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Coumarin-Derived Fluorescent Chemosensors

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1. Introduction

Fluorescent chemosensors are highly valuable in a variety of fields including environmental chemistry, analytical chemistry, and bio-medicinal science. They have provided accurate, on-line, and low-cost detection of toxic heavy metal ions, anions, and enzymes with high selectivity and sensitivity. Coumarins, with the structure of benzopyrone, have many advantages including high fluorescence quantum yield, large Stokes shift, excellent light stability, and less toxicity. Therefore coumarins have been widely used in the fields of biology, medicine, perfumes, cosmetics, and fluorescent dyes. By far coumarin derivatives have been used as fluorescent probes of pH, for detection of nitric oxide, nitroxide, and hydrogen peroxide. Moreover, coumarin derivatives have served as good chemosensors of anions including cyanide, fluoride, pyrophosphate, acetate, benzoate, and dihydrogenphosphate as well as various metal ions comprised of Hg(II), Cu(II), Zn(II), Ni(II), Ca(II), Pb(II), Mg(II), Fe(III), Al(III), Cr(III), and Ag(I). Several systems containing coumarin exhibited simultaneous sensitivity toward two or more different metal ions, e.g. Ca(II) and Mg(II), Ni(II) and Co(II), Cu(II) and Hg(II), Na(I) and K(I), Cu(II) and Ni(II), Hg(II) and Ag(I), Cu(II)/Ni(II)/Cd(II), Zn(II)/Cd(II)/Pb(II), or Ni(II)/Pd(II)/Ag(I). Herein a brief review of fluorescent chemical sensors derived from coumarins is presented.

2. Structural characteristics of coumarin

The fusion of a pyrone ring with a benzene ring gives rise to a class of heterocyclic compounds known as benzopyrones, of which two distinct types are recognized, namely benzo-α-pyrones, commonly called coumarins, and benzo-γ-pyrones, called chromones, the latter differing from the former only in the position of the carbonyl group in the heterocyclic ring as shown in Fig. 1 (Sethna & Shah, 1945). It is well known that stilbene with a *trans* conformation is highly fluorescent. From the viewpoint of molecular structure, coumarins bear a carbon-carbon double bond which is fixed as *trans* conformation as in *trans*-stilbene through a lactone structure. This can help to avoid the *trans*-*cis* transformation of the double bond under ultraviolet (UV) irradiation as observed in stilbene compounds and results in strong fluorescence and high fluorescence quantum yield and photostability in most of coumarin derivatives.

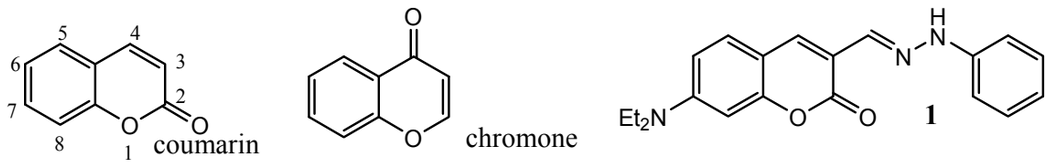


Fig. 1. Structures and numbering scheme of coumarin and related compounds

It was showed in the late 1950s that substitutions on the coumarin structure shifted the fluorescence band. For instance, adding a methyl group to the 4-position of 7-hydroxy- or 7-methoxycoumarin red shifts the fluorescence spectra. Addition of electron-repelling groups in the 4-, 6-, or 7-position or electron-attracting groups in the 3-position all shifts the fluorescence band to longer wavelengths. When the carbonyl is substituted with a thione, the absorbance was red shifted and the fluorescence was quenched (Trenor et al., 2004). The reduction of the acceptor strength of the substituent at the 3-position, as in a 7-diethylaminocoumarin dye **1** (the structure of which is shown in Fig. 1) does not always result in sustained fluorescence in polar, aprotic solvents. Thus 7-diethylamino-3-styrylcoumarin dyes are not technically important as laser dyes; however, the extreme sensitivity of coumarin **1** to the medium polarity could provide an opportunity to probe the microenvironment experienced by the molecule (Bangar Raju & Varadarajan, 1995).

Changing the solvent or the solution pH also affected the fluorescence spectra. Study on the effect of solution pH on 7-hydroxy-4-methylcoumarin showed that increasing the solution pH raised the fluorescence intensity. Studies on the effect of changing the solvent polarity on 13 coumarin derivatives revealed that increasing solvent polarity red shifted the absorbance as well as red shifted and broadened the emission of the coumarins due to increased hydrogen bonding. Studies on the excited-state properties of 4- and 7-substituted coumarin derivatives revealed that solvent polarity shifted both the emission and absorption peaks, with a greater shift observed in the emission spectra, indicating that the excited- state dipole moment of the solute molecule was greater than the ground-state dipole moment (Trenor et al., 2004).

3. Coumarin-derived fluorescent chemosensors

3.1 Coumarin-derived fluorescent chemosensors for metal ions

Considering the threat of mercury to the environment and human health, a great effort has been devoted to the utilization of fluorescent methods for detection of Hg^{2+} ions. More than ten coumarin-derived fluorescent chemosensors for Hg^{2+} ions have been reported. The structures and references of these chemical sensors are listed in Table 1.

The recognition mechanisms of these chemosensors mainly involve photoinduced electron transfer (PET), intramolecular charge transfer (ICT), fluorescence resonance energy transfer (FRET), coordination, and desulfurization. For instance, the fluorescence detection of **2** upon Hg^{2+} addition is promoted by a Hg^{2+}-induced desulfurization of the thiourea moiety, leading to a decrease in an ICT character of the excited-state coumarin moiety (Shiraishi et al., 2010). Coumarin-thiazolobenzo-crown ether based chemosensor **3** has been developed for Hg(II) ions that utilizes the strong coordination of Hg(II) ions on the crown oxygen and thiazole nitrogen. The complexation of Hg(II) disrupts the ICT from the oxygen donor to the

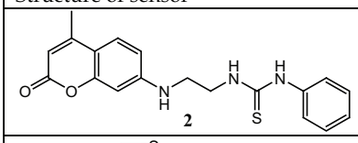
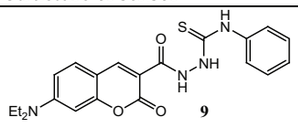
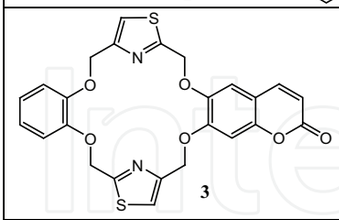
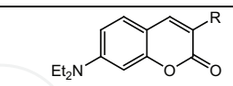
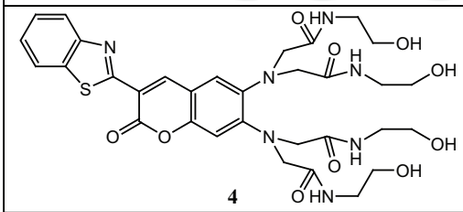
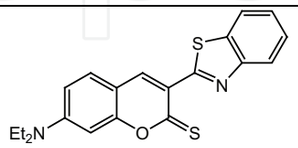
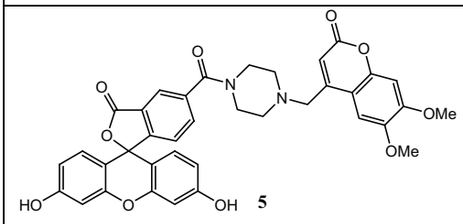
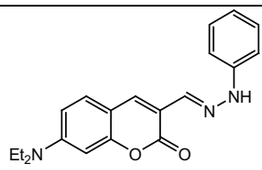
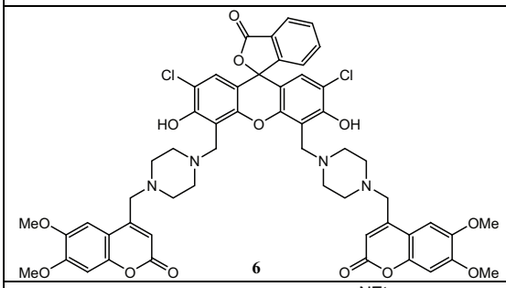
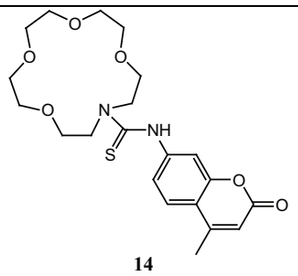
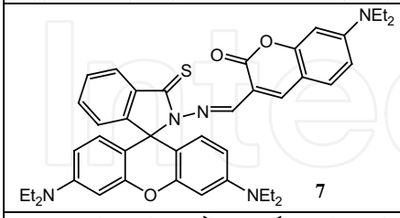
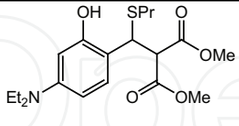
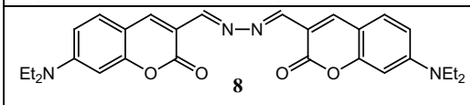
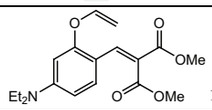
Structure of sensor	Reference	Structure of sensor	Reference
 **2**	Shiraishi et al., 2010	 **9**	W. Ma et al., 2010
 **3**	S. H. Lee et al., 2010	 **10**: R = acetylene  **11**: R = 1,3-dithiane-2-yl 	D.-N. Lee et al., 2009 J. H. Kim et al., 2009
 **4**	Wang et al., 2006	 **12**	M. G. Choi et al., 2009
 **5**	Ryu et al., 2010	 **13**	H. J. Kim et al., 2010
 **6**	H. J. Kim et al., 2009a	 **14**	Voutsadaki et al., 2010
 **7**	Q.-J. Ma et al., 2010	 **15**	Jiang & Wang, 2009
 **8**	R. Sheng et al., 2008	 **16**	Cho & Ahn, 2010

Table 1. Structures and references of coumarin-derived chemosensors for Hg(II) ions

coumarin fluorophore resulting in blue-shift in absorption and quenching of the fluorescence (S. H. Lee et al., 2010). The fluorescent ratiometric Hg^{2+} ion sensor **4**, based on a coumarin platform coupled with a tetraamide receptor, can specifically detect Hg^{2+} ions through the ICT mechanism (Wang et al., 2006). Fluorescein-coumarin chemodosimeter **5** for

signaling Hg^{2+} ions is designed based on FRET arising from the interaction between a pair of fluorophores (Ryu et al., 2010). Rhodamine-coumarin conjugate **7** was developed as a probe for Hg(II) ions. The fluorescence response to Hg(II) ions is attributed to the 1:1 complex formation between probe **7** and Hg^{2+} (Q.-J. Ma et al., 2010). Chemosensor **9** based on the coumarin thiosemicarbazide displays a selective fluorescence enhancement for Hg^{2+}, which is attributed to the transformation of thiosemicarbazide unit to 1,3,4-oxadiazoles via Hg^{2+}-induced desulfurization reaction in aqueous media (W. Ma et al., 2010). Coumarinyldithiane **11** and thiocoumarin **12** selectively sense Hg^{2+} also due to the Hg^{2+}-induced desulfurization reaction. Probe **14** belongs to the turn-on class of sensors, functioning via a PET process (Voutsadaki et al., 2010).

Chemosensors **15** and **16** are not coumarin derivatives but in the presence of Hg(II) ions the weakly fluorescent precursor **15** can be transformed to strongly fluorescent coumarin **17** via a desulfurization-lactonization cascade reaction as shown in Fig. 2 (Jiang & Wang, 2009). Similarly, **16** selectively senses inorganic mercury in the turn-on mode through a Hg(II) ion-promoted hydrolysis-cyclization reaction that leads to coumarin **17** as shown in Fig. 3 (Cho & Ahn, 2010).

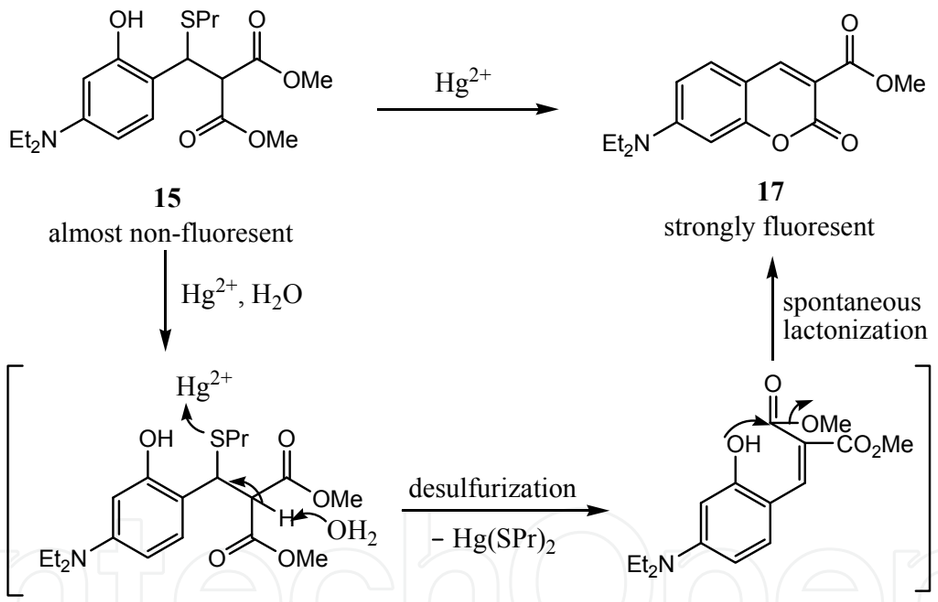


Fig. 2. Transformation of sensor **14** to fluorescent coumarin **16** via Hg(II)-induced desulfurization-lactonization

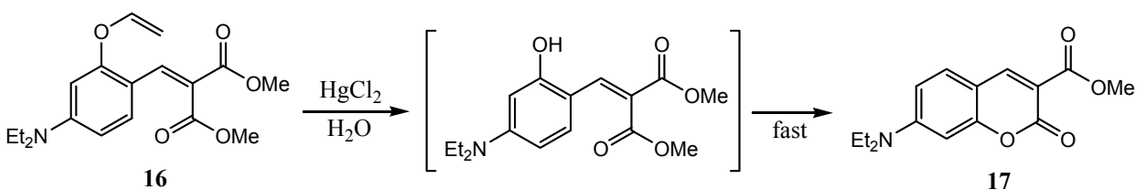


Fig. 3. The reaction of probe **16** with $HgCl_2$

Detection of trace amount of Cu^{2+} is important not only for environmental applications, but also for toxicity determination in living organs. Following the report that a new cavitand bearing four coumarin groups acts as fluorescent chemosensor for Cu^{2+} (Jang et al., 2006), over ten more coumarin-derived fluorescent chemosensors for Cu(II) ions have been envisaged. The structures and references of these chemical sensors are listed in Table 2.

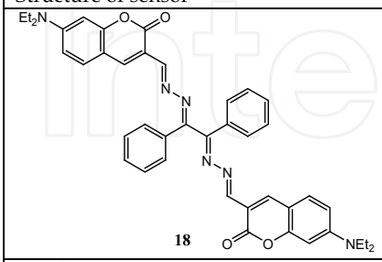
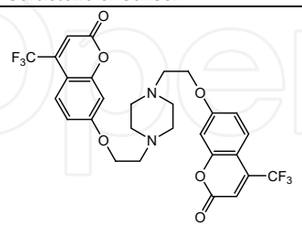
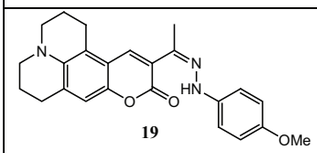
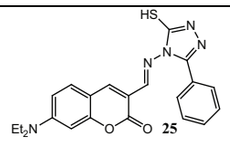
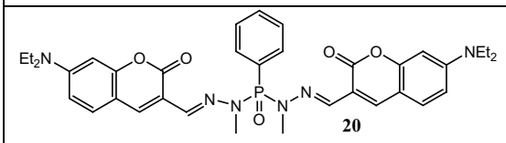
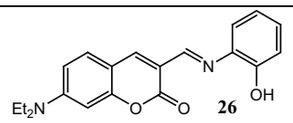
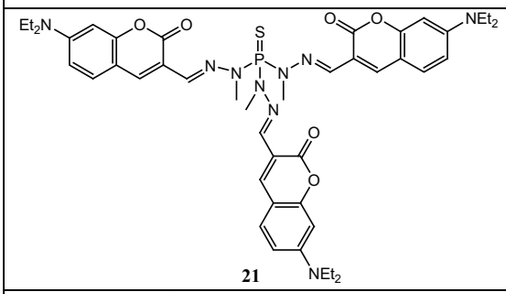
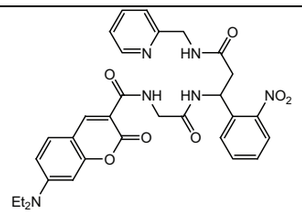
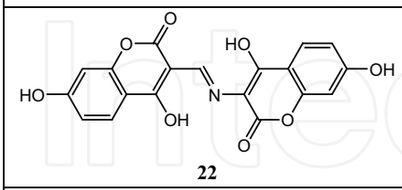
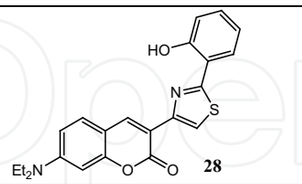
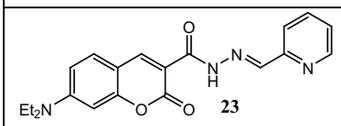
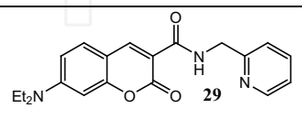
Structure of sensor	Reference	Structure of sensor	Reference
 **18**	G. He et al., 2010a	 **24**	X. Chen et al., 2011
 **19**	M. H. Kim et al., 2009	 **25**	Ko et al., 2011
 **20**	Chandrasekhar et al., 2009	 **26**	N. Li et al., 2010
 **21**	Chandrasekhar et al., 2009	 **27**	Ciesienski et al., 2010
 **22**	J. R. Sheng et al., 2008	 **28**	Helal et al., 2011
 **23**	Zhao et al., 2010	 **29**	Jung et al., 2009

Table 2. Structures and references of coumarin-derived chemosensors for Cu(II) ions

A turn-on fluorescent probe **18** for Cu^{2+} is presented by incorporating coumarin fluorophores within the benzyl dihydrazone moiety. It is among the brightest Cu^{2+} binding sensors in aqueous media reported to date (G. He et al., 2010a). Coumarin **19** is a highly effective turn-on fluorescent sensor that is catalytically hydrolyzed by Cu^{2+} leading to a

large increase in the fluorescence intensity (M. H. Kim et al., 2009). Studies on interaction of phosphorus-supported multidentate coumarin-containing fluorescent sensors **20** and **21** with various transition metal ions reveal substantial fluorescence enhancement upon interaction with Cu^{2+} enabling a selective detection mechanism for Cu^{2+} (Chandrasekhar et al., 2009). Biscoumarin **22** linked by a C=N double bond is highly sensitive and selective to Cu^{2+} and the fluorescent sensing mechanism is based on C=N isomerization (J. R. Sheng et al., 2008). Coumarin probe **23** is highly selective for Cu^{2+} over biologically relevant alkali metals, alkaline earth matals and the first row transition metals due to the formation of a 1:2 complex between Cu^{2+} and **23** (Zhao et al., 2010). Fluorescent biscoumarin **24** linked by a piperazine unit shows high selectivity towards Cu^{2+} (Chen et al., 2011). Rationally designed iminocoumarin fluorescent sensor **25** displays high selectivity for Cu^{2+} over a variety of competing metal ions in aqueous solution with a significant fluorescence increase (Ko et al., 2011). Nonfluorescent coumarin derivative **26** is synthesized as an efficient turn-on fluorescent chemodosimeter for Cu^{2+} in water. Mechanism studies suggest that **26** forms a complex with Cu^{2+} in a 1:2 metal-to-ligand ratio, and a 50-fold fluorescence enhancement is observed when the complex simultaneously undergoes Cu^{2+}-promoted hydrolysis (N. Li et al., 2010). Sensor **27** relies on a coumarin-tagged ligand that selectively binds Cu^{2+} over other biometals to induce fluorescence quenching, which is subsequently relieved upon UV irradiation to provide the turn-on response (Ciesienski et al., 2010). For chemosensor **28** the mechanism of fluorescence is based on ICT, which is modified by the introduction of an electron-donating diethylamino group making it chromogenic and increasing the binding affinity (Helal et al., 2011). Coumarin **29** appending 2-picolylamide enables efficient tridentate complexation for Cu(II) in preference to a variety of other common heavy and toxic metal ions (Jung et al., 2009).

Owing to the important role of zinc, the second most abundant transition metal in the human body, more and more attention has been paid to development of Zn^{2+}-specific chemosensors including coumarin-derived fluorescent chemosensors for Zn(II) ions, the structures and references of which are listed in Table 3.

Study on the sensory capabilities of two novel di(2-picolyl)amine (DPA)-substituted coumarins **30** and **31** shows that the variation of the point of attachment of the DPA group to the coumarin framework controls their sensing behavior: the 4-subsituted system **30** is a chelation-enhanced fluorescence (CHEF)-type sensor which shows a significant increase in fluorescence intensity upon Zn^{2+} binding, whereas the 3-substituted coumarin **31** is a ratiometric sensor (N. C. Lim & Brückner, 2004). Coumarin Schiff-base **32** acts as a turn-on fluorescent chemosensor for Zn(II) ions (H. Li et al., 2009) and **33** does not show any two-photon activity in the wavelength range 760-860 nm but in the presence of Zn(II) **33** exhibits large two-photon absorption as well as emission in the same wavelength range (Ray et al., 2010). Another coumarin Schiff-base **43** is a highly sensitive and selective fluorescent probe for Zn^{2+} in tetrahydrofuran (THF) (Yan et al., 2011). In coumarin Schiff-base **34** the fluorescence quenching is dominant because of the nitrogen lone pair orbital contribution to the excitation. Upon Zn^{2+} coordination **34** shows a significant fluorescence enhancement due to the blocking of the nitrogen lone pair orbital by metal coordination (Jung et al., 2010). A series of coumarin-based fluorescent probes **35-38** for detecting Zn^{2+} with high affinities show the ratiometric fluorescent properties (Mizukami et al., 2009). Another series of coumarin-derived chemosensors **39-42** belong to the CHEF-type and have been showed to

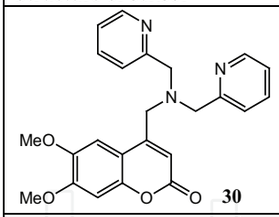
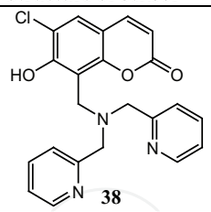
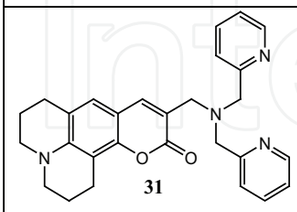
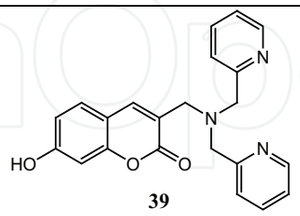
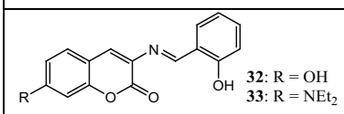
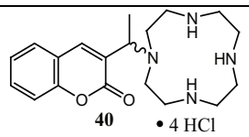
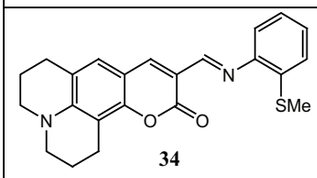
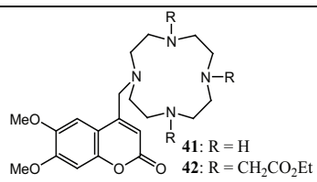
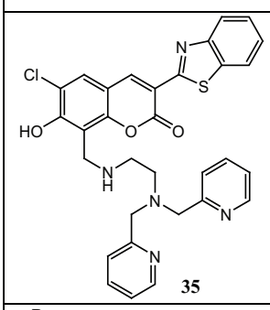
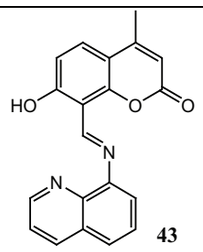
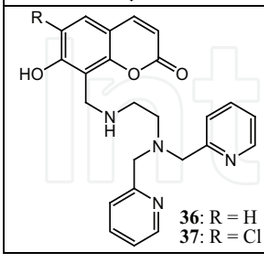
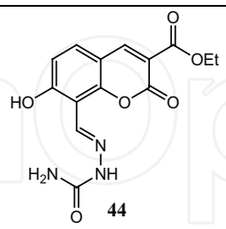
Structure of sensor	Reference	Structure of sensor	Reference
 **30**	N. C. Lim & Brückner, 2004	 **38**	Mizukami et al., 2009
 **31**	N. C. Lim & Brückner, 2004	 **39**	N. C. Lim et al., 2005
 **32**: R = OH **33**: R = NEt_2	H. Li et al., 2009 Ray et al., 2010	 **40** • 4 HCl	N. C. Lim et al., 2005
 **34**	Jung et al., 2010	 **41**: R = H **42**: R = CH_2CO_2Et	N. C. Lim et al., 2005
 **35**	Mizukami et al., 2009	 **43**	Yan et al., 2011
 **36**: R = H **37**: R = Cl	Mizukami et al., 2009	 **44**	Su et al., 2010

Table 3. Structures and references of coumarin-derived chemosensors for Zn(II) ions

be competent for detecting zinc pools in cultured rat pituitary (GH3) and hepatoma (H4IIE) cell lines (N. C. Lim et al., 2005). Coumarin **44** is a fluorescent sensor for Zn^{2+} and exhibits lower background fluorescence due to intramolecular PET but upon mixing with Zn^{2+} in aqueous ethanol, a turn-on fluorescence emission is observed (Su et al., 2010). Recently it was reported that a biscoumarin linked by bi-thiazole acted as a colorimetric receptor selectively for Zn^{2+} (Upadhyay & Mishra, 2010).

Structures of several coumarin-derived fluorescent chemosensors for iron(III) are shown in Fig. 4. Squarate hydroxamate-coumarin conjugate **45** is designed as a CHEF-type sensor for Fe(III). Due to a PET process, **45** possesses a low fluorescence yield but upon exposure of **45** to Fe(III), an irreversible 9-fold fluorescence intensity increase is observed as the result of an oxidation/hydrolysis reaction (N. C. Lim et al., 2009). Coumarin derivative **46** exhibits high selectivity for Fe^{3+} and the selectivity is not affected by the presence of representative alkali metals, alkali earth metals and other transition metal salts (Yao t al., 2009). Mugineic acid-coumarin derivative **47** synthesized by click chemistry acts as a fluorescent probe for Fe^{3+} (Namba et al., 2010). Coumarin-based hexadentate fluorescent probes for selective quantification of iron(III) have also been designed and synthesized (Y. M. Ma & Hider, 2009).

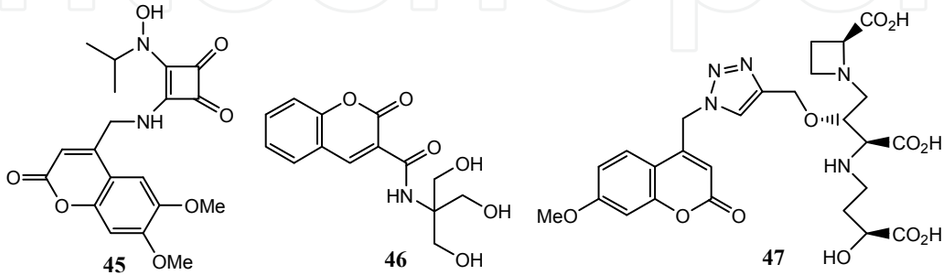


Fig. 4. Structures of coumarin-derived fluorescent chemosensors for iron(III) ion

Structures of coumarin-derived fluorescent chemosensors for Mg(II) are shown in Fig. 5. Coumarin-based two-photon probe **48** is developed for the detection of free Mg^{2+} ions in living cells and living tissues. The probe can be excited by 880 nm laser photons, emits strong two-photon excited fluorescence in response to Mg^{2+} ions (H. M. Kim et al., 2007). Coumarin Schiff-base **49**, without two-photon activity in the wavelength range 760-860 nm, exhibits large two-photon absorption as well as emission in the presence of Mg^{2+} (Ray et al., 2010). Coumarin-based chromoionophore **50** implemented in a transparent membrane can be used as an optical one-shot sensor for Mg^{2+} (Capitán-Vallvey, 2006). Two coumarin salen-based sensors **51** and **52** exhibit a pronounced fluorescence enhancement response toward Mg^{2+} in the presence of Na^{+} as a synergic trigger (Dong et al., 2011). Coumarin-derived fluorescent molecular probes **53** and **54** can be used for highly selective detection of Mg^{2+} versus Ca^{2+} by means of monitoring the absorption and fluorescence spectral change (Suzuki et al., 2002).

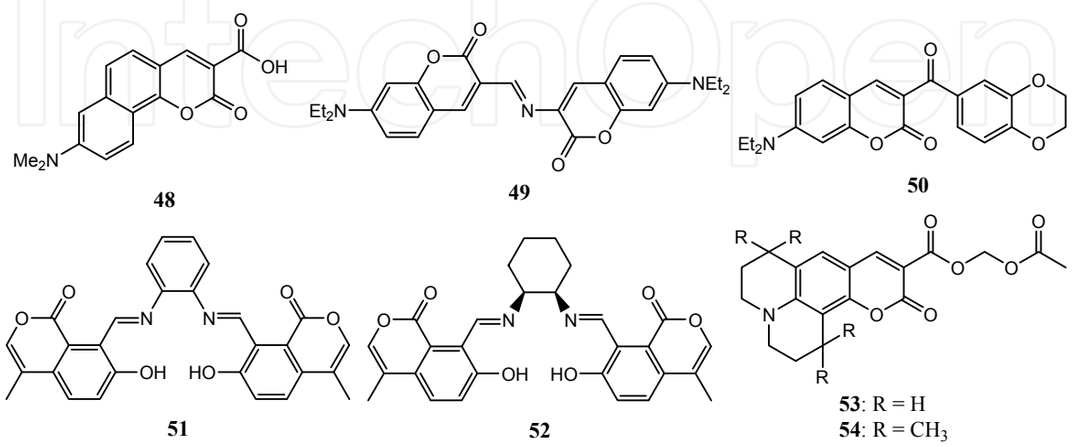


Fig. 5. Structures of coumarin-derived fluorescent chemosensors for Mg(II) ion

Fig. 6 shows the structures of coumarin-derived fluorescent chemosensors for Ag(I). A highly sensitive and selective fluorescent chemosensor **55** for Ag^+ based on a coumarin-Se_2N chelating conjugate is developed. Due to inhibiting a PET quenching pathway, a fluorescent enhancement of 4-fold is observed under the binding of the Ag^+ cation to **55** with a detection limit down to the 10^{-8} M range (S. Huang et al., 2011). Coumarin **56** and **57** are highly silver ion selective fluorescence ionophores (Sakamoto et al., 2010). By a microwave-assisted dual click reaction, fluorogenic 3-azidocoumarin can be rapidly introduced onto a 3,4-dipropargylgluco- or galactosyl scaffold with restored fluorescence. Subsequent desilylation leads to water soluble sugar-bis-triazolocoumarin conjugates which are applicable toward selective Ag^+ detection in aqueous media via fluorescence spectroscopy (X.-P. He et al., 2011).

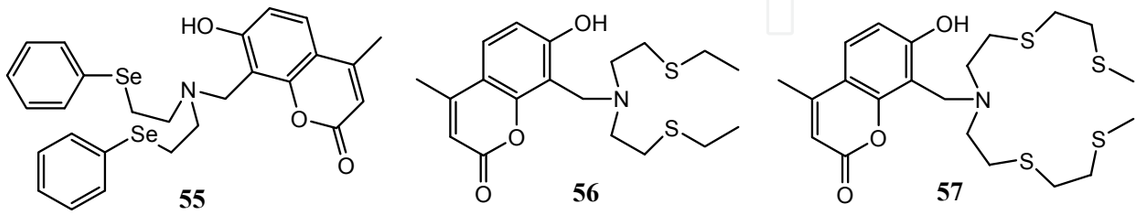


Fig. 6. Structures of coumarin-derived fluorescent chemosensors for silver(I) ion

Structures of coumarin-derived fluorescent chemosensors for lead(II) are shown in Fig. 7. Fluorescent chemosensor **58** based on a coumarin-crown ether conjugate exhibits a high affinity and selectivity for Pb^{2+} (C.-T. Chen & W.-P. Huang, 2002). Coumarin dyes **59**-**61** seem to fulfill most of the criteria required for intracellular lead indicators, as they exhibit high selectivity for Pb^{2+} (Roussakis et al., 2008). Ion competition studies and fluorescence experiments show that a fullerene-coumarin dyad is selective for Pb^{2+} complexation (Pagona et al., 2010).

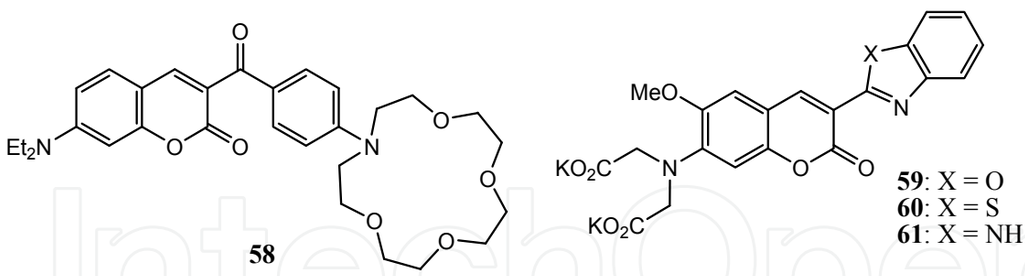


Fig. 7. Structures of coumarin-derived fluorescent chemosensors for lead(II) ion

Apart from the above-mentioned metal ions, coumarin-derived fluorescent chemosensors have been used for detection of other metal ions including Cd^{2+} (Taki et al., 2008), Al^{3+} (Maity & Govindaraju, 2010), and Cr^{3+} (Hu et al., 2011). Some coumarin-derived fluorescent chemosensors exhibit simultaneous sensitivity toward two or more different metal ions, e.g. Cu(II) and Hg(II) based on FRET mechanism (G. He et al., 2010b) or via selective anion-induced demetallation (Lau et al., 2011), Cu^{2+} and Ni^{2+} (H. Li et al., 2011), Ni^{2+} and Zn^{2+} (Chattopadhyay et al., 2006), Ni^{2+} and Co^{2+} (Lin et al., 2009), Ca^{2+} and Mg^{2+} (Suresh & Das, 2009), Na^+ and K^+ (Ast et al., 2011), Hg^{2+} and Ag^+ (Tsukamoto et al., 2011), $Cu^{2+}/Ni^{2+}/Cd^{2+}$ (Lin et al., 2008), $Zn^{2+}/Cd^{2+}/Pb^{2+}$ (Kulatilleke et al., 2006), or $Ni^{2+}/Pd^{2+}/Ag^+$ (Santos et al., 2009).

3.2 Coumarin-derived fluorescent chemosensors for anions

Development of highly efficient chemosensors for cyanide is of extreme significance due to the detrimental aspect of cyanide. Much attention has been paid to the utilization of fluorescent methods for the detection of cyanide. Several coumarin-derived fluorescent chemosensors for CN^- have been reported, the structures of which are shown in Fig. 8.

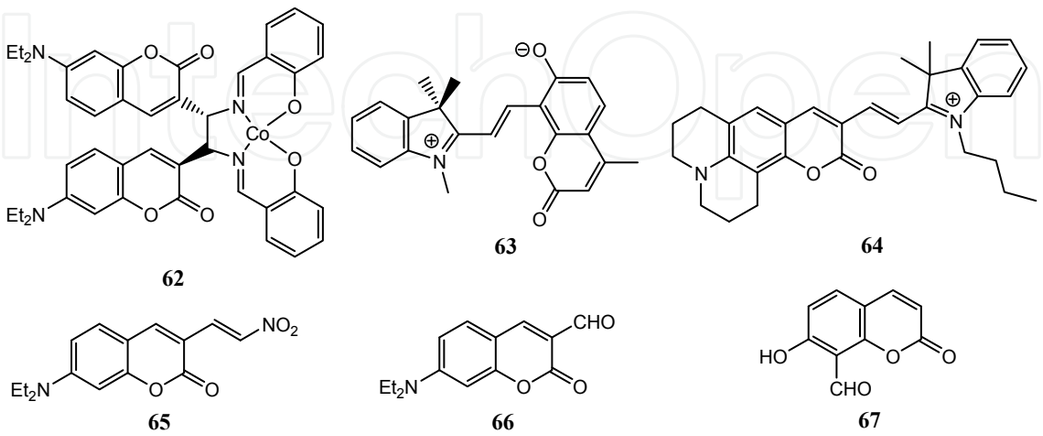


Fig. 8. Structures of coumarin-derived fluorescent chemosensors for cyanide

Cobalt(II)-coumarinylsalen complex **62** exhibits selective and tight binding to a cyanide anion and displays a significant fluorescence enhancement upon the addition of cyanide owing to the interruption of PET from the coumarin fluorophore to the cobalt(II)-salen moiety (J. H. Lee et al., 2010). Coumarin-spiropyran conjugate **63** is a highly sensitive chemosensor for CN^- and shows a CN^--selective fluorescence enhancement under UV irradiation (Shiraishi et al., 2011). An indole conjugated coumarin **64** for KCN chemodosimeter displays considerable dual changes in both absorption (blue-shift) and emission (turn-on) bands exclusively for KCN. The fluorescence enhancement of the **64**-KCN is mainly due to blocking of the ICT process (H. J. Kim et al., 2011). Doubly activatived coumarin **65** acts as a colorimetric and fluorescent chemodosimeter for cyanide (G.-J. Kim & H.-J. Kim, 2010a). A simple aldehyde-functionalized coumarin **66** has been utilized as a doubly activated Michael acceptor for cyanide (G.-J. Kim & H.-J. Kim, 2010b). Coumarin-based fluorescent chemodosimeter **67** with a salicylaldehyde functionality as a binding site has shown selectivity for cyanide anions over other anions in water at biological pH (K.-S. Lee et al., 2008a).

Recognition and detection of fluoride, the smallest anion with unique chemical properties is of growing interest. Several coumarin-derived fluorescent chemosensors for F^- have been developed, the structures of which are shown in Fig. 9.

Coumarin derivative **68** has been developed as a fluorescent probe for detection of F^- ion in water and bioimaging in A549 human lung carcinoma cells (S. Y. Kim et al., 2009). Coumarin **69** is a simple, highly selective, and sensitive chemosensor for fluoride anions in organic and aqueous media based on the specific affinity of fluoride anion to silicon (Sokkalingam & Lee, 2011). Coumarin-derived chemosensor **70** shows an obvious color change from yellow to blue upon addition of F^- ion with a large red shift of 145 nm in acetonitrile (Zhuang et al., 2011). Coumarin-based hydrazone **71** is an ICT probe for fluoride in aqueous medium (Upadhyay et al., 2010a). Coumarin-based system **72** has been developed as a novel turn-on fluorescent and colorimetric sensor for fluoride anions (J. Li et al., 2009).

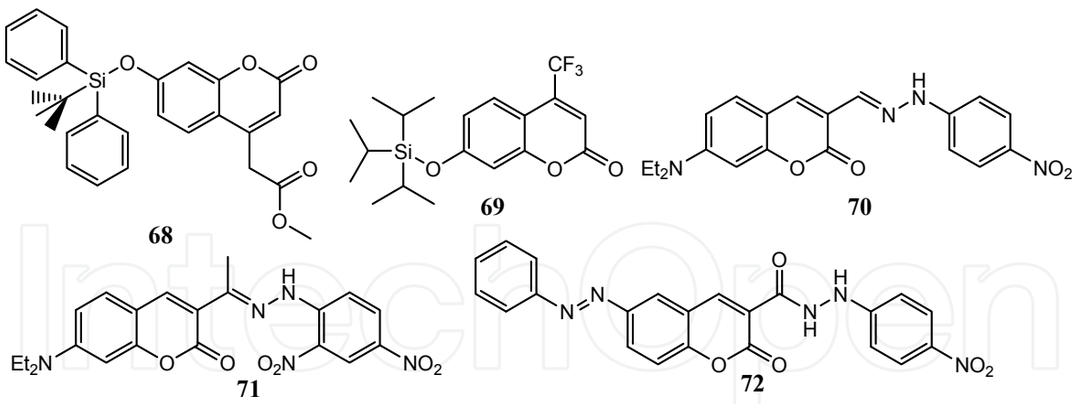


Fig. 9. Structures of coumarin-derived fluorescent chemosensors for F- ion

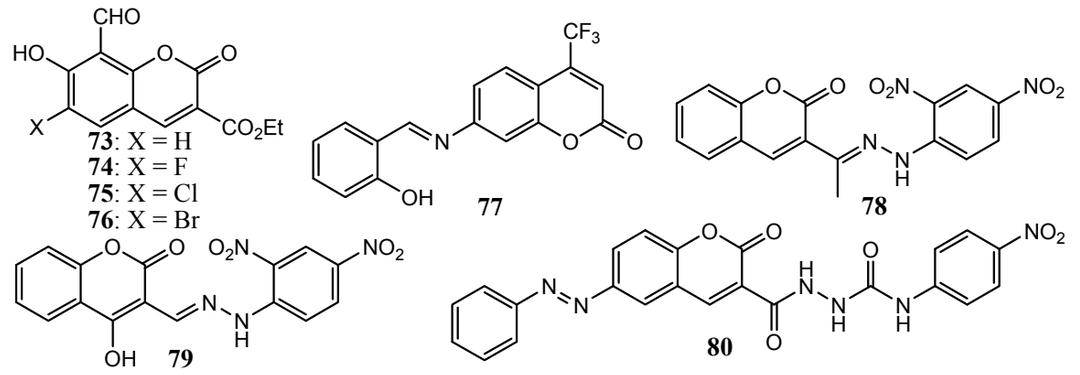


Fig. 10. Structures of coumarin-derived fluorescent chemosensors for anions other than CN- and F-

Structures of coumarin-derived fluorescent chemosensors for detection of anions other than CN- and F- have been shown in Fig. 10. Coumarin-based fluorescent probes **73-76** with salicylaldehyde functinoality as recognition unit have been developed for selective detection of bisulfite anions in water (K. Chen et al., 2010). Coumarin Schiff-base **77** is a highly selective and sensitive turn-on fluorogenic probe for detection of HSO_4^- ions in aqueous solution (H. J. Kim et al., 2009b). Coumarin-based hydrazone **78** acts as an ICT probe for detection of acetate, benzoate, and dihydrogenphosphate (Upadhyay et al., 2010b). Another coumarin-based hydrazone **79** has been utilized as both a colorimetric and ratiometric chemosensor for acetate and a selective fluorescence turn-on probe for iodide (Mahapatra et al., 2011). Compound **80** is a colorimetric and fluorescence anion sensor with the urea group as binding site and the coumarin moiety as signal unit. The sensor displays significant fluorescence enhancement response to anions such as acetate, because of complex formation (Shao, 2010). Coumarin-derived fluorescent chemosensors have also been used for detection of pyrophosphate (S. K. Kim et al., 2009), $H_2PO_4^-$ and $PhPO_3H^-$ (K. Choi & Hamilton, 2001), and multiple anions including pyrophosphate, citrate, ATP and ADP (Mizukami et al., 2002). A new Zn^{II}-2,2':6',2''-terpyridine complex, derivatized with a coumarin moiety, acts as a fluorescent chemosensor for different biologically important phosphates like PPi, AMP and ADP in mixed aqueous media (Das et al., 2011). A strapped calix[4]pyrrole-coumarin conjugate has been developed as a fluorogenic anions (Cl^-, Br^- and AcO^-) receptor modulated by cation and anion binding (Miyaji et al., 2005).

3.3 Coumarin derivatives as fluorescent probes of pH

Structures of coumarin-derived fluorescent chemosensors for sensing pH are shown in Fig. 11. Several iminocoumarin (**81**) derivatives **82-84** have been synthesized as a new type of fluorescent pH indicator. The indicators possess moderate to high brightness, excellent photostability and compatibility with light-emitting diodes. The indicators can be covalently immobilized on the surface of amino-modified polymer microbeads which in turn are incorporated into a hydrogel matrix to afford novel pH-sensitive materials. When a mixture of two different microbeads is used, the membranes are capable of optical pH sensing over a very wide range comparable to the dynamic range of the glass electrode (pH 1-11) (Vasylevska et al., 2007). Coumarin derivative **85** containing piperazine and imidazole moieties has been developed as a fluorophore for hydrogen ions sensing. The fluorescence enhancement of the sensor with an increase in hydrogen ions concentration is based on the hindering of PET from the piperazinyl amine and the imidazolyl amine to the coumarin fluorophore by protonation. The sensor **85** has a novel molecular structure design of fluorophore-spacer-receptor(1)-receptor(2) format and therefore is proposed to sense two range of pH from 2.5 to 5.5 and from 10 to 12 instead of sensing one pH range (Saleh et al., 2008). By using rational molecular design, two molecular functions, the transport by vesicular monoamine transporter (VMAT) and ratiometric optical pH sensing, have been integrated to develop ratiometric pH-responsive fluorescent false neurotansmitter (FFN) probes (M. Lee et al., 2010). A FRET sensor with a donor and an acceptor attached to each end of pH-sensitive polysulfoamides exhibits an instantaneous conformation change from coil to globule at a specific pH, which results in the drastic on-and-off FRET efficiency. To detect a specific pH region, sulfadimethoxine and sulfamethizole are selected among various sulfonamides since their pK_a values are in the physiological pH. For tuning the emission color arising from FRET, 7-hydroxy-4-bromomethylcoumarin and coumarin 343 are used as a FRET donor and an acceptor, respectively, for a blue-to-green FRET sensor (Hong & Jo, 2008).

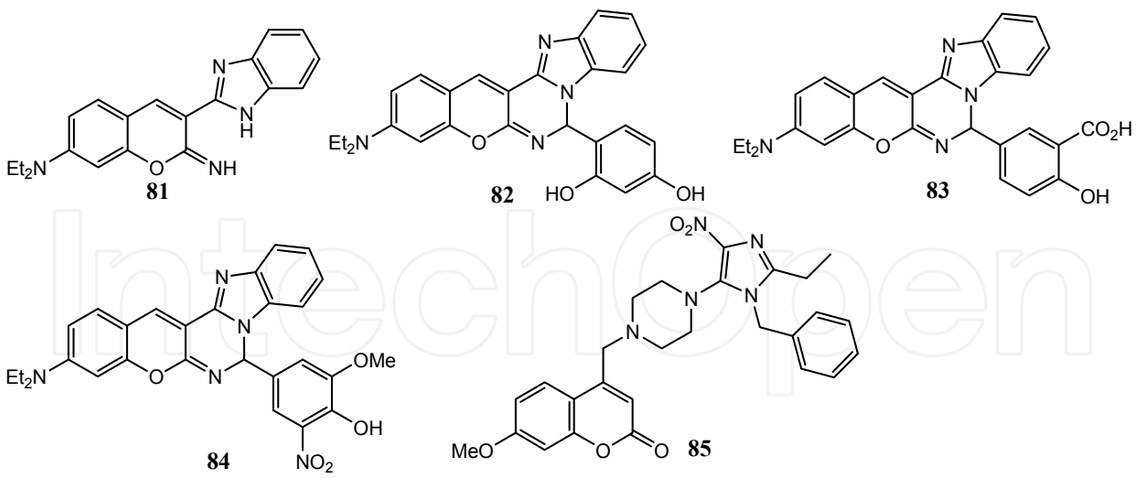


Fig. 11. Structures of coumarin-derived fluorescent chemosensors for sensing pH

3.4 Coumarin-derived fluorescent chemosensors for thiols

Biothiols such as cysteine (Cys), homocysteine (Hcy), and glutathione (GSH) are of great significance because they are involved in myriad vital cellular processes including redox homeostasis and cellular growth. Alteration of the cellular biothiols is also implicated in

cancer and AIDS. Study on fluorescent and colorimetric probes for detection of thiols has received much attention and many coumarin-derived fluorescent chemosensors for detection of thiols have been reported. The structures of these chemical sensors are shown in Fig. 12.

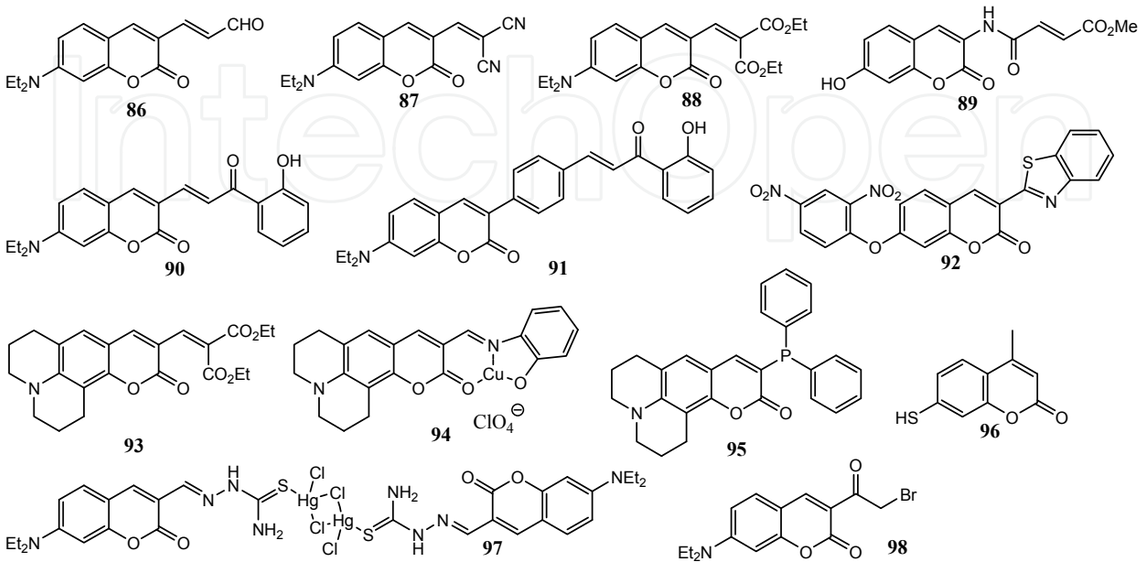


Fig. 12. Structures of coumarin-derived chemosensors for detection of thiols

Generally detection of thiols by optical probes is based on two features of thiols, their strong nucleophilicity and high binding affinity toward metal ions. Accordingly, most of the fluorescent probes for thiols are in fact chemodosimeters, which involve specific reactions between probes and thiols, such as Michael addition, cyclization with aldehyde (or ketone), cleavage of disulfide by thiols, metal complexes-displace coordination, demetalization from Cu-complex, thiolysis of dinitrophenyl ether, and Staudinger ligation. For instance, detection of thiols by chemosensors **87-91** and **93** involves Michael addition between the probes and thiols. For sensors **67** (Fig. 8), **86** and **98**, cyclization reactions occur between the sensors and thiols in the detection process. Coumarin **86** is a ratiometric fluorescent probe for specific detection of Cys over Hcy and GSH based on the drstic distinction in the kinetic profiles (Yuan et al., 2011). Nonfluorescent coumarin-malonitrile conjugate **87** can be transformed into a strongly fluorescent molecule through the Michael addition and thus exhibits a highly selective fluorescence response toward biothiols including Cys, Hcy and GSH with micromolar sensitivity (Kwon et al., 2011). Similarly, nonfluorescent **88** displays a highly selective fluorescence enhancement with thiols and has been successfully applied to thiols determination in intracellular, in human urine and blood samples (Zuo et al., 2010). Coumarin **89** has been developed as a water-soluble, fast-response, highly sensitive and selective fluorescence thiol quantification probe (Yi et al., 2009). Compound **90** (G.-J. Kim et al., 2011) and **91** (S. Y. Lim et al., 2011) with a hydrogen bond act as highly selective ratiometric fluorescence turn-on probes for GSH. Structure **92** has been judiciously designed and synthesized as a new type of selective benzenethiol fluorescent probe based on the thiolysis of dinitrophenyl ether (Lin et al., 2010a). Coumarin-based chemodosimeter **93** effectively and selectively recognizes thiols based on a Michael type reaction, showing a preference for Cys over other biological materials including Hcy and GSH (Jung et al.,

2011a). Iminocoumarin-Cu(II) ensemble-based chemodosimeter **94** sensitively senses thiols followed by hydrolysis to give a marked fluorescence enhancement over other amino acids based on demetalization from Cu-complex (Jung et al., 2011b). Nonfluorescent coumarin-phosphine dye **95** reacts with S-nitrosothiols (RSNOs) to form a fluorescent coumarin derivative and thus may be used as a tool in the detection of RSNOs. The reaction mechanism is similar to the well-known Staudinger ligation (Pan et al., 2009). 7-Mercapto-4-methylcoumarin **96** is a reporter of thiol binding to the CdSe quantum dot surface (González-Béjar et al., 2009). Coumarin-derived complex **97** has been developed as a reversible fluorescent probe for highly selective and sensitive detection of mercapto biomolecules such as Cys, Hcy and GSH (J. Wu et al., 2011). A simple coumarin derivative **98** is the first fluorescence turn-on probe for thioureas by the double functional group transformation strategy. The probe exhibits high sensitivity and selectivity for thioureas over other structurally and chemically related species including urea and thiophenol (Lin et al., 2010b). The simple coumarin sensor **67** (Fig. 8) has shown fluorescence selectivity for not only cyanide anions but also Hcy and Cys in water (K.-S. Lee et al., 2008b). A new coumarin-containing zinc complex has been developed as a colorimetric turn-on and fluorescence turn-off sensor which shows high selectivity for hydrogen sulfide in the presence of additional thiols like Cys or GSH (Galardon et al., 2009).

3.5 Coumarin-derived fluorescent chemosensors for H_2O_2, O_2, hydroxyl radicals or chemical warfare agents

Structures of coumarin-derived fluorescent chemosensors for hydrogen peroxide, oxygen, hydroxyl radicals or chemical warfare agents are shown in Fig. 13. Water-soluble umbelliferone-based fluorescent probe **99** shows very large increase (up to 100-fold) in fluorescent intensity upon reaction with hydrogen peroxide, and good selectivity over other reactive oxygen species (Du et al., 2008). Another water-soluble fluorescent hydrogen peroxide probe **100** based on a 'click' modified coumarin fluorophore shows significant intensity increases (up to fivefold) in near-green fluorescence upon reaction with H_2O_2, and good selectivity over other reactive oxygen species (Du Ý et al., 2010). More recently a simple and highly sensitive fluorometric method was proposed for the determination of H_2O_2 in milk samples. In this method, nonfluorescent coumarin was oxidized to highly fluorescent 7-hydroxycoumarin by hydroxyl radicals generated in a Fenton reaction, and the oxidation product had strong fluorescence with a maximum intensity at 456 nm and could be used as a fluorescent probe for H_2O_2 (Abbas et al., 2010). Thiazo-coumarin ligand directly cyclometallated Pt(II) complex **101** has been used for luminescent O_2 sensing (W. Wu et al., 2011). A hybrid coumarin-cyanine platform **102** has been developed as the first ratiometric fluorescent probe for detection of intracellular hydroxyl radicals (Yuan et al., 2010). More recently a coumarin-neutral red (CONER) nanoprobe was developed for detection of hydroxyl radical based on the ratiometric fluorescence signal between 7-hydroxy coumarin 3-carboxylic acid and neutral red dyes. Biocompatible poly lactide-*co*-glycolide nanoparticles containing encapsulated neutral red were produced using a coumarin 3-carboxylic acid conjugated poly(sodium *N*-undecylenyl-Nε-lysinate) as moiety reactive to hydroxyl radicals. The response of the CONER nanoprobe was dependent on various parameters such as reaction time and nanoparticle concentration. The probe was selective for hydroxyl radicals as compared with other reactive oxygen species including $O_2^{\bullet -}$, H_2O_2, $^1O_2$ and OCl^- (Ganea et al., 2011).

The current rise in international concern over criminal terorist attacks using chemical warfare agents has brought about the need for reliable and affordable detection methods of toxic gases. One of the applicable technologies is the design of fluorogenic chemosensors for the specific detection of nerve agents (Royo et al., 2007). A coumarin oximate **103** has been developed for detection of chemical warfare simulants based on the PET mechanism that gives an "off-on" fluorescent response with a half-time of approximately 50 ms upon phosphorylation of a reactive oximate functionality (Wallace et al., 2006). Coumarin-derived hydroxy oxime **104** serves as a nerve agent sensor based on the reaction of β-hydroxy oxime with organophosphorus agent mimics (Dale & Rebek, 2009). A FRET approach towards potential detection of phosgene has been developed as shown in Fig. 14. When both coumarins **105** and **106** are mixed together with triphosgene in the presence of Et_3N in $CHCl_3$, hybrid urea **107** forms in a statistical yield. Significant fluorescence enhancement is detected which is particularly important since the acceptor unit alone does not emit under the same condition. The fluorescence increase is obviously due to the formation of urea **107**. Simultaneously, the fluorescence from the donor unit decreases due to the quenching, indicating that efficient energy transfer takes place from the donor to the acceptor. This system is selective, since other gases/agents rarely can serve for cross-linking (Zhang & Rudkevich, 2007).

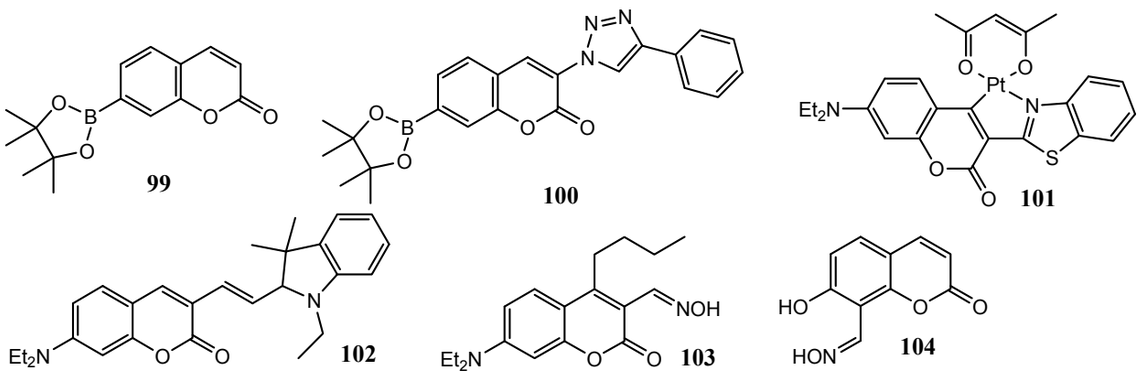


Fig. 13. Structures of coumarin-derived fluorescent sensors for H_2O_2, O_2, hydroxyl radicals or chemical warfare agents

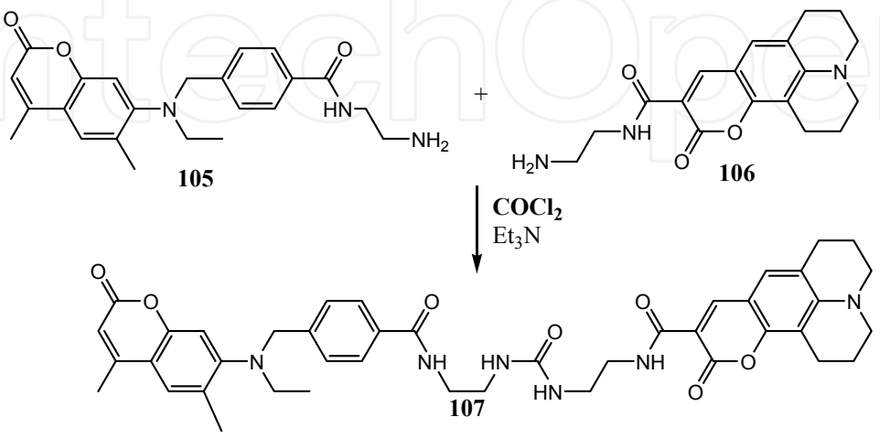


Fig. 14. Coumarins **105** and **106** react with phosgene to form urea **107**

3.6 Coumarin-derived fluorescent chemosensors for amines, amino acids or other organic compounds

Structures of coumarin-derived fluorescent chemosensors for amines, amino acids or other organic compounds are shown in Fig. 15. Butyl-subsituted coumarin aldehyde **108** is an excellent chemosensor for detection of amines and unprotected amino acids in aqueous conditions by formation of highly fluorescent iminium ions (Feuster & Glass, 2003). Boronic acid-containing coumarin aldehyde **109** binds to primary catecholamines with good affinity and acts as an effective colorimetric sensor for dopamine and norepinephrine with excellent selectivity over epinephrine, amino acids, and glucose. In the fluorescence manifold, sensor **109** responds differentially to catechol amines over simple amines, giving a fluorescence decrease in response to catechol-containing compounds and a fluorescence increase with other amines (Secor & Glass, 2004). Coumarin-based fluorescent functional monomers containing a carboxylic acid functionality, **110** and **111** have been synthesized, which allow for the preparation of fluorescent imprinted polymer sensors for chiral amines (Nguyen & Ansell, 2009). Coumarin aldehyde **66** (Fig. 8) can be utilized as not only a doubly activated Michael acceptor for cyanide but also a highly selective and sensitive fluorescence turn-on probe for proline (G.-J. Kim & H.-J. Kim, 2010c). Coumarin-azacrown ether conjugate **112** has been developed as a fluorescent probe for identifying melamine (Xiong et al., 2010). Thiocoumarin **113** can be efficiently desulfurized to its corresponding coumarin by the reaction with mCPBA, and results in a pronounced fluorescence turn-on type signaling. The conversion also provides a significant change in absorption behavior which allows a ratiometric analysis, providing a convient detection method for mCPBA in aqueous environment (Cha et al., 2010). Polymers containing 4,8-dimethylcoumarin have been developed for detection of 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT).

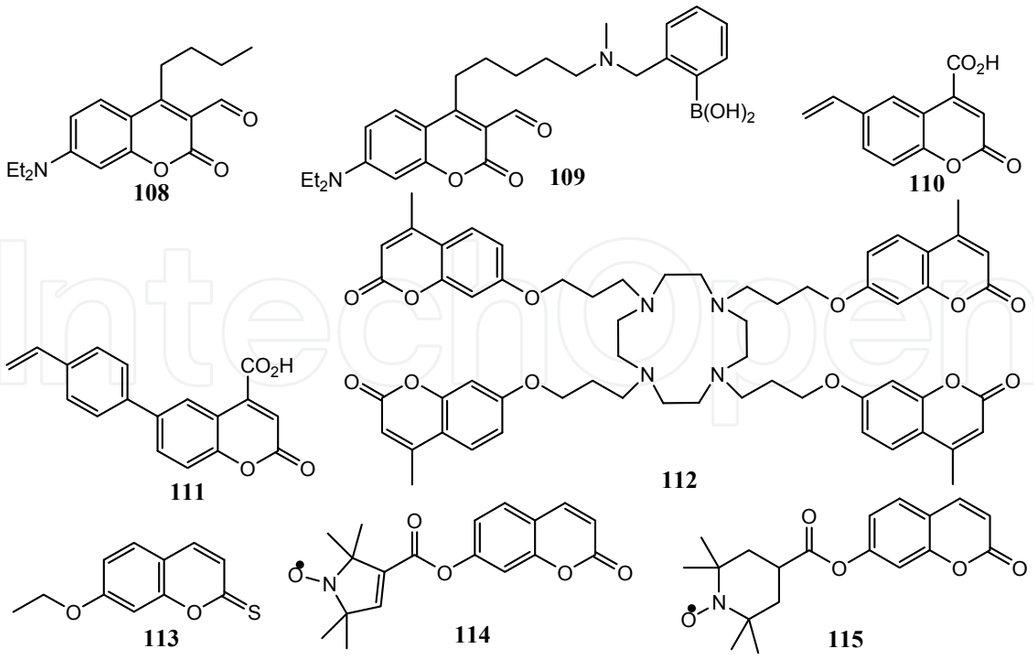


Fig. 15. Structures of coumarin-derived fluorescent chemosensors for amines, amino acids or other organic compounds

The fluorescence quenching of these copolymers in solution can be attributed to the collisional quenching. The response of these polymeric sensors is promising and can easily detect DNT and TNT at few parts per billion levels (Kumar et al., 2010). A novel kind of luminescent vesicular chemosensors for the recognition of biologically important ions and molecules such as imidazoles has been developed by the self-assembly of lipids, amphiphilic binding sites, and fluorescent coumarin reporter dyes that are sensitive to their environment (Gruber et al., 2010). Two hybrid compounds **114** and **115**, linked via an ester-bond between the 7-hydroxyl residue of an umbelliferone and a carboxylic acid residue of two nitroxide radicals, act as fluorescence and spin-label probes. The ESR intensities of **114** and **115** are proportionally reduced after the addition of ascorbic acid sodium salt, and their fluorescence intensities are increased maximally by eight- and nine-fold, respectively (Sato et al., 2008).

3.7 Coumarin-derived fluorescent chemosensors for TiO_2, monolayer, polymerization or polymeric micelles

Structures of coumarin-derived fluorescent chemosensors for detection of TiO_2, monolayer, or photopolymerization are shown in Fig. 16. A novel acac-coumarin chromophore linker **116** for robust sensitization of TiO_2 has been developed to find molecular chromophores with suitable properties for solar energy conversion. The synthesis and spectroscopic characterization confirms that **116** yields improved sensitization to solar light and provides robust attachment to TiO_2 even in aqueous conditions (Xiao et al., 2011). A new amphiphilic coumarin dye, 7-aminocoumarin-4-acetic acid octadecylamide (**117**) forms a stable monolayer at the air-water interface and may be utilized as an efficient fluorescent probe for monolayer studies (Kele et al., 2001). Performance of amidocoumarins **118**-**120** as probes for monitoring of cationic photopolymerization of monomers by fluorescence probe technology has been investigated. 7-Diethylamino-4-methylcoumarin **118** can be used for monitoring cationic photopolymerization of monomers using the fluorescence intensity ratio as an indicator of the polymerization process. The replacement of diethylamino group in **118** with benzamido or acetamido groups eliminates the effect of the probe protonation on kinetics of cationic photopolymerization. 7-Benzamido-4-methylcoumarin **119** and 7-acetamido-4-methylcoumarin **120** can be used as fluorescent probes for monitoring progress of cationic polymerization of vinyl ethers under stationary measurement conditions, using normalized fluorescence intensity as an indicator of the polymerization progress (Ortyl et al., 2010). Coumarin 153 has been used as a fluorescent probe molecule to monitor the possible micellization of several amphiphilic block copolymers (Basu et al., 2009).

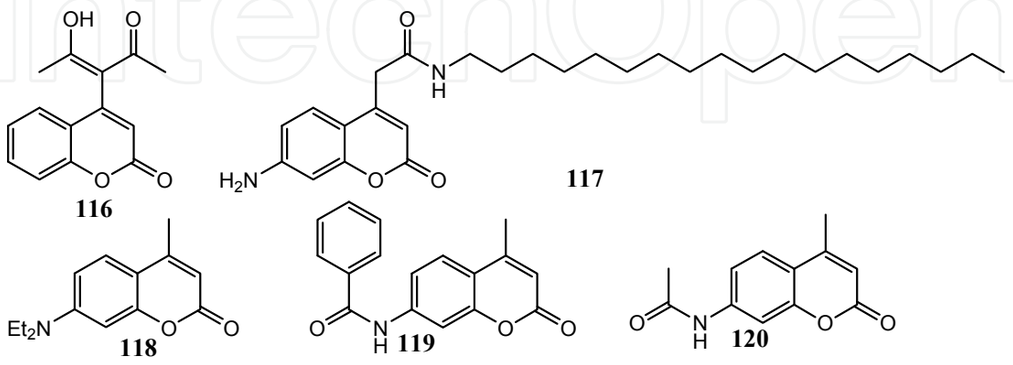


Fig. 16. Structures of coumarin-derived fluorescent sensors for detection of TiO_2, monolayer, or photopolymerization

3.8 Coumarin-derived fluorescent chemosensors for enzymes

Structures of coumarin-derived fluorescent chemosensors for enzymes are shown in Fig. 17. Hemicyanine-coumarin hybrid **121** represents a new class of far-red emitting fluorogenic dyes whose fluorescence is unveiled through an enzyme-initiated domino reaction and thus acts as a fluorogenic probe for penicillin G acylase (Richard et al., 2008). Similarly novel self-immolative spacer systems **122** and **123** have been developed and are utilized as fluorogenic probes for sensing penicillin amidase (Meyer et al., 2008). A library of 6-arylcoumarins has been developed as candidate fluorescent sensors of which **124** has the strongest fluorescence intensity, whose quantum yield is similar to that of ethyl 7-diethylaminocoumarin-3-carboxylate, a well-known fluorophore as labeling or sensing biomolecule. The transormation of the methoxy group (**125**) to a hydroxyl group (**126**) induces a change of fluorescence intensity, which suggests that **125** may be useful as a fluorescent sensor for dealkylating enzymes such as glycosidase. Coumarin **127** shows 50% decrease of the fluorescence intensity at pH 8.0 compared with that at pH 6.0 and this decrease may be derived from the deprotonation of the triazole ring. Thus **127** may be used as a fluorescent sensor for nitric oxide (Hirano et al., 2007). Histone deacetylases are intimately involved in epigenetic regulation and, thus, are one of the key therapeutic targets for cancer. Coumarin-suberoylanilide hydroxamic acid **128** is a fluorescent probe for determining binding affinities and off-rates of histone deacetylase inhibitors (Singh et al., 2011). A quinone-methide-rearrangement reaction as the off-on optical switch has been successfully implemented into the design of the first long-wavelength latent fluorogenic substrate **129** which is a sensitive fluorimetric indicator for analyte determination in salicylate hydroxylase-coupled dehydrogenase assay (S.-T. Huang et al., 2010). Another switch-on long-wavelength latent fluorogenic substrate **130** is a fluorescent probe for nitroreductase (H.-C. Huang et al., 2011).

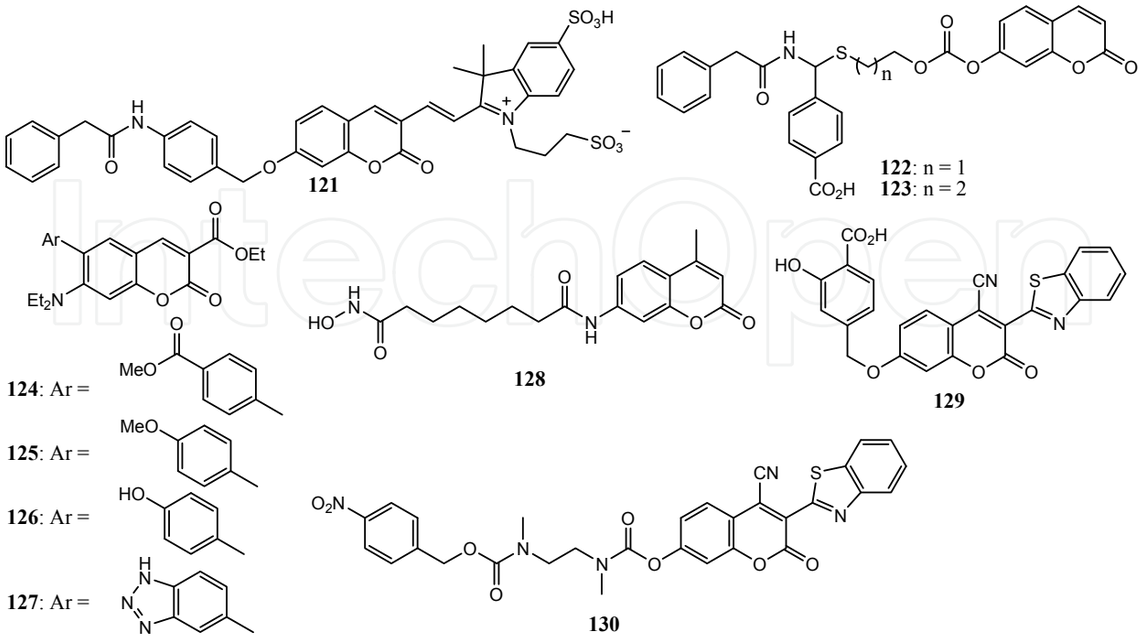


Fig. 17. Structures of coumarin-derived fluorescent chemosensors for enzymes

Apart from the above-mentioned coumarin-derived fluorescent chemosensors for enzymes, clikable biocompatible nanoparticles have been prepared in a one-pot process by microemulsion polymerization, which are then readily modified by the Huisgen Cu(I)-catalyzed azide-alkyne cycloaddition reaction to afford a coumarin-containing subtilisin responsive nanosensor (Welser et al., 2009). A coumarin-containing time-resolved fluorescence probe for dipeptidyl peptidase 4 has also been reported (Kawaguchi et al., 2010). A coumarin-derived triple-signaling fluorescent probe has been successfully applied for intracellular measurement of different enzyme activity (Y. Li et al., 2011). As shown in Fig. 18, a sensitive, selective, and fluorogenic probe **131** has been developed for monoamine oxidases (MAO A and B). Nonfluorescent aminocoumarin **131** can be converted to fluorescent pyrrolocoumarin **132** in the presence of MAO A and B (G. Chen et al., 2005). A new fluorogenic transformation based on a quinone reduction/lactonization sequence as shown in Fig. 19 has been developed and evaluated as a tool for probing redox phenomena in a biochemical context.



Fig. 18. Systematic mapping of aminocoumarin **131** and the corresponding pyrrolocoumarin **132**

3.9 Coumarin-derived fluorescent chemosensors for proteins, DNA, RNA and other uses

Structures of coumarin-derived fluorescent chemosensors for DNA, RNA, nitroxyl and proteins are shown in Fig. 20. A novel coumarin C-riboside **133** is designed and synthesized based on the well-known photoprobe Coumarin 102. The coumarin C-glycoside **133** has been incorporated synthetically into DNA oligomers, and has been used to probe ultrafast dynamics of duplex DNA using time-resolved Stokes shift methods (Coleman et al., 2007). Coumarin-triazole **134** reacts with $CuCl_2$ to form a chelated Cu(II)-**134** complex which shows highly selective turn-on type fluorogenic behavior upon addition of Angeli's salt ($Na_2N_2O_3$) and can be used for detection of nitroxyl in living cells (Zhou et al., 2011). A simple coumarin derivative 7-diethylaminocoumarin-3- carboxylic acid **135** has been used as an acceptor to construct a useful and effective FRET system for detection of RNA-small molecule binding (Xie et al., 2009). Coumarin dye bearing an indolenine substituent **136** displays high emission and bright fluorescence and offers promise as an fluorescent chemosensor for protein detection (Kovalska et al., 2010). Coumarin-containing trifunctional probe **137**, assembled using a cleavable linker, is useful for efficient enrichment and detection of glycoproteins (Tsai et al., 2010). Coumarin 6 has been used as a fluorescent probe to monitor protein aggregation and can distinguish between both amorphors and fibrillar aggregates (Makwana et al., 2011). An S_NAr reaction-triggered fluorescence probe is developed using a new fluorogenic compound derivatized from 7-aminocoumarin for oligonucleotides detection (Shibata et al., 2009). Coumarin C343 has been conjugated to silica nanoparticles and entrapped in a sol-gel matrix to produce a nanosensor capable of monitoring lipid peroxidation (Baker et al., 2007). Coumarin-containing dual-emission chemosensors for nucleoside polyphosphates have been developed based on a new

mechanism involving binding-induced recovery of FRET. These sensors demonstrate that binding-induced modulation of spectral overlap is a powerful strategy for the rational design of FRET-based chemosensors (Kurishita et al., 2010).

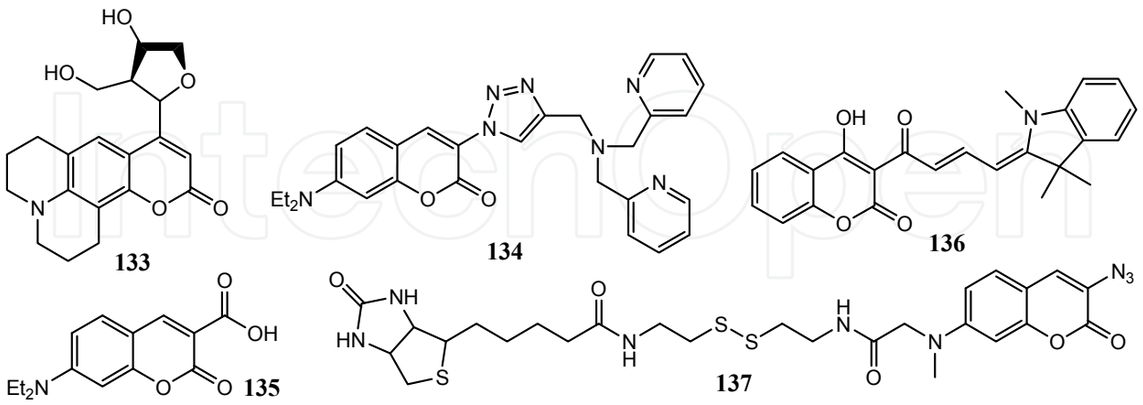


Fig. 19. Structures of coumarin-derived fluorescent chemosensors for DNA, RNA, nitroxyl and proteins

4. Conclusions

Coumarin-derived fluorescent chemosensors have been extensively applied in a variety of fields. Though these sensors are effective for detection of many species, their performance toward different species might decrease in the following order: metal ions, anions, biothiols, enzymes, pH, amines and amino acids, chemical warfare agents, proteins, hydrogen peroxide, hydroxyl radicals, polymerization and polymeric micelles, DNA and RNA, oxygen, titania. Continuous efforts will be devoted to development of fluorescent chemosensors with higher selectivity and sensitivity for more single target or simultaneously for multiple targets, thus providing practical fluorescent chemosensors for application in environmental chemistry, analytical chemistry, and bio-medicinal science.

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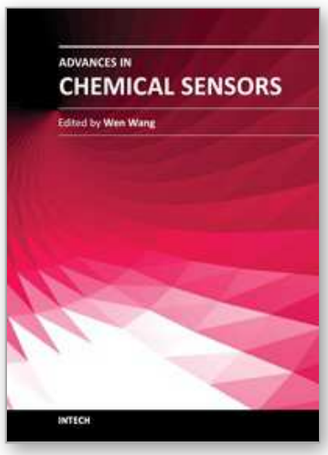
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The chemical sensor plays an essential role in the fields of environmental conservation and monitoring, disaster and disease prevention, and industrial analysis. A typical chemical sensor is a device that transforms chemical information in a selective and reversible way, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. Much research work has been performed to achieve a chemical sensor with such excellent qualities as quick response, low cost, small size, superior sensitivity, good reversibility and selectivity, and excellent detection limit. This book introduces the latest advances on chemical sensors. It consists of 15 chapters composed by the researchers active in the field of chemical sensors, and is divided into 5 sections according to the classification following the principles of signal transducer. This collection of up-to-date information and the latest research progress on chemical sensor will provide valuable references and learning materials for all those working in the field of chemical sensors.

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