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Highly Selective and Stable Florescent Sensor for Cd(II) Based on Poly(azomethine-urethane)

İsmet Kaya · Musa Kamacı

Abstract In this study a kind of poly(azomethine-urethane); (E)-4-((2 hydroxyphenylimino) methyl)-2-methoxyphenyl 6-acetamidohexylcarbamate (HDI-*co*-3-DHB-2-AP) was prepared as in the literature and employed as a new fluorescent probe for detection of Cd(II) concentration. The photoluminescence (PL) measurements were carried out in the presence of several kinds of heavy metals. HDI-*co*-3-DHB-2-AP gave a linearly and highly stable response against Cd(II) as decreasing a new emission peak at 562 nm. Possible interferences of other ions were found too low. Detection limit of the sensor was found as $8.86 \times 10^{-4} \, \mathrm{mol \, L^{-1}}$. Resultantly, HDI-*co*-3- DHB-2-AP could be effectively used as an optical Cd(II) sensor.

Keywords Poly(azomethine-urethane) · Fluorescence sensor · Cd(II) sensor · optical sensor

Introduction

The detection and quantification of heavy metal ions are of great importance in any kind of biological and environmental analysis due to these ions affect biological systems in many different ways ranging from being essential trace elements to being acute toxins [1]. To determine these kinds of ions a lot of analytical methods including atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission or mass spectroscopy (ICP-AES, ICP-MS) have been widely used at very low concentrations. Although these methods have good

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sensitivity and fast measurement capabilities, they require expensive instruments, well-controlled experimental conditions, complicated sample-pretreatment procedures and higher sample volume [2–4]. As an alternative to these expensive methods a lot of optical sensors have been developed so far [5–7]. Optical sensors have a lot of advantages such as cheapness, fine sensitivity and freedom from electrical interference, safety and being easy to apply [8]. In addition, a lot of analytes could be analyzed by optical sensors which can not be detected by another method. Also, polymeric compounds were used in this field to obtain more selective-sensitive sensors [9].

A number of metal ion sensors based on metal-ligand coordination or chemical reaction have been designed and reported, especially for detecting transition and heavy metal ions, such as mercury, lead and copper ions so far [10–12]. However, relatively few examples of ion sensors for Cd^{2+} have been reported [13, 14]. Cadmium is one of the important resources and currently used in many processes such as nickel-cadmium batteries, rods, electroplating, metallurgy, war industry and agriculture [15, 16]. Also, cadmium is a component of semiconductors quantum dots such as cadmium sulfide [17], cadmium selenide [18] and cadmium telluride [19] which are used for light detection or solar cell [20]. Exposure of cadmium can contaminate food, water and the use of cadmium causes serious environmental and health problems such as lung, prostatic and renal cancers [21, 22]. The determination of cadmium has become increasingly important because its toxicity and the increasing level of extended use in industry. Also, cadmium can accumulate, store in living organisms and may lead to cancer [23]

In this study we proposed an easy recognition and detection of Cd(II) in aqueous solutions via one step fluorescence measurement of the synthesized poly(azomethine-urethane) (HDI-*co*-3-DHB-2-AP). The polymeric sensor was prepared as in the literature [12] and found as good candidate for optical detection of Cd(II). An important advantage of the proposed Cd(II) sensor is easy production (only one step

reaction) with fine sensing and stable properties. Selectivity study of the new Cd(II) sensor was investigated and a considerable selectivity was obtained according to relative intensity change values.

Experimental

Materials

3,4-Dihydroxybenzaldehyde (3-DHB), hexamethylenediisocyanate (HDI), 2-aminophenol, dimethylformamide (DMF), Pb(CH$_3$COO)$_2$.3H$_2$O, Mn(CH$_3$COO)$_2$.H$_2$O, CuCl and HgCl$_2$ were supplied from Merck Chemical Co. (Germany), Cu(CH$_3$COO)$_2$.H$_2$O, Zn(CH$_3$COO)$_2$.2H$_2$O, Co(CH$_3$COO)$_2$.4H$_2$O, Cd(CH$_3$COO)$_2$.2H$_2$O, and Ni(CH$_3$COO)$_2$.4H$_2$O were from Fluka, and ZrCl$_4$ and CrCl$_3$ were from Riedel Dehaen and they were used as received.

Synthesis of the poly(azomethine-urethane) (HDI-co-3-DHB-2-AP)

HDI-co-3-DHB-2-AP was synthesized in two steps [24]. The first step consists of the copolymerization reaction of 3,4-dihydroxybenzaldehyde (3-DHB) with hexamethylenediisocyanate (HDI) to form the novel polyurethane. The second step includes the graft copolymerization reaction of 2-aminophenol (2-AP) with the prepared polyurethane to form poly(azomethine-urethane) (PAMU). At the first step 3.0 g of HDI (1.8×10^{-2} mol) was dissolved in 50 ml THF and added into a 250 ml three-necked round-bottom flask which was fitted with condenser, magnetic stirrer, and inert argon gas supplier. The solution was heated up to 333 K and equivalent amount 2.5 g of 3-DHB (1.8×10^{-2} mol) was added into the flask. Reaction was maintained for 6 h under argon atmosphere, cooled at the room temperature, and kept for 24 h. THF was removed using an evaporator. Obtained polyurethane (PU) was washed with methanol (2×50 ml), acetonitrile (2×50 ml) and water (2×100 ml) to remove the unreacted components. The product was dried in a vacuum oven at 348 K for 24 h (yields 97 %). At the second step 0.93 g of PU (3×10^{-3} mol) was dissolved in 60 ml DMF/MeOH (1/3) mixture and added into a 250 ml three-necked round-bottom flask which was fitted with condenser and magnetic stirrer. The solution was heated up to 333 K and equivalent amount 0.327 g of 2-AP (3×10^{-3} mol) was added into the flask. Reaction was maintained for 3 h, cooled at the room temperature. The obtained PAMU

Scheme 1 Synthesis of HDI-co-3-DHB and HDI-co-3-DHB-2-AP
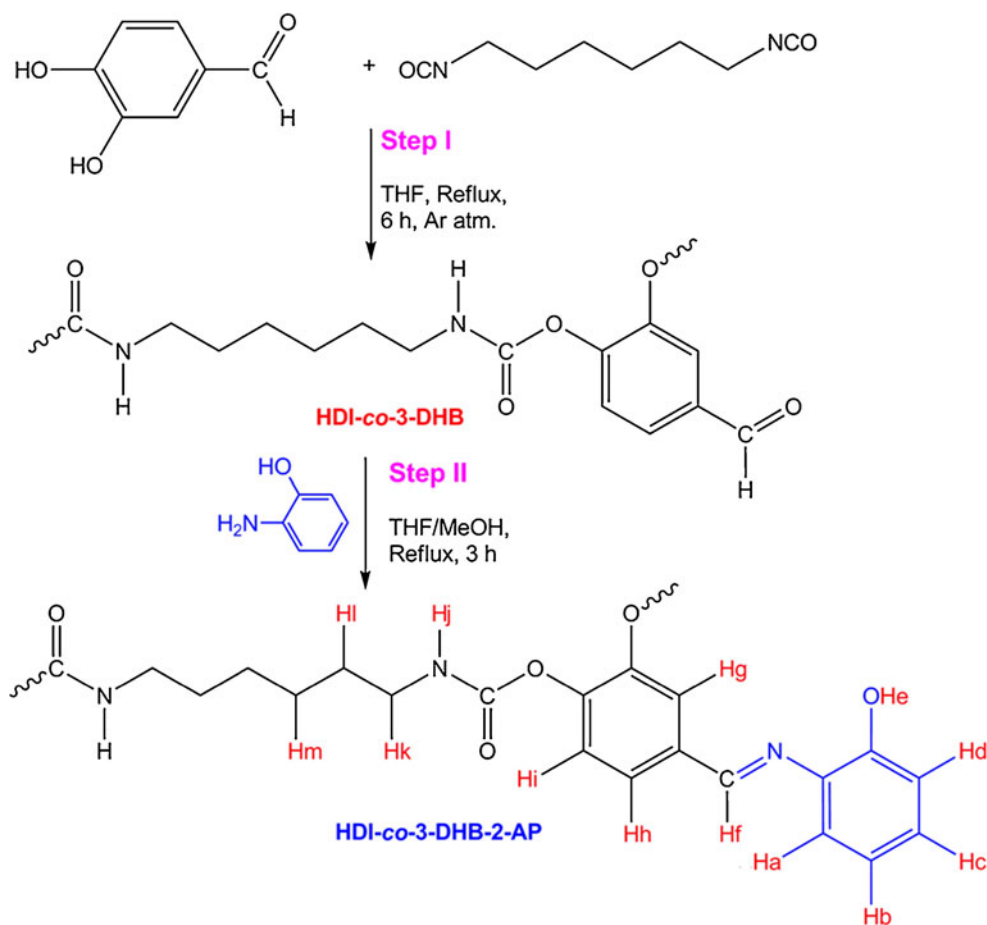
was washed by methanol (2×50 ml), acetonitrile (2×50 ml) and distilled water (2×100 ml) to remove the unreacted components. The product was dried in a vacuum oven at 348 K for 24 h (yields 91 %) [25]. All the synthesized procedures were summarized in Scheme 1.

FT-IR (cm^{-1}): 3305 (N-H, urethane), 1690 (C = O, urethane), 1647 (HC = N, imine), 2930 and 2850 (C-H, methyl), 1591, 1543, 1499 (C = C, aromatic).

^{1}H-NMR (DMSO): δ ppm, 9.83 (s, -OH, He), 7.96 (s, -N = CH, Hf), 7.86 (s, Ar-Hg), 6.79 (d, Ar-Hh), 6.77 (t, Ar-Hc), 6.73 (d, Ar-Hi), 6.71 (d, Ar-Ha), 6.68 (t, Ar-Hb), 6.64 (d, Ar-Hd), 6.62 (t, -NHCO, Hj), 3.18 (m, Al-Hk), 2.09 (m, Al-Hl), 1,32 (m, Al-Hm).

Characterization

The structure of HDI-co-3-DHB-2-AP was characterized by infrared (IR) and NMR spectra. FT-IR analysis was carried out by Perkin Elmer FT-IR Spectrum one using universal ATR sampling accessory (4000–550 cm^{-1}). ^{1}H spectrum (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) was obtained by using deuterated DMSO-d$_6$ as a solvent at 298 K. The tetramethylsilane was used as internal standard.

Fluorescence Measurements

A Shimadzu RF-5301PC spectrofluorophotometer was used in fluorescence measurements. Measurements were carried out in DMF solutions of HDI-co-3-DHB-2-AP. The influence of the poly(azomethine-urethane) concentration on the fluorescence intensity was determined by measuring of the emission peak intensities when excited at 503 nm. The effects of transition metal ions on emission intensity of the emission spectra were investigated in 1:2 (v:v) DMF/ deionized water solutions each of which containing 2.40 mgL^{-1} of HDI-co-3-DHB-2-AP and 6.66×10^{-2} molL^{-1} metal ion. The changes of fluorescence intensities depending on the concentration of Cd(II) ions were determined using a series of different concentrations of metal solutions in 1:2 (v:v) DMF/ deionized water mixtures. Slit width was 5 nm in the mentioned experiments. Another series of Cd(II) containing poly(azomethine-urethane) solutions were prepared to determine the detection limit. For this purpose several solutions with different concentrations of Cd(II) in the range of 5.86×10^{-5}–6.00×10^{-2} molL^{-1} were used.

Calculation of Nitrogen and Oxygen Atoms Charges

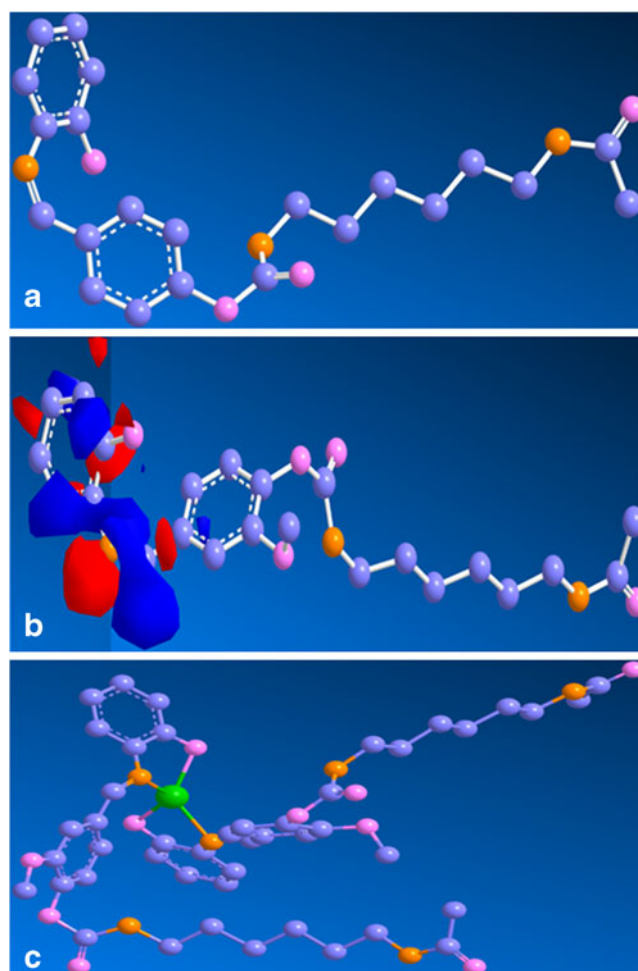The charges of nitrogen and oxygen atoms in the structure were determined by using Huckel calculation

Fig. 1 3-D image of HDI-co-3-DHB-2-AP (**a**), HOMO-LUMO image of HDI-co-3-DHB-2-AP (**b**) and the possible structure of Cd^{2+} with HDI-co-3-DHB-2-AP (**c**). (Purple carbon, pink oxygen, orange nitrogen and green Cd atom (M) (hydrogen atoms are not shown)

method. For this reason, Chem Office v12 program was used.
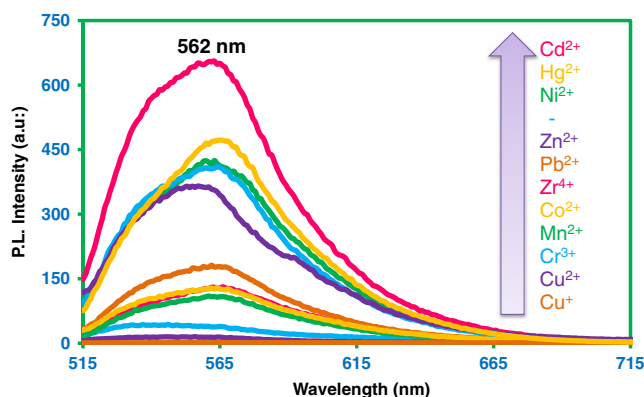

Fig. 2 Fluorescence emission spectra (λ$_{Ex}$=503 nm, λ$_{Em}$=524 nm) of HDI-co-3-DHB-2-AP (2.40 mgL^{-1}) with presence of 6.66×10^{-2} molL^{-1} metal ions. The excitation and emission slit widths were 5 nm

Table 1 PL intensities of the polymer solutions in the presence of different cations

Metal content	Cd(II)	Ni(II)	–	Zn(II)	Pb(II)	Co(II)	Zr(IV)	Mn(II)	Cu(II)	Cr(III)
[a]I_{em} (562)	676	415	405	358	181	140	128	108	38	14

λ_{Ex}=503 nm, slit width=5 nm. Polymer conc.: C_{Pol}=2.40 mg L^{-1} and Metal conc.: C_M=6.66 x 10^{-2} mol L^{-1}

[a] Emission intensity at 562 nm

Results and Discussion

Fluorescence Characteristics of HDI-co-3-DHB-2-AP

The optimal excitation and emission wavelengths in DMF solution of HDI-*co*-3-DHB-2-AP: 2.4 mg L^{-1} were found as 503 and 524 nm, respectively. Also, the Stoke's shift value of HDI-*co*-3-DHB-2-AP is found as 59 cm^{-1}. Stoke's shift is important for a fluorescence sensor. The higher Stoke's shift value supplies very low background signals and resultantly allows the usage of the material in construction of a fluorescence sensor [26]. HDI-*co*-3-DHB-2-AP has a few chelating groups including the imine nitrogens and urethane linkages for complexation with metal ions. Huckel calculation method was used to calculate the charge density of HDI-*co*-3-DHB-2-AP [27]. Also, 3-D image of HDI-*co*-3-DHB-2-AP, HOMO-LUMO image of HDI-*co*-3-DHB-2-AP and the possible structure of HDI-*co*-3-DHB-2-AP with Cd(II) atom were shown in Fig. 1. According to Huckel calculation and Fig. 1, the charges of nitrogen atom in imine group and oxygen atom in hydroxyl group (−OH) were calculated as −0.481 and −0.653, respectively. Also, the charges of nitrogen and oxygen atoms in the urethane linkage were calculated as −0.186 and −0.249. According to these results, imine nitrogen quite higher negative charge than in the urethane group nitrogen. This indicates that possible complexation could be mainly carried out between nitrogen atom in imine group, oxygen atom and Cd(II) metal ions [26].

Cd(II) Selectivity of HDI-co-3-DHB-2-AP

The synthesized polymer is exposed to different transition metal ions such as Cd(II), Co(II), Cr(III), Cu(II), Mn(II), Ni(II), Pb(II), Zn(II) and Zr(IV) and the changes in emission spectra are recorded and shown in Fig. 2. The polymer concentration was chosen very low to minimize the photo luminescence (PL) intensity of metal-free polymer solution in working range. The results are also summarized in Table 1. The obtained results show that when the polymer is exposed to Cd(II), Ni(II) and Hg(II) ions the emission peak is increased at 562 nm. On the other hands, the emission peak is decreased at 562 nm when it exposed Zn(II), Pb(II), Co(II), Zr(IV), Mn(II), Cu(II), Cu(I) and Cr(III) ions. The obtained peak intensity decreases with increasing Cd(II)

concentration. This result indicates that HDI-*co*-3-DHB-2-AP could be used as very selective Cd(II) sensor in aqueous solutions.

Concentration effect of Cd(II) ion in the emission spectrum of the polymer was given in Fig. 3. Relative emission intensities (I-I$_0$/I$_0$) at 562 nm obtained from Fig. 3 are plotted vs. Cd(II) concentration and a linear spectrofluorometric response for Cd(II) concentration at 562 nm is obtained with a very good regression coefficient as R= 0.9589 (Fig. 4a) and R=0.9981 (Fig. 4b). This linear response could be used for detection of Cd(II) concentration using the following equation for concentration range between $1.50 \times 10^{-2} - 9.375 \times 10^{-4}$ mol L^{-1} (a) and $4.69 \times 10^{-4} - 5.86 \times 10^{-5}$ mol L^{-1} (b) (Eqs. 1 and 2, respectively):

$$\frac{I - I_o}{I_o} = 25.033 \left[Cd^{2+} \right] - 0.7162 \qquad (1)$$

$$\frac{I - I_o}{I_o} = 229.91 \left[Cd^{2+} \right] - 0.8979 \qquad (2)$$

where I is the emission intensity of tested sample at 562 nm and I$_0$ is the emission intensity of metal free polymer solution.

The detection limit of the proposed sensor was determined by using these two equations and the intersection of
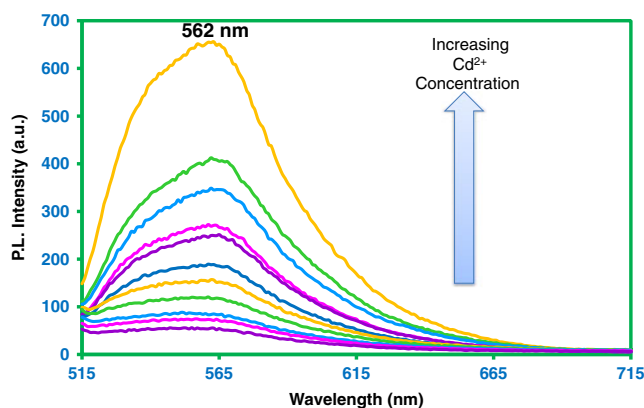

Fig. 3 Fluorescence emission spectra of HDI-*co*-3-DHB-2AP in the presence Cd^{+2} ion with different concentrations (mol.L^{-1}, from bottom to top): 5.86×10^{-5}, 1.17×10^{-4}, 2.34×10^{-4}, 4.68×10^{-4}, 9.38×10^{-4}, 1.88×10^{-3}, 3.75×10^{-3}, 7.50×10^{-3}, 1.50×10^{-2}, 3×10^{-2} and 6×10^{-2} Conditions: Slit: λ_{Ex}=5 nm, λ_{Em}=5 nm, λ_{Ex}=503 nm, λ_{Em}=524 nm, concentration of HDI-*co*-3-DHB-2-AP: 2.40 mg L^{-1}
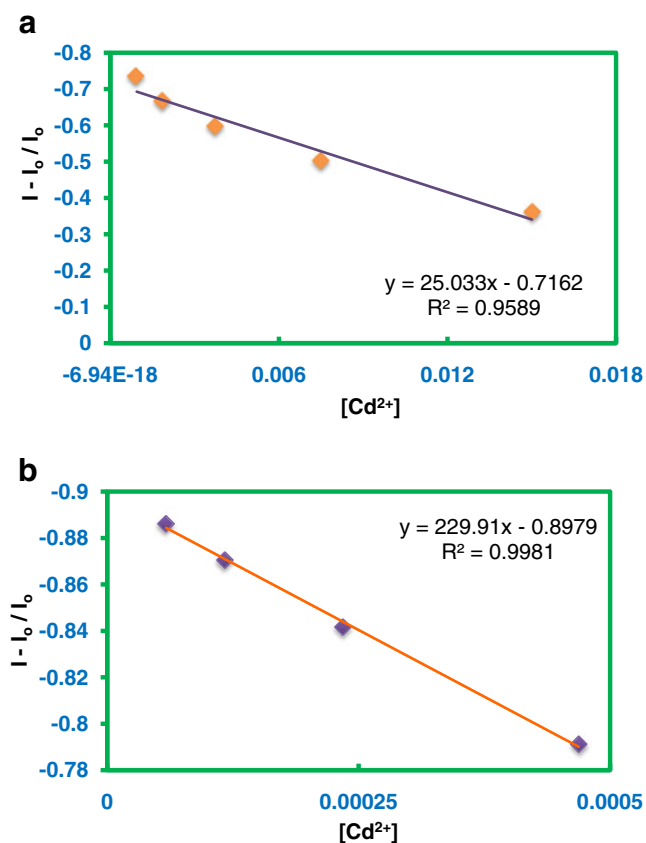
a

$y = 25.033x - 0.7162$
$R^2 = 0.9589$

b

$y = 229.91x - 0.8979$
$R^2 = 0.9981$

Fig. 4 Linearized responses of HDI-*co*-3-DHB-2AP to Cd^{2+} ion (Concentration range between $1.50 \times 10^{-2} – 9.375 \times 10^{-4} \, molL^{-1}$ (**a**) and $4.69 \times 10^{-4} – 5.86 \times 10^{-5} \, molL^{-1}$ (**b**))

the extrapolated linear regions. Firstly, these two equations were equalized each other, after detection limit was calculated. According to the calculation, detection limit of sensor was found as $8.86 \times 10^{-4} \, molL^{-1}$. Also, 3-D graphic of increasing Cd(II) concentration was obtained by using Origin Pro 8 SR6 program and shown in Fig. 5.

Possible interference of the other transition metals used at the same wavelength (562 nm) is also shown in Fig. 6.
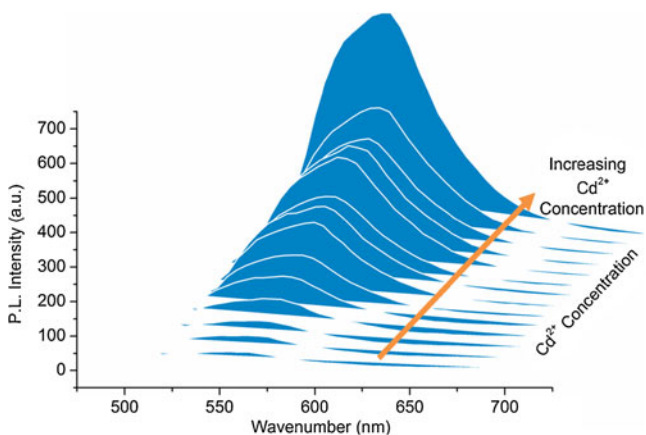

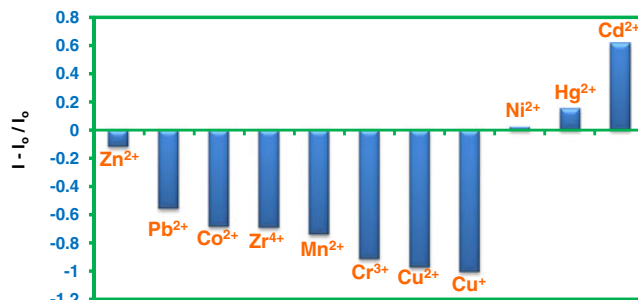**Fig. 5** 3-D graphic of increasing Cd(II) concentration

Fig. 6 Relative intensity change of HDI-*co*-3-DHB-2-AP on exposure to $6.66 \times 10^{-2} \, molL^{-1}$ different transition metal cations

Measurements were carried out using the same concentrated ($6.66 \times 10^{-2} \, molL^{-1}$) metal ions and the polymer concentration of $2.40 \, mgL^{-1}$. As seen in Fig. 6 with exception of Cd (II) the other transition metal ions have no response in the used wavelength. However, Cd(II) has quite high relative response in this region allowing performing the synthesized polymer as highly selective Cd(II) sensor. As known, cadmium and zinc have very similar chemical properties because of electronic configuration. Both of these metal(II) ions have d^{10} electronic structure in last orbits. Because of
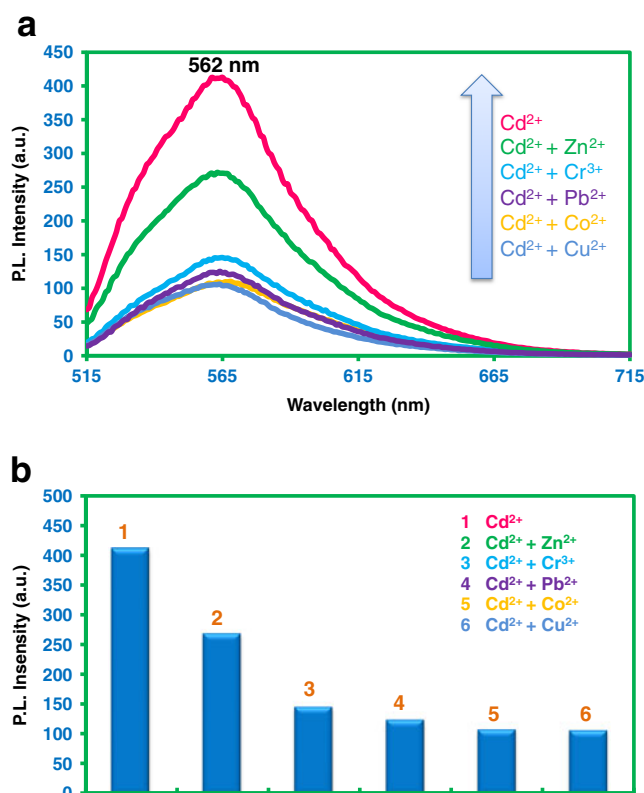

a

562 nm

Cd^{2+}
$Cd^{2+} + Zn^{2+}$
$Cd^{2+} + Cr^{3+}$
$Cd^{2+} + Pb^{2+}$
$Cd^{2+} + Co^{2+}$
$Cd^{2+} + Cu^{2+}$

b

1   Cd^{2+}
2   $Cd^{2+} + Zn^{2+}$
3   $Cd^{2+} + Cr^{3+}$
4   $Cd^{2+} + Pb^{2+}$
5   $Cd^{2+} + Co^{2+}$
6   $Cd^{2+} + Cu^{2+}$

Fig. 7 Fluorescence emission spectra of HDI-*co*-3-DHB-2AP in the presence Cd^{+2} ion and Cd^{2+} ion with the other quenching ion such as Zn^{2+}, Cr^{3+}, Pb^{2+}, Co^{2+}, Cu^{2+}. Conditions: Slit: λ_{Ex}=5 nm, λ_{Em}=5 nm, λ_{Ex}=503 nm, λ_{Em}=524 nm, concentration of HDI-*co*-3-DHB-2-AP: $3.00 \, molL^{-1}$ (**a**). The obtained results representation as column chart (**b**)
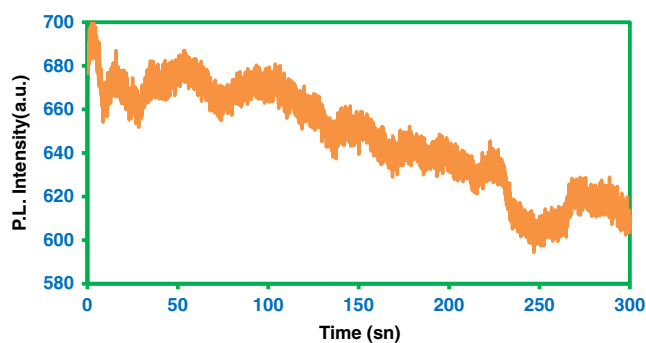
Fig. 8 The time resolved fluorescence spectroscopy of HDI-co-3-DHB-2-AP and its Cd(II) complex in DMF

this property, Cd(II) sensor can also respond to Zn(II) [28]. But this study, as seen Fig. 6 the proposed Cd(II) sensor was not responded to Zn(II).

Oehme and Wolfbeis have presented a wide list for the published optical ion sensors which were classified according to the analyte types [29]. According to their study a selective complexation of the sensor with some particular ions depends on different reasons like soft or hard metal kinds. Selectivity of a sensor should basically follow the hard-soft acid-base principle, which states that hard acids prefer to bind to hard bases and vice versa. The classification of the used ions in this study are as follows: Cr(II), Mn(II) and Zr(IV) are hard acid, Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) are border-line acid and Cd(II), Cu(I) and Hg(II) are soft acid [30]. According to this classification, cadmium (II) is clearly a soft Lewis acid, which more readily binds uncharged nitrogen donors than negatively-charged oxygen through electrostatic bonds [31]. We explained that the possible complexation could be mainly carried out between the nitrogen atom in imine group, oxygen atom and Cd(II) metal ion. These two last sentences could be an explanation for how the proposed sensor only have selectivity against Cd(II) ions. On the other hand, Hg(II) ion forms stable coordination complex with N and S atoms [32]. As seen in Scheme 1, the synthesized poly(azomethine-urethane) contains N and O atoms.

Reversibility is also another important property for a sensor. Ion binding reactions based on chelators are reversible in principle and this is desired for continuous monitoring. In practice, however, most chelating reactions are irreversible [29]. Reversible ion sensors are generally developed as active sensing layer immobilized on any polymeric membrane. Optical sensors could be applied to flow systems

(with the analyte solution passing a detection cell) or in a batch mode (where the sensor is exposed to a fixed volume of the analyte solution) [29]. Reversibility of a sensor could be determined using the flow systems. In this study we envisaged a disposable sensor which is useful in solution form and used the batch mode. However, as mentioned above very low-concentrated polymer solution is needed for detection of Cd(II) content. This makes the new method inexpensive and resultantly may be favored. However, the selectivity, easy and cheap production as well as easy sensing application makes the present sensor superior candidate for Cd(II) sensing.

Fluorescence emission spectra of HDI-co-3-DHB-2AP in the presence Cd^{+2} ion and Cd^{2+} ion with the other quenching ion such as Zn^{2+}, Cr^{3+}, Pb^{2+}, Co^{2+}, Cu^{2+} were shown in Fig. 7. These spectra were obtained using 3.00 mol.L^{-1} HDI-co-3-DHB-2-AP concentration, 6.66×10^{-2} mol.L^{-1} Cd^{2+} concentration and 1 mg $Pb(CH_3COO)_2.3H_2O$, $Cu(CH_3COO)_2.H_2O$, $Co(CH_3COO)_2.4H_2O$, $Zn(CH_3COO)_2.2H_2O$ or $CrCl_3$. According to Fig. 7, in spite of the emission intensity decrease there is selectivity.

The time resolved fluorescence spectroscopy of the proposed sensor in DMF is shown in Fig. 8 and the time resolved fluorescence spectroscopy data are summarized in Table 2. According to the Fig. 8 and Table 2, the time resolved fluorescence spectroscopy data of the presented sensor were found as 0.89, 1.92, 4.73, 9.61 and 10.65 % for 60, 120, 180, 240 and 300 s, respectively. According to these results, the formed between HDI-co-3-DHB-2AP and Cd(II) complex is stable and no reaction takes places within the first 120 s.

Conclusions

A new selectively polymeric Cd(II) sensor was developed using the optical methods. The obtained results showed that this toxic and harmful ion could be successfully detected by optical measurements using the synthesized polymer (HDI-co-3-DHB-2AP). The other tested ions had very low interference in the measuring wavelength. This indicated that the new sensor was very selective. The Stoke's shift value ($\Delta\lambda_{ST}$) in DMF solution was 59 cm^{-1}. Detection limit of the proposed sensor was found as 8.86×10^{-4} molL^{-1}. Stability of the sensor was determined using fluorescence lifetime data. According to these data stability of the proposed ion was found quite high. As a result, HDI-co-3-DHB-2AP could be effectively used as an optical Mn(II) sensor.

Table 2 The time resolved fluorescence spectroscopy data of HDI-co-3-DHB-2-AP and its Cd(II) complex

Time (s)	0	30	60	90	120	150	180	210	240	270	300
Wavelength (nm)	676	673	670	668	663	650	644	632	611	608	604
Degradation (%)	–	0.44	0.89	1.18	1.92	2,37	4.73	6.51	9.61	10.06	10.65

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