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Hg(II) sensing platforms with improved photostability: The combination of rhodamine derived chemosensors and up-conversion nanocrystals

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ABSTRACT

This paper reported two nanocomposite sensing platforms for Hg(II) detection with improved photostability, using two rhodamine derivatives as chemosensors and up-conversion nanocrystals as excitation host, respectively. There existed a secondary energy transfer from this excitation host to these chemosensors, which was confirmed by spectral analysis, energy transfer radius calculation and emission decay lifetime comparison. In this case, chemosensor photostability was greatly improved. Further analysis suggested that these chemosensors recognized Hg(II) following a simple binding stoichiometry of 1:1. Hg(II) sensing performance of these sensing platforms was analyzed through their emission spectra upon various Hg(II) concentrations. Emission spectral response, Stern-Volmer equation, emission stability and sensing selectivity were discussed in detail. It was finally concluded that these chemosensors showed emission turn on effect towards Hg(II), with high photostability, good selectivity and linear response.

1. Introduction

By showing advantages of instant response, low need for equipment and immunity to electromagnetic interference, optical sensing has been recommended as a promising analytical method [1–3]. Among the numerous target species, heavy metal ions have attracted much attention due to their participation in vital biological reactions, making them a potential biohazard for human beings [4–7]. For example, Hg contamination is a well-established biohazard which can be released through both natural and anthropogenic activities. Additionally, inorganic contaminations may be absorbed and converted into organic ones by microbes and bacteria. After being accumulated through food chain, more harm will be brought to human beings [8].

There are precursive efforts focusing on optical sensing platforms for heavy metal ion detection [1–3,9–10]. Regardless of their promising results, defects are found, such as underdeveloped photostability and limited selectivity towards a specific analyte. These sensing platforms are usually emission turn off ones. These chemosensors lose their emission intensity after meeting analyte. Considering that competing matters and emission killers can quench chemosensor emission as well, these emission turn-off sensing platforms suffer from limited selectivity. Additionally, these chemosensors need excitation of short wavelength radiation, such as UV light. This exposure to high energy light makes these chemosensors suffer from photobleaching effect and thus underdeveloped photostability. When designing new sensing platforms, selectivity and photostability shall be taken into consideration.

It seems that the combination of a chemosensor with emission turn on effect and an up-conversion excitation host may well solve the above problems [11,12]. In a representative example for emission turn on chemosensor, its emission is rather weak in the absence of target analyte. After meeting its target analyte, chemosensor emission is increased and proportional to analyte concentration, showing emission turn on effect. While such effect cannot be triggered by competing matters, resulting in good selectivity. A typical up-conversion excitation host absorbs low energy radiation, such as near infrared laser, and transfers this energy to chemosensors for sensing purpose. This secondary energy transfer mechanism avoids any excitation on competing chromophores and fluophors, showing minimal background light interference and improved photostability. After consulting previous reports on superior chemosensors, rhodamine molecules have been usually suggested due to their highly emissive performance and emission turn on effect triggered by Hg(II) [11,13–16]. Up-conversion $NaYF_4$ lattice is usually adopted as excitation host owing to its high stability and efficient up-conversion emission.

Guided by the above results, this work designs two composite sensing platforms for Hg(II) sensing, using two rhodamine derivatives as chemosensors, up-conversion $NaYF_4$ nanocrystals as excitation host,

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respectively, as depicted by Scheme 1. Chemosensor sensing mechanism is discussed, the secondary energy transfer between up-conversion host and chemosensors is confirmed. Corresponding sensing behavior towards Hg(II) and some competing metal ions is revealed.

2. Experimental Details

2.1. General Information: Chemicals and Equipment

Starting chemicals of AR grade were purchased from Dayuan Chemical Company (Shanghai, China) and used for sample synthesis in this work, including rhodamine 6G, anhydrous hydrazine (95 wt%), 3,5-dichloro-2-hydroxybenzaldehyde and Lawesson's reagent. The other compounds were bought from Shanghai Chemical Company (Shanghai, China), including mercury nitrate, NaOH, HCl, Triton X-100, ethanol, acetonitrile, toluene, rare earth and inorganic metal salts. Organic solvents and water were purified before use.

A Varian INOVA 300 spectrometer and an Agilent 1100 MS spectrometer (COMPACT) were used for NMR and MS spectral record, respectively. Emission and absorption spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer and a HP 8453 UV–Vis-NIR diode array spectrophotometer, respectively. Emission decay lifetimes were analyzed on a two-channel TEKTRONIX TDS-3052 oscilloscope, using a Continuum Sunlite OPO tunable laser as excitation module ($\lambda = 980$ nm). A Hitachi S-4800 microscope and a JEM-2010 transmission election microscope were applied for sample morphology and energy-dispersive X-ray (EDX) analysis.

2.2. Synthesis of Chemosensors 3 and 4

2-Amino-3′,6′-bis(ethylamino)-2′,7′-dimethylspiro[isoindoline-1,9′-xanthen]-3-one (1) and 2-amino-3′,6′-bis(ethylamino)-2′,7′-dimethylspiro[isoindoline-1,9′-xanthene]-3-thione (2) were firstly synthesized as starting compounds [16,17]. A mixture of rhodamine 6G (2 g) and anhydrous hydrazine (15 mL) in ethanol (50 mL) was heated at 80 °C under N_2 protection for 10 h. After cooling, plenty of cold water was added. The resulting crude product was purified from ethanol/water (V/V = 4:6) to give 1. Yield (74%). ^{1}HNMR ($CDCl_3$), δ (ppm): 1.22–1.25 (t, 6H, NCH$_2$*CH*$_3$), 1.91 (s, 6H, xanthene-*CH*$_3$), 3.20–3.23 (q, 4H, N*CH*$_2$CH$_3$), 4.78 (s, N-*NH*$_2$), 5.32 (s, *NH*CH$_2$CH$_3$), 6.21 (s, 2H, xanthene-H), 6.42 (s, 2H, xanthene-H), 7.14 (dd, 1H, Ar-H), 7.52 (dd, 2H, Ar-H), 8.21 (dd, 1H, Ar-H). MS *m/z*: [m]$^+$ calc. for $C_{26}H_{28}N_4O_2$, 428.2; found, 428.3.

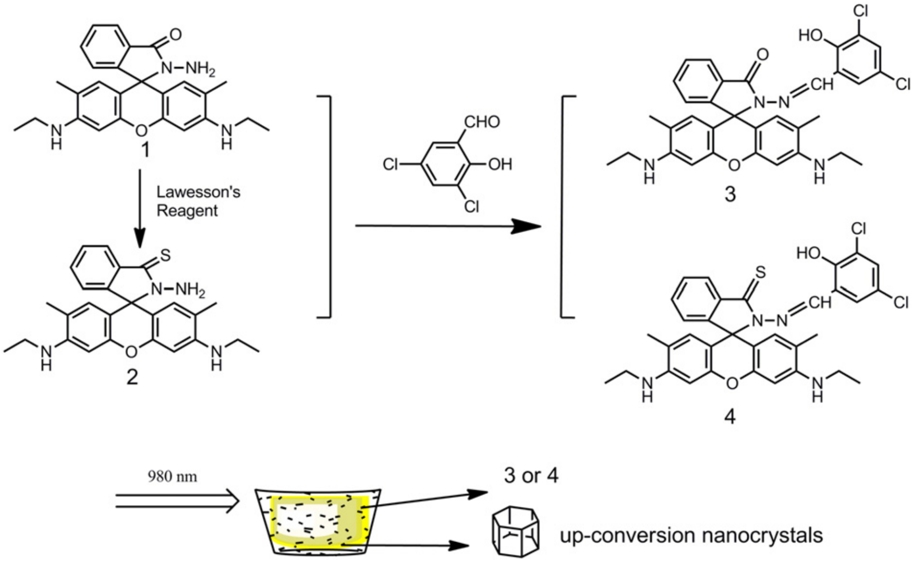
The above obtained 1 (5 mmol) was mixed with Lawesson's reagent (7 mmol) and anhydrous toluene (40 mL) [18]. This mixture was heated at 120 °C under N_2 protection for 8 h. Solvent was extracted by rotary evaporation. Crude product was purified on a silica gel column to give 2. Yield (62%). ^{1}HNMR ($CDCl_3$), δ (ppm): 1.24–1.36 (t, 6H, NCH$_2$*CH*$_3$), 1.93 (s, 6H, xanthene-*CH*$_3$), 3.23–3.25 (q, 4H, N*CH*$_2$CH$_3$), 4.75 (s, N-*NH*$_2$), 5.37 (s, *NH*CH$_2$CH$_3$), 6.19 (s, 2H, xanthene-H), 6.43 (s, 2H, xanthene-H), 7.15 (dd, 1H, Ar-H), 7.57 (dd, 2H, Ar-H), 8.26 (dd, 1H, Ar-H). MS *m/z*: [m]$^+$ calc. for $C_{26}H_{28}N_4OS$, 444.2; found, 445.5.

2-((3,5-Dichloro-2-hydroxybenzylidene)amino)-3′,6′-bis(ethylamino)-2′,7′-dimethylspiro[isoindoline-1,9′-xanthen]-3-one (3) was synthesized following below method [18]. A mixture of the above obtained 1 (10 mmol), 3,5-dichloro-2-hydroxybenzaldehyde (10 mmol) and ethanol (50 mL) was refluxed for 8 h under N_2 atmosphere. After solvent evaporation under reduced pressure, solid residue was separated on a silica gel column using CH_2Cl_2 as eluent. Yield (45%). ^{1}HNMR ($CDCl_3$), δ (ppm): 1.21–1.23 (t, 6H, NCH$_2$*CH*$_3$), 1.92 (s, 6H, xanthene-*CH*$_3$), 3.21–3.22 (q, 4H, N*CH*$_2$CH$_3$), 5.35 (s, *NH*CH$_2$CH$_3$), 6.23 (s, 2H, xanthene-H), 6.44 (s, 2H, xanthene-H), 7.15 (dd, 1H, Ar-H), 7.50 (dd, 2H, Ar-H), 7.65–7.68 (m, 2H, xanthene-H), 8.12 (dd, 1H, Ar-H), 9.11 (s, 1H, Ar-H), 11.20 (s, 1H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 13.45, 16.78, 41.58, 72.33, 100.63, 113.31, 116.51, 121.12, 126.27, 127.16, 128.31, 128.77, 129.25, 130.19, 131.31, 132.36, 134.71, 134.61, 143.15, 143.88, 148.47, 157.26, 163.61. MS *m/z*: [m]$^+$ calc. for $C_{33}H_{30}Cl_2N_4O_3$, 600.2; found, 600.3.

The synthetic procedure for 2-((3,5-dichloro-2-hydroxybenzylidene) amino)-3′,6′-bis(ethylamino)-2′,7′-dimethylspiro[isoindoline-1,9′-xanthene]-3-thione (4) was similar to that for 3, except that 2 was used as a starting chemical in this run, not 1. Yield (45%). ^{1}HNMR ($CDCl_3$), δ (ppm): 1.22–1.24 (t, 6H, NCH$_2$*CH*$_3$), 1.93 (s, 6H, xanthene-*CH*$_3$), 3.24–3.26 (q, 4H, N*CH*$_2$CH$_3$), 5.39 (s, *NH*CH$_2$CH$_3$), 6.22 (s, 2H, xanthene-H), 6.44 (s, 2H, xanthene-H), 7.13 (dd, 1H, Ar-H), 7.52 (dd, 2H, Ar-H), 7.75–7.77 (m, 2H, xanthene-H), 8.25 (dd, 1H, Ar-H), 9.12 (s, 1H, Ar-H), 11.23 (s, 1H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 14.61, 16.99, 39.31, 81.35, 100.92, 113.41, 119.33, 121.33, 125.71, 126.19, 127.11, 128.02, 128.79, 130.22, 130.98, 132.27, 134.51, 141.47, 142.48, 143.53, 144.27, 148.38, 157.39, 160.31. MS *m/z*: [m]$^+$ calc. for $C_{33}H_{30}Cl_2N_4O_2S$, 616.2; found, 616.2.

2.3. Preparation of $NaYF_4$ Up-conversion Host

Up-conversion $NaYF_4$ nanocrystals were obtained in accordance with a literature procedure [10]. Below solutions were mixed together



Scheme 1. Synthetic and construction route for chemosensors (3 and 4) and their sensing platforms.