu(II) [20–22], Zn(II) [23,24], Ni(II) [25], Hg(II) [26–28], Pb(II) [29], Mg(II) [30], Fe(III) [31], and Ag(I) [32,33]. Several systems containing coumarin exhibited simultaneous sensitivity towards two or three different metal ions, e.g. Ca(II) and Mg(II) [34], Ni(II) and Co(II) [35], Cu(II) and Hg(II) [36], Cu(II)/Ni(II)/Cd(II) [37], Zn(II)/Cd(II)/Pb(II) [38], or Ni(II)/Pd(II)/Ag(I) [39].

In continuation to our interest in study on fluorescent coumarin dyes [40], we have designed and synthesized a series of novel coumarin dyes. Herein we report the synthesis, structural characterization and recognition behavior towards metal ions of the dyes.

2. Experimental section

2.1. Materials and instruments

All chemicals and solvents employed in this study were of analytical grade and were used as received unless other statements. Benzoylhydrazine and 4,4,4-trifluoroacetoacetate were obtained from Bangcheng Chemicals Co. Ltd (China). Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. Melting points were determined on a WRS-2A capillary melting apparatus and the quoted temperatures were uncorrected. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AM 400 spectrometer. $CDCl_3$ was used as solvent and chemical shifts recorded were internally referenced to Me_4Si (0 ppm). IR spectra were obtained on a Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. Mass spectra were obtained on an Agilent 6000 LC–MS instrument (ESI, pos mode, 70–1000 amu). Fluorescence spectra were recorded on a Hitachi F-4500 spectrofluorometer. UV–Vis spectra were recorded on a JASCO V530 spectrometer. X-Ray crystal strcture was measured on a Bruker Smart CCD diffractometer by using Mo K_{α} radiation at 293 K.

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* Corresponding author. Tel.: +86 21 67792594; fax: +86 21 67792608.
E-mail address: hongqili@dhu.edu.cn (H. Li).

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2.2. Synthesis of compound **1**

A mixture of 4-diethylaminosalicylaldehyde (1.93 g, 10 mmol), ethyl trifluoroacetoacetate (2.02 g, 11 mmol) and piperidine (4 mg, 0.05 mmol) in EtOH (50 mL) was refluxed for 5 h. After evaporation to remove solvent, the resulted solid was washed with water and purified by column chromatography on silica gel (petroleum ether/ ethyl acetate, 70:1, v/v) to give **1a** (3.3 g, 92%) as lemon yellow solid. Mp 92–93 °C. IR (KBr): 3442, 2982, 1673, 1605, 1524, 1222, 1197, 1174, 1099 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.19 (*t*, 6H, J = 7.2 Hz, CH$_3$), 1.37 (*t*, 3H, J = 7.2 Hz, CH$_3$), 3.32–3.44 (*m*, 4H, CH$_2$), 4.32 (*q*, 2H, J = 7.2 Hz, CH$_2$), 6.27 (*s*, 1H, CH), 6.30 (*d*, 1H, J = 2.4 Hz, CH), 7.04 (*d*, 1H, J = 8.4 Hz, CH), 7.70 (*s*, 1H, CH), 7.73 (*s*, 1H, OH). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.57 (CH$_3$), 14.19 (CH$_3$), 44.77 (NCH$_2$), 61.51 (OCH$_2$), 95.61 (Ph–C), 95.95 (Ph–C), 97.32 (Ph–C), 106.10 (Ph–C), 106.35 (Ph–C), 106.73 (Ph–C), 131.10 (CF$_3$), 140.01 (Ph–C), 152.64 (=C–N), 155.10 (C–OH), 167.65 (C=O); ^{19}F NMR (376 MHz, CDCl$_3$): δ = −87.40 (*s*, 3F, CF$_3$). MS (ESI): m/z 360.2 (M$^+$ + 1).

Compound **1b** was obtained by the above-mentioned procedure as colorless block crystal in 82% yield. Mp: 87–89 °C. IR (KBr) ν = 3447, 1684, 1625, 1572, 1454, 1184, 1168, 1155, 1090, 1020 cm^{-1}; MS (ESI): m/z 311.1 (M$^+$ + 23).

2.3. Synthesis of compound **2**

A mixture of chromene **1a** (1.80 g, 5 mmol) and TsOH·H$_2$O (10 mg, 0.05 mmol) in chlorobenzene (50 mL) was refluxed for 4 h. After evaporation to remove solvent, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 20:1, v/v) to give **2a** (1.42 g, 91%) as yellow solid. Mp 125–127 °C. IR (KBr): 3435, 2986, 1736, 1675, 1619, 1566, 1152, 1176, 1136, 1082 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.26 (*t*, 6H, J = 7.2 Hz, CH$_3$), 3.50 (*q*, 4H, J = 7.2 Hz, CH$_2$), 6.47 (*d*, 1H, J = 2.4 Hz, CH), 6.66 (dd, 1H, J = 2.4 and 9.2 Hz, CH), 7.41 (*d*, 1H, J = 9.2 Hz, CH), 8.38 (*s*, 1H, CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.47 (CH$_3$), 45.48 (CH$_2$), 96.80 (Ph–C), 108.02 (Ph–C), 109.37 (Ph–C), 110.52 (Ph–C), 132.65 (CF$_3$), 150.56 (Ph–C), 150.58 (Ph–C), 154.54 (Ph–C), 157.37 (=C–N), 159.31 (OC=O), 178.47 (C=O). ^{19}F NMR (376 MHz, CDCl$_3$): δ = −72.47 (*s*, 3F, CF$_3$). MS (ESI): m/z 314.1 (M$^+$ + 1).

Compound **2b** was obtained similarly as pale grayish yellow solid in 88% yield. Mp: 95–96 °C. IR (KBr) ν = 3447, 1684, 1647, 1568, 1454, 1184, 1168, 1152, 1017 cm^{-1}; MS (ESI): m/z 243.1 (M$^+$ + 1).

2.4. General synthesis of the target compounds (3–10)

Phenylhydrazine hydrochloride compound (1 mmol), compound **2a** (1 mmol) and TsOH·H$_2$O (1 mg, 0.005 mmol) were mixed in chlorobenzene (20 mL) and then heated to reflux. Reactions were usually completed within 0.5–4 h. The solvent was removed by evaporation and the residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate, 10:1, v/v).

2.4.1. 3-(2-Nitrophenylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (**3**)

Obtained as brick red acicular crystal from **2a** and 2-nitrophenylhydrazine hydrochloride in 92% yield. Mp: 144–146 °C. IR (KBr) ν = 3318, 3093, 2987, 2940, 2912, 1742, 1610, 1584, 1450, 1500, 1333, 1197, 1174, 1099, 1146, 1047 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.26 (*t*, 6H, CH$_3$, J = 7.2 Hz), 3.48 (*q*, 4H, CH$_2$, J = 7.2 Hz), 6.56 (*d*, 1H, CH, J = 2.4 Hz), 6.67 (dd, 1H, CH, J = 2.4 and 8.8 Hz), 6.96–6.99 (*m*, 1H, CH), 7.35 (*d*, 1H, CH, J = 8.8 Hz), 7.61 (*m*, 1H, CH), 7.83 (*s*, 1H, CH), 7.97–8.00 (*m*, 1H, CH), 8.14–8.16 (*m*, 1H, CH), 11.07 (*s*, 1H, NH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 12.47 (CH$_3$), 45.17 (CH$_2$), 97.34 (Ph–C), 106.05 (Ph–C), 107.37 (Ph–C), 109.73 (Ph–C), 116.60 (Ph–C), 120.47 (Ph–C), 121.39 (*q*, CF$_3$, J = 263.7 Hz), 125.81 (Ph–C), 130.31 (Ph–C), 132.94 (Ph–C), 136.15 (Ph–C), 140.36 (Ph–C), 146.70 (=C–NH), 152.51 (=C–N), 154.76 (*q*, C=N, J = 31 Hz), 157.69 (=C–O), 158.15 (O–C=O). ^{19}F NMR (376 MHz, CDCl$_3$): δ = −66.13 (*s*, 3F, CF$_3$). MS (ESI): m/z 449.2 (M$^+$ + 1).

2.4.2. 3-(4-Methoxyphenylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (**4**)

Obtained as orange–red acicular crystal from **2a** and 4-methoxyphenylhydrazine hydrochloride in 76% yield. Mp: 154–156 °C. IR (KBr) ν = 3367, 2989, 1688, 1582, 1458, 1236, 1142, 1051, 1027 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.25 (*t*, 6H, CH$_3$, J = 7.2 Hz), 3.47 (*q*, 4H, CH$_2$, J = 7.2 Hz), 3.93 (*s*, 3H, OCH$_3$), 6.54 (*d*, 1H, CH, J = 2.4 Hz), 6.66 (dd, 1H, CH, J = 2.4 and 8.8 Hz), 6.84 (dd, 2H, CH, J = 2.0 and 6.8 Hz), 7.09 (dd, 2H, CH, J = 2.0 and 6.8 Hz), 7.35 (d, 1H, CH, J = 8.8 Hz), 7.82 (*s*, 1H, CH), 8.27 (*s*, 1H, NH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 12.41 (CH$_3$), 45.10 (CH$_2$), 55.63 (OCH$_3$), 96.94 (Ph–C), 107.71 (Ph–C), 109.86 (Ph–C), 114.58 (Ph–C), 115.27 (Ph–C), 123.37 (*q*, CF$_3$, J = 266.6 Hz), 128.33 (Ph–C), 130.26 (Ph–C), 137.52 (Ph–C), 146.29 (=C–NH), 152.17 (=C–N), 155.10 (=C–OCH$_3$), 155.86 (*q*, C=N, J = 31.8 Hz), 157.24 (=C–O), 159.51 (O–C=O). ^{19}F NMR (376 MHz, CDCl$_3$): δ = −64.25 (*s*, 3F, CF$_3$). MS (ESI): m/z 434.2 (M$^+$ + 1).

2.4.3. 3-(4-Bromophenylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (**5**)

Obtained as yellow solid from **2a** and 4-bromophenylhydrazine hydrochloride in 92% yield. Mp: 162–164 °C. IR (KBr) ν = 3446, 1736, 1654, 1623, 1560, 1454, 1250, 1184,1135, 1099, 1057 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.26 (*t*, 6H, CH$_3$, J = 7.2 Hz), 3.47 (*q*, 4H, CH$_2$, J = 7.2 Hz), 6.52 (*d*, 1H, CH, J = 2.4 Hz), 6.67 (dd, 1H, CH, J = 2.4 and 8.8 Hz), 7.03–7.06 (*m*, 2H, CH), 7.34–7.38 (*m*, 3H, CH), 7.84 (*s*, 1H, CH), 8.47 (*s*, 1H, NH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 12.42 (CH$_3$), 45.17 (CH$_2$), 96.93 (Ph–C), 107.66 (Ph–C), 110.05 (Ph–C), 115.69 (Ph–C), 120.39 (*q*, CF$_3$, J = 278.7 Hz), 128.56 (Ph–C), 130.44 (Ph–C), 132.06 (Ph–C), 133.26 (Ph–C), 142.76 (=C–NH), 146.43 (=C–N), 152.36 (=C–OCH$_3$), 154.43 (q, C=N, J = 41.7 Hz), 157.31 (=C–O), 159.61 (O–C=O). ^{19}F NMR (376 MHz, CDCl$_3$): δ = −64.44 (*s*, 3F, CF$_3$). MS (ESI): m/z 484.2 (M$^+$ + 1).

2.4.4. 3-(4-Fluorophenylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (**6**)

Obtained as yellow solid from **2a** and 4-fluorophenylhydrazine hydrochloride in 95% yield. Mp: 148–150 °C. IR (KBr) ν = 3446, 2982, 1696, 1624, 1518, 1418, 1294, 1180, 1133, 1094 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.25 (*t*, 6H, CH$_3$, J = 7.2 Hz), 3.47 (*q*, 4H, CH$_2$, J = 7.2 Hz), 6.53 (*d*, 1H, CH, J = 2.0 Hz), 6.67 (dd, 1H, CH, J = 2.0 and 8.8 Hz), 6.96–7.00 (*m*, 2H, CH), 7.09–7.12 (*m*, 2H, CH), 7.36 (*d*, 1H, CH, J = 8.8 Hz), 7.84 (*s*, 1H, CH), 8.40 (*s*, 1H, NH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 12.41 (CH$_3$), 45.13 (CH$_2$), 96.88 (Ph–C), 107.14 (Ph–C), 107.63 (Ph–C), 109.96 (Ph–C), 115.15 (Ph–C), 115.90 (Ph–C), 117.20 (Ph–C), 120.55 (*q*, CF$_3$, J = 271.2 Hz), 123.15 (Ph–C), 129.15 (Ph–C), 130.38 (Ph–C), 139.90 (Ph–C), 146.36 (=C–NH), 152.28 (=C–N), 155.31 (*q*, C=N, J = 40.5 Hz), 157.27 (=C–O), 159.59 (C=O). ^{19}F NMR (376 MHz, CDCl$_3$): δ = −64.37 (*s*, 3F, CF$_3$), −62.76 (*s*, 1F, Ph–F). MS (ESI): m/z 422.2 (M$^+$ + 1).

2.4.5. 3-(4-Methylphenylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (**7**)

Obtained as yellow solid from **2a** and 4-methylphenylhydrazine hydrochloride in 94% yield. Mp: 161–162 °C. IR (KBr) ν = 3446, 1695, 1623, 1518, 1457, 1244, 1178, 1133, 1105 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.25 (*t*, 6H, CH$_3$, J = 7.2 Hz), 2.29 (*s*, 3H, CH$_3$), 3.47 (*q*, 4H, CH$_2$, J = 7.2 Hz), 6.53 (*d*, 1H, CH, J = 2.4 Hz), 6.67 (dd, 1H, CH, J = 2.4 and 8.8 Hz), 7.04 (*d*, 2H, CH, J = 8.6 Hz), 7.08 (*d*, 2H, CH, J = 8.6 Hz), 7.35 (*d*, 1H, CH, J = 8.8 Hz), 7.82 (*s*, 1H, CH), 8.29 (*s*, 1H, NH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 12.41 (CH$_3$), 45.13 (CH$_2$), 96.92

(Ph—C), 107.32 (Ph—C), 107.66 (Ph—C), 109.82 (Ph—C), 114.00 (Ph—C), 123.32 (Ph—C), 126.75 (*q*, CF_3, *J* = 201.9 Hz), 129.68 (Ph—C), 130.27 (Ph—C), 131.37 (Ph—C), 136.36 (Ph—C), 141.22 (Ph—C), 146.34 (=C—NH), 152.16 (=C—N), 154.49 (q, C=N, *J* = 24 Hz), 157.25 (=C—O), 159.46 (C=O). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -64.39$ (*s*, 3F, CF_3). MS (ESI): m/z 418.3 ($M^+ + 1$).

2.4.6. 3-(2-Chlorophenylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (*8*)

Obtained as orange–red columnar crystal from **2a** and 2-chlorophenylhydrazine hydrochloride in 96% yield. Mp: 150–152 °C. IR (KBr) ν = 3446, 1652, 1636, 1558, 1454, 1136, 1127,1102, 1053 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (*t*, 6H, CH_3, *J* = 7.2 Hz), 3.46 (*q*, 4H, CH_2, *J* = 7.2 Hz), 6.54 (*d*, 1H, CH, *J* = 2.4 Hz), 6.66 (dd, 1H, CH, *J* = 2.4 and 8.8 Hz), 6.88–6.90 (*m*, 1H, CH), 7.24–7.27 (*m*, 2H, CH), 7.36 (*d*, 1H, CH, *J* = 8.8 Hz), 7.61–7.63 (*m*, 1H, CH), 8.86 (*s*, 1H, CH), 8.82 (*s*, 1H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.41 (CH_3), 45.11 (CH_2), 96.99 (Ph—C), 106.73 (Ph—C), 107.56 (Ph—C), 109.94 (Ph—C), 115.19 (Ph—C), 118.84 (Ph—C), 120.28 (*q*, CF_3, *J* = 283.6 Hz), 122.03 (Ph—C), 127.85 (Ph—C), 128.10 (*q*, C=N, *J* = 34.4 Hz), 129.14 (Ph—C), 130.42 (Ph—C), 139.71 (Ph—C), 146.33 (=C—NH), 152.40 (=C—N), 157.38 (=C—O), 159.07 (C=O). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -64.62$ (*s*, 3F, CF_3). MS (ESI): m/z 438.2 ($M^+ + 1$).

2.4.7. 3-(3-Chlorophenylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (*9*)

Obtained as orange acicular crystal from **2a** and 3-chlorophenylhydrazine hydrochloride in 88% yield. Mp: 186–187 °C. IR (KBr) ν = 3446, 3282, 2974, 2925, 1694, 1598, 1516, 1418, 1244, 1175, 1134, 1060 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (*t*, 6H, CH_3, *J* = 7.2 Hz), 3.48 (*q*, 4H, CH_2, *J* = 7.2 Hz), 4.48 (*s*, 1H, NH), 6.55 (*d*, 1H, CH, *J* = 2.4 Hz), 6.68 (dd, 1H, CH, *J* = 2.4 and 9.2 Hz), 6.90–6.93 (*m*, 1H, CH), 6.97–7.00 (*m*, 1H, CH), 7.16–7.18 (*m*, 1H, CH), 7.20–7.22 (*m*, 1H, CH), 7.37 (*d*, 1H, CH, *J* = 9.2 Hz), 7.85 (*s*, 1H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.41 (CH_3), 45.16 (CH_2), 96.93 (Ph—C), 106.99 (Ph—C), 107.63 (Ph—C), 110.05 (Ph—C), 112.29 (Ph—C), 114.22 (Ph—C), 121.91 (Ph—C), 123.12 (*q*, CF_3, *J* = 102 Hz), 126.76 (*q*, C=N, *J* = 22.8 Hz), 130.18 (Ph—C), 130.45 (Ph—C), 135.10 (Ph—C), 144.80 (Ph—C), 146.41 (=C—NH), 152.38 (=C—N), 157.32 (=C—O), 159.59 (C=O). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -64.41$ (s, 3F, CF_3). MS (ESI): m/z 437.11 (M^+).

2.4.8. 3-(2,4-Dimethylphenylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (*10*)

Obtained as yellow solid from **2a** and 2,4-dimethylphenylhydrazine hydrochloride in 88% yield. Mp: 159–160 °C. IR (KBr) ν = 3448, 1701, 1623, 1521, 1454, 1254, 1160, 1139, 1061 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (*t*, 6H, CH_3, *J* = 7.2 Hz), 2.19 (*s*, 3H, CH_3), 2.23 (*s*, 3H, CH_3), 3.47 (*q*, 4H, CH_2, *J* = 7.2 Hz), 6.55 (*d*, 1H, CH, *J* = 2.4 Hz), 6.68 (dd, 1H, CH, *J* = 2.4 and 8.8 Hz), 6.88 (dd, 1H, CH, *J* = 2.0 and 8.0 Hz), 6.96 (*d*, 1H, CH, *J* = 2.0 Hz), 7.02 (*d*, 1H, CH, *J* = 8.0 Hz), 7.35 (*d*, 1H, CH, *J* = 8.8 Hz), 7.81 (*s*, 1H, CH), 8.23 (*s*, 1H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.41 (CH_3), 19.03 (CH_3), 19.96 (CH_3), 45.10 (CH_2), 96.93 (Ph—C), 107.68 (Ph—C), 109.81 (Ph—C), 111.43 (Ph—C), 115.39 (Ph—C), 123.51 (*q*, CF_3, *J* = 108.5 Hz), 124.07 (Ph—C), 127.74 (Ph—C), 130.25 (Ph—C), 137.45 (Ph—C), 138.82 (Ph—C), 141.46 (Ph—C), 146.35 (=C—NH), 152.14 (=C—N), 155.60 (*q*, C=N, *J* = 24.9 Hz), 157.26 (=C—O), 159.45 (C=O). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -64.33$ (*s*, 3F, CF_3). MS (ESI): m/z 432.3 ($M^+ + 1$).

2.5. Synthesis of 3-(2-benzoylhydrazonotrifluoroethyl)-7-(N,N-diethylamino)coumarin (*11*)

A mixture consisting of **2a** (0.31 g, 1 mmol), benzhydrazide (0.14 g, 1 mmol) and TsOH·H_2O (1 mg, 0.005 mmol) in chlorobenzene (20 mL) was refluxed for 2 h. The solvent was removed by evaporation and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 10:1, v/v) to give **11** (0.42 g, 97%) as golden solid. Mp 148–150 °C. IR (KBr): 3446, 1707, 1654, 1617, 1584, 1450, 1262, 1176, 1135, 1078 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (*t*, 6H, CH_3, *J* = 7.2 Hz), 3.48 (*q*, 4H, CH_2, *J* = 7.2 Hz), 6.55 (*d*, 1H, CH, *J* = 2.4 Hz), 6.70 (dd, 1H, CH, *J* = 2.4 and 9.2 Hz), 7.39 (*d*, 1H, CH, *J* = 9.2 Hz), 7.44–7.46 (*m*, 1H, CH), 7.48 (*s*, 1H, CH), 7.52–7.55 (*m*, 2H, CH), 7.91–7.92 (*m*, 2H, CH), 7.94 (*s*, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.41 (CH_3), 45.25 (CH_2), 96.79–110.51 (Ph—C), 127.20 (CF_3), 128.64–132.41 (Ph—C), 146.97 (C=N), 153.03 (O—C=O), 157.55 (N—C=O). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -64.29$ (*s*, 3F, CF_3). MS (ESI): m/z 432.3 ($M^+ + 1$).

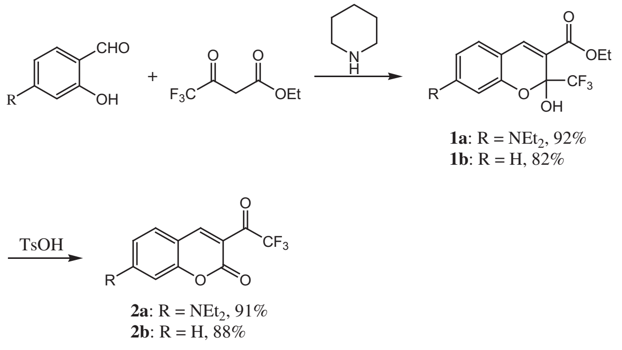
2.6. Synthesis of 3-(2-hydroxyphenyliminotrifluoroethyl)-7-(N,N-diethylamino)coumarin (*12*)

A mixture consisting of **2a** (0.31 g, 1 mmol), 2-aminophenol (0.11 g, 1 mmol) and TsOH·H_2O (1 mg, 0.005 mmol) in chlorobenzene (20 mL) was refluxed for 6 h. The solvent was removed by evaporation and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 10:1, v/v) to give **12** (0.38 g, 94%) as greenish-yellow crystal. Mp: 145–146 °C. IR (KBr) ν = 3446, 2974, 1697, 1620, 1593, 1486, 1250, 1188, 1168, 1082 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20–1.24 (*m*, 6H, CH_3), 3.41–3.46 (*m*, 4H, CH_2), 6.49–6.51 (*m*, 1H, CH), 6.62–6.64 (*m*, 2H, CH), 6.74–6.76 (*m*, 2H, CH), 6.81 (*s*, 1H, CH), 6.82–6.83 (*m*, 1H, CH), 7.35–7.38 (*m*, 1H, CH), 8.06 (*s*, 1H, OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.39 (CH_3), 45.00 (CH_2), 96.83 (Ph—C), 107.77 (Ph—C), 108.28 (Ph—C), 109.65 (Ph—C), 110.16 (Ph—C), 112.17 (Ph—C), 120.33 (Ph—C), 122.45 (Ph—C), 124.03 (*q*, CF_3, *J* = 272.8 Hz), 130.16 (Ph—C), 144.72 (Ph—C), 146.41 (*q*, C=N, *J* = 95.3 Hz), 148.28 (=C—N), 151.95 (=C—O), 156.90 (C—OH), 160.71 (O—C=O). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -84.75$ (s, 3F, CF_3). MS (ESI): m/z 405.2 ($M^+ + 1$).

3. Results and discussion

3.1. Synthesis and structural characterization of coumarins *3*–*12*

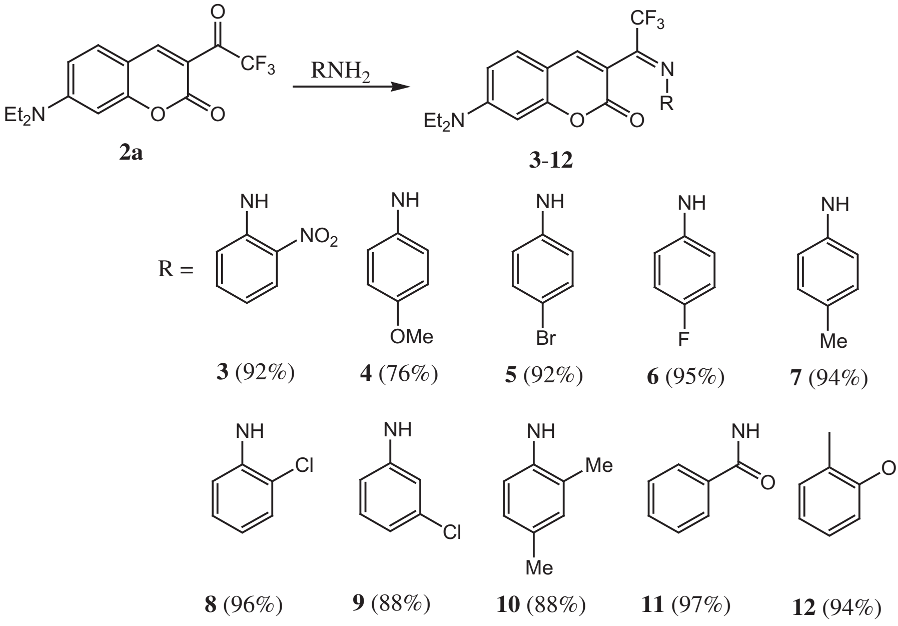
The novel coumarin dyes **3**–**12** were synthesized by a three-step protocol, as shown in Scheme 1 and Scheme 2. Knoevenagel condensation between 4-diethylaminosalicylaldehyde and ethyl trifluoroacetoacetate catalyzed by piperidine (5 mol%) in ethanol for 5 h did not produce trifluoroacetylcoumarin **2a** directly. Instead 2-hydroxyl-2-trifluoromethyl-3-ethoxycarbonyl-7-(*N*,*N*-diethylamino)-2*H*-1-chromene (**1a**) was obtained in 92% yield, which upon treatment with TsOH·H_2O (2 mol%) in chlorobenzene to afford coumarin **2a** in 91% yield. Compound **1b** and **2b** were prepared similarly and the results were in good accordance with



1a: R = NEt_2, 92%
1b: R = H, 82%

2a: R = NEt_2, 91%
2b: R = H, 88%

Scheme 1. Synthesis of coumarins **2**.



Scheme 2. Synthesis of the coumarin dyes **3**–**12**.

those reported in the literature [41]. Finally, the novel coumarin dyes (**3**–**12**) were prepared from coumarin **2a** and compounds containing an amino group with chlorobenzene as the solvent in good to excellent yields.

The chemical structures of coumarin **3**–**12** were fully characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR and mass spectrum. All of the data in the spectra were in good accordance with the structures.

Single crystals of coumarin **3** suitable for X-ray crystal diffraction measurement were obtained by slow evaporation of a solution of **3** in 1:1 petroleum ether and ethyl acetate. X-Ray data for crystals of **3** were collected by graphite-monochromatized Mo K_α radiation at 293 K and the crystal data and experimental details for compound **3** were summarized in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic temperature factors for the non-hydrogen atoms. The hydrogen atoms bonded to the carbon atoms were assigned based on the expected bonding geometry. The hydrogen atoms were refined isotropically in the final least-squares cycles.

Table 1
Crystal data and experimental details for coumarin **3**.

Empirical formula	$C_{21}H_{18}F_3$ N_4O_4
Formula weight	447.39
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2 (1)2 (1)2 (1)
Unit cell dimensions	$a = 7.942$ (4) Å, $\alpha = 90°$
	$b = 12.473$ (6) Å, $\beta = 90°$
	$c = 20.670$ (9) Å, $\gamma = 90°$
Volume	2047.7 (16) Å^3
Z, Calculated density	4, 1.451 mg/m^3
Absorption coefficient	0.120 mm^{-1}
F (000)	924
Crystal size	0.12 × 0.10 × 0.08 mm
Theta range for data collection	2.56–25.00°
Limiting indices	$-9 <= h <= 9$, $-12 <= k <= 14$, $-24 <= l <= 15$
Reflections collected/unique	9627/3615 [R (int) = 0.0746]
Completeness to θ = 26.00	99.9%
Absorption correction	None
Max. and min. transmission	0.9904 and 0.9857
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3615/0/292
Goodness-of-fit on F^2	1.004
Final R indices [I > 2σ (I)]	$R1 = 0.0584$, $wR2 = 0.1132$
R indices (all data)	$R1 = 0.1135$, $wR2 = 0.1386$
Absolute structure parameter	0.8 (14)
Extinction coefficient	0.0070 (13)
Largest diff. peak and hole	0.227 and −0.202 e.Å^{-3}

The crystal structure and molecular packing of coumarin **3** were showed in Fig. 1 and Fig. 2, respectively. It can be seen that the benzopyrone skeleton in the molecule is essentially planar. The molecule adopts a *trans* configuration about both the central C=C olefinic bond and the C=N imine bond. Molecules of compound **3** are packed in a face-to-face arrangement and form a layered stack. CCDC-824461 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

3.2. UV–Vis absorption spectra of the novel compounds

UV–Vis absorption spectra of compounds **1a**, **2a**, **9**, **11** and **12** in EtOH were measured and showed in Fig. 3. The maximum absorption

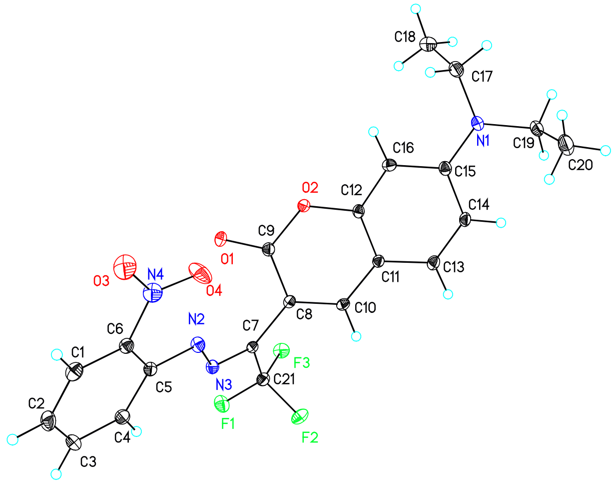


Fig. 1. Crystal structure of compound **3**.

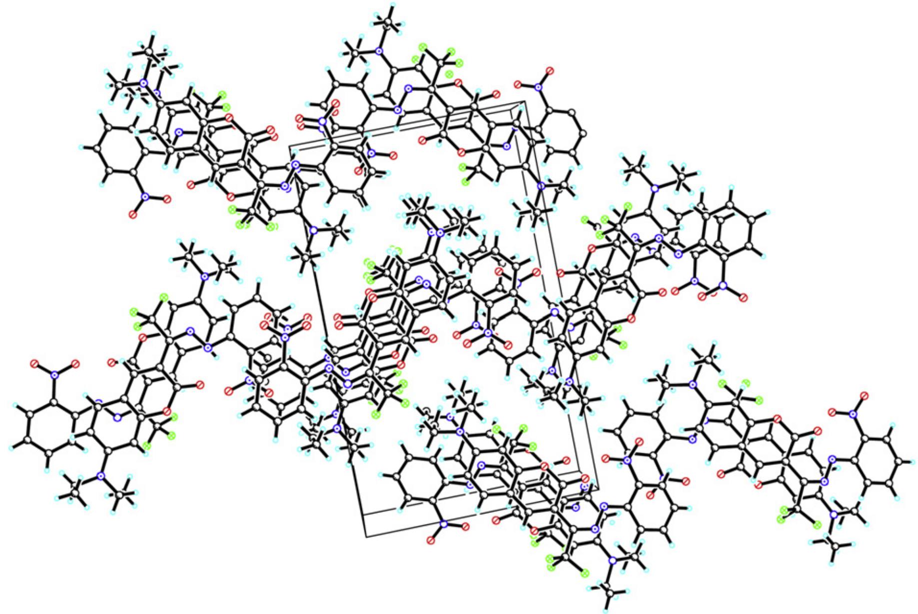


Fig. 2. View of the molecular packing in coumarin **3**.

wavelength of compounds **1a**, **2a**, **9**, **11** and **12** was 392, 398, 405, 413 and 399 nm, respectively. The remarkable bathochromatic shift of the maximum absorption wavelengths of compounds **1a**, **2a**, **9**, **11** and **12** relative to the maximum absorption wavelength at 275 nm of coumarin without substitution was attributed to the formation of the push–pull system based on the electron-donating diethylamino group and the electron-withdrawing trifluoroethyl substituent in the compounds.

3.3. Emission spectra and fluorescence quantum yields of the coumarins

Fluorescence emission spectra of compounds **1a**, **2a**, **9**, **11** and **12** in EtOH were measured at an excitation wavelength of 370 nm and were showed in Fig. 4. It can be found that compound **1a** and **2a** exhibited strong fluorescence intensity while coumarin **9**, **11** and **12** showed relatively weak fluorescence intensity. The fluorescence emission wavelengths of the new compounds were around 460 nm, except for coumarin **11** undergoing a bathochromatic shift to a wavelength of about 490 nm.

For the new compounds **1a**, **2a**, **9**, **11** and **12**, the fluorescence quantum yield, which is defined as the ratio of the number of photons of light emitted from a photoluminescent sample to those absorbed by the sample and can be calculated by the following equation for an unknown sample (Φ_u) was studied.

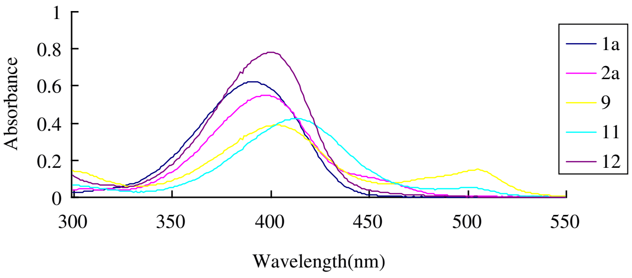


Fig. 3. UV–Vis absorption spectra of **1a**, **2a**, **9**, **11** and **12** in EtOH (20 uM).

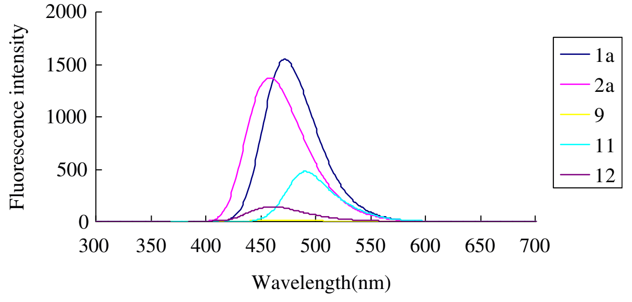


Fig. 4. Emission ($\lambda_{ex} = 370$ nm) spectra of **1a**, **2a**, **9**, **11** and **12** in EtOH (20 uM).

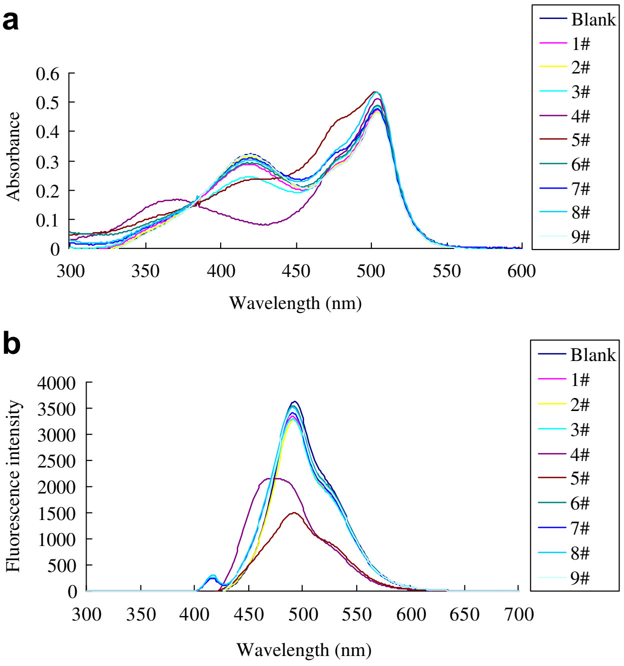


Fig. 5. Absorption (a) and emission ($\lambda_{ex} = 411$ nm) (b) spectra of 11 upon addition of different metal ions (1 equiv to **11**). Experimental conditions: 2×10^{-5} mol/L 11, 0.1 mol/L HEPES buffer in EtOH/H_2O (9:1, v/v), pH = 7.16. 1#: Mg^{2+}; 2#: Zn^{2+}; 3#: Ca^{2+}; 4#: Cu^{2+}; 5#: Ni^{2+}; 6#: Hg^{2+}; 7#: Co^{2+}; 8#: Fe^{3+}; 9#: Al^{3+}.

$$\Phi_u = \Phi_s \cdot \frac{F_u}{F_s} \cdot \frac{A_s}{A_u}$$

wherein A is the absorbance at the excitation wavelength, F is the area under the fluorescence curve and Φ_s is the quantum yield of the standard. Subscripts s and x refer to the standard and sample, respectively. The above data should be obtained under identical conditions. In the study 9,10-diphenylanthracene was chosen as the standard, with its fluorescence quantum yield Φ_s being 1.000. Compound **1a** and **2a** had relatively high fluorescence quantum yield of 0.194 and 0.269, respectively. Among the derivatives of coumarin **2a**, compound **11** afforded a relatively high fluorescence quantum yield of 0.185 while coumarin **9** and **12** showed very low fluorescence quantum yield of 0.009 and 0.023, respectively.

*3.4. Spectroscopic recognition of coumarin **11** towards metal ions*

The recognition behavior of coumarin **11** towards various metal ions was investigated. The fluorescence titration experiments were performed in 0.1 mol/L HEPES buffer solution ($EtOH/H_2O = 9:1$, v/v, pH = 7.16) at an excitation wavelength of 411 nm. The slit of both excitation and emission was 5.0 nm. The changes in the absorption (a) and emission (b) spectra of coumarin **11** upon addition of equal equivalent of different metal ions including Mg^{2+}, Zn^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Hg^{2+}, Co^{2+}, Fe^{3+} and Al^{3+} were showed in Fig. 5.

The maximum absorption wavelength of coumarin **11** was 505 nm and its maximum excitation and emission wavelength were 411 and 492 nm, respectively. The addition of different metal ions induced varied changes in both the absorption and emission spectra of **11**. Addition of Cu^{2+} or Ni^{2+} brought marked changes to both the absorption and emission spectra of **11** while other metal ions did not cause distinct change in the spectra of **11**. Upon addition of Cu^{2+} to **11** the absorption peak blue-shifted from 420 nm to 373 nm and the emission band shifted from 492 nm to 471 nm with decrease in the fluorescence intensity. In the case of Ni^{2+}, upon addition of Ni^{2+} to **11** a bathochromic shift of the absorption peak from 420 nm to 478 nm was observed. Meanwhile the fluorescence intensity decreased drastically. The color of **11** in $EtOH/H_2O$ (9:1, v/v) was orange and after addition of Cu^{2+} the color of the solution changed to red obviously. However, the color of the solution of **11** remained basically unchanged upon addition of other metal ions. These results indicated that coumarin **11** showed effective selectivity for Cu^{2+} and Ni^{2+} over other metal ions including Mg^{2+}, Zn^{2+}, Ca^{2+}, Hg^{2+}, Co^{2+}, Fe^{3+} and Al^{3+}.

In order to further inquire into the spectral characteristics of coumarin **11** upon addition of Cu^{2+} and Ni^{2+}, influences of the amount of Cu^{2+} and Ni^{2+} (0.1–1 equivalent to **L**) on the absorption and emission spectra of **11** were measured and showed in Fig. 6 and Fig. 7, respectively. With the gradual addition of Cu^{2+} to **11**, the absorption band at 420 nm decreased gradually in intensity and a new absorption peak at 373 nm was developed (Fig. 6a).

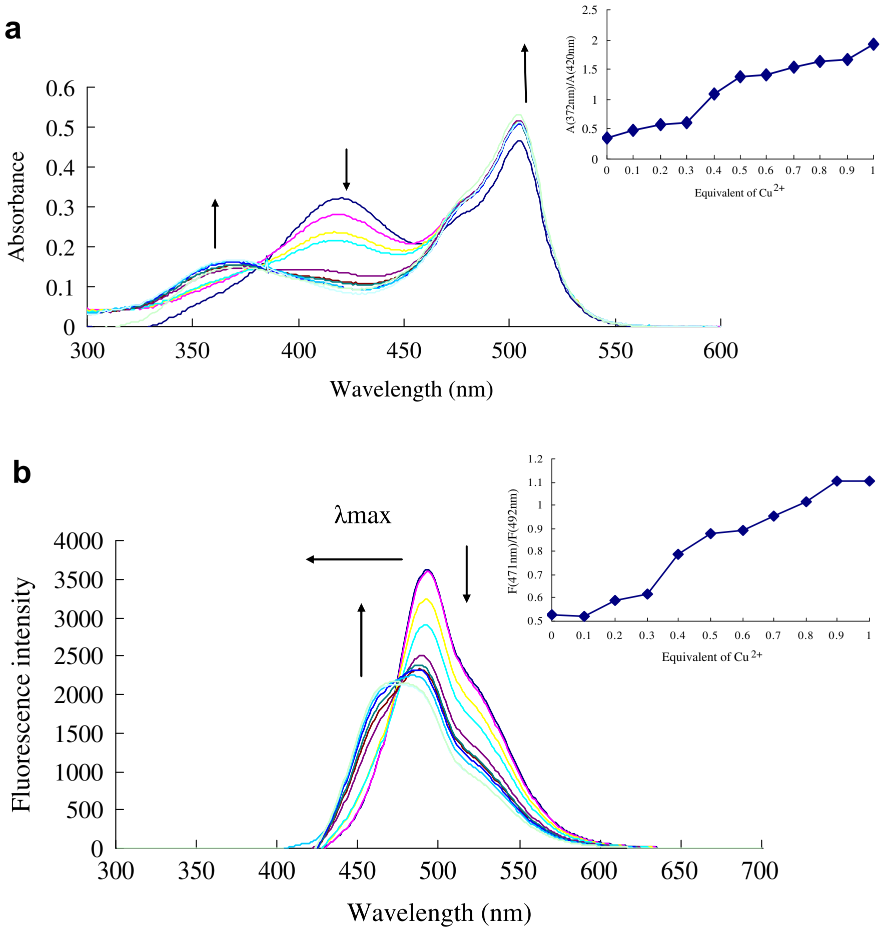


Fig. 6. Absorption (a) (inset: plot of absorbance ratio (372 nm/420 nm) versus equivalent of Cu^{2+}) and emission ($\lambda_{ex} = 411$ nm) (b) (inset: plot of fluorescence intensity ratio (471 nm/492 nm) versus equivalent of Cu^{2+}) spectra of 11 upon addition of Cu^{2+} (0.1–1 equivalent to **11**). Experimental conditions: 2×10^{-5} mol/L 11, 0.1 mol/L HEPES buffer in $EtOH/H_2O$ (9:1, v/v), pH = 7.16.

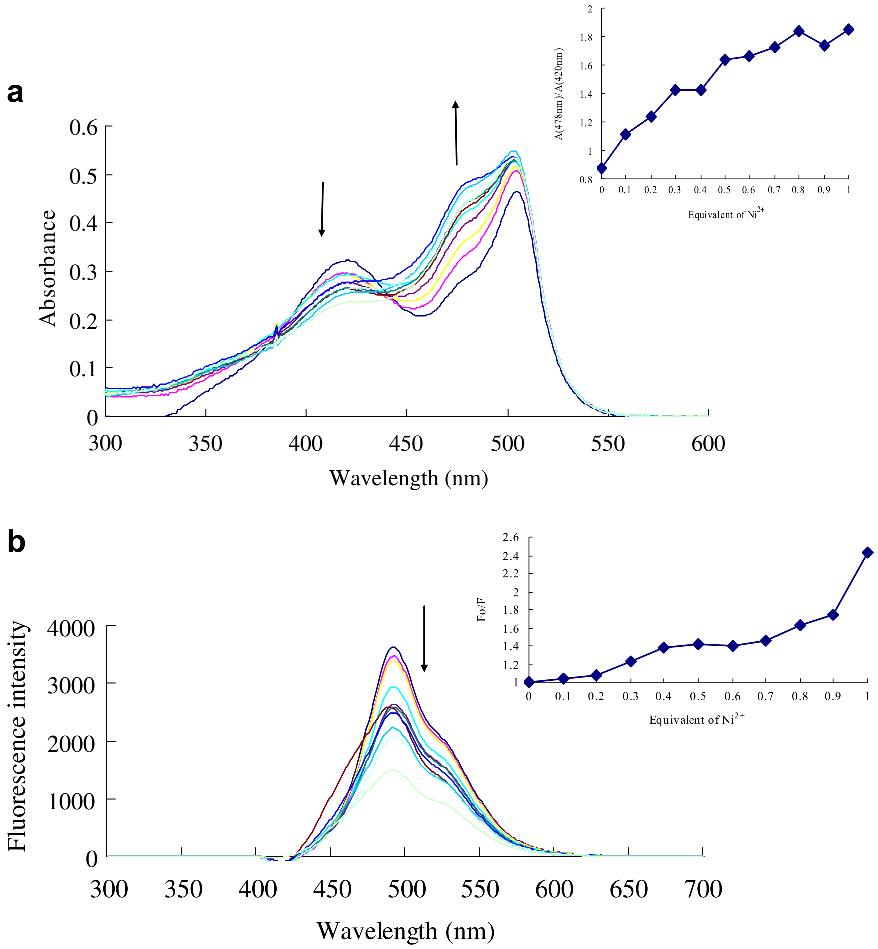


Fig. 7. Absorption (a) (inset: plot of absorbance ratio (478 nm/420 nm) versus equivalent of Ni^{2+}) and emission ($\lambda_{ex} = 411$ nm) (b) (inset: plot of relative fluorescence intensity at 492 nm versus equivalent of Ni^{2+}) spectra of 11 upon addition of Ni^{2+} (0.1–1 equivalent to **11**). Experimental conditions: 2×10^{-5} mol/L 11, 0.1 mol/L HEPES buffer in EtOH/H_2O (9:1, v/v), pH = 7.16.

Meanwhile the maximum emission wavelength shifted from 492 nm to 471 nm gradually (Fig. 6b).

Remarkable influences of Ni^{2+} on the absorption and emission spectra of **11** were also observed, as shown in Fig. 7a and b. The gradual addition of Ni^{2+} to **11** resulted in significant fluorescence quenching and a bathochromatic shift of the absorption peak from 420 nm to 478 nm. The interaction between **11** and Cu^{2+} or Ni^{2+} enhanced the fluorescence quenching and the bonding between **11** and Cu^{2+} or Ni^{2+} and led to the changes in the absorption and emission spectra. Therefore **11** could be used as an optical chemosensor for Cu^{2+} and Ni^{2+} with high sensitivity.

4. Conclusions

A series of novel coumarin dyes (**3**–**12**) were designed and synthesized in high yields by a three-step protocol. 3-(2-Benzoylhydrazono-trifluoroethyl)-7-(*N*,*N*-diethylamino)coumarin (**11**) was found to be able to recognize Cu^{2+} and Ni^{2+} selectively in aqueous solution. Upon addition of Cu^{2+} or Ni^{2+} to **11** a blue shift or a bathochromatic shift of the absorption band was observed while the emission band blue-shifted with decrease in the fluorescence intensity. Upon addition of Cu^{2+}, the color of the solution of **11** changed from orange to red. The results showed that **11** could serve as an optical chemosensor of Cu^{2+} and Ni^{2+}.

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