

Sensing of Metal Ions by Hybrid Systems of a Chiral Schiff Base Zn(II) Complex and Spiropyran

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Abstract: We have constructed three (hybrid) systems for quantitative fluorescence sensing of metal ions by using chiral Schiff base Zn(II) complexes. System 1 is a hybrid system composed of a trans-type chiral Schiff base Zn(II) complex and merocyanine (Mc), which is open-form of spiropyran (Sp) after photoisomerization. Depending on intermolecular interactions and quenching, increase (Zn^{2+}) or decrease (Cu^{2+} and Gd^{3+}) of fluorescence intensity of Zn(II) complex could be observed as functions of concentration of metal ions. System 2 is a sole component of a salen-type chiral Schiff base Zn(II) complex which can coordinate metal ions. After coordination of Zn^{2+} , Cu^{2+} , and Gd^{3+} ions, decreasing of fluorescence intensity could be found for all the cases for system 2 under the same condition to system 1. System 3 is a hybrid system being consisted of a salen-type chiral Schiff base Zn(II) complex and Mc. Decrease or increase of fluorescence intensity is in agreement with intermolecular interactions, namely affinity for the Zn(II) complex is $Zn^{2+} > Cu^{2+} > Gd^{3+}$, whereas it is reverse order for Mc. The quantitative spectroscopic nature (detected as absorption, CD, and fluorescence) of these systems is predominantly attributed to both organic ligands and Zn(II) center in a probe complex.

Keywords: Ion sensor, Fluorescence spectra, Zn(II) complexes, Schiff base, Photochromism.

1. INTRODUCTION

We make use of finding and collection of metal ions in environment and human body, of which importance is increasing year by year [1-5]. For this reason specific detection of metal ions in complicate systems composed of many components is needed.

Moreover, a way for detection of specific metal ions controlled by external stimuli is also needed in order to avoid interference of other components. Among many metal ions as mentioned in the text of inorganic chemistry, Zn(II) ion is one of typical example of a trace essential element in human body [6], in particular important for metabolism [7] and parenteral nutrition [8]. Indeed, many fluorescent sensors for Zn(II) ion used in solutions have been reported so far [9-14], and one of typical recent examples exhibit a strong fluorescence response after coordination Zn(II) ion to non-fluorescent organic ligand [15]. This organic probe is a typical example of self-response fluorescent sensors to detect existence or concentration of Zn(II) ion in a pure system, which cannot control on purpose by external stimuli. Therefore, new ideas or ways for detection should be proposed to make use of external control [16-24]. In order to realize such requirement, we will examine multi-functional compounds or hybrid functional systems composed of both fluorescent part of Zn(II) ion and external controlling parts of several mechanisms.

In the course studies on organic/inorganic hybrid functional materials composed on photochromic organic compounds and chiral metal complexes [25], the present target is aiming at application for fluorescent probes for trace metal ions. According to this concept providing benefits to realize the requirement above, we have proposed and constructed three systems, System 1, System 2, and System 3 (Figures 1-3) working well as fluorescent sensors for specific metal ions after screening tests. Coordination of metal ions to be analyzed and emission of not only chiral Schiff base Zn(II) complexes [25, 26] but also photochromic spiropyran (Sp) or merocyanine (Mc) [27-30] (quenching by energy transfer [31-33] between these components) as well as Schiff base [34] are a key principle of the present strategy of system design. Characteristic features and benefit if any of each system are summarized below:

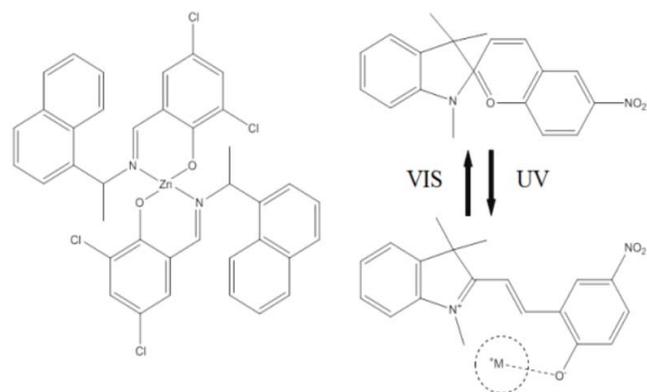


Figure 1: System 1: Trans-type chiral Schiff base Zn(II) complex (left) and Sp or Mc (right).

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Figure 2: System 2: Salen-type chiral Schiff base Zn(II) complex.

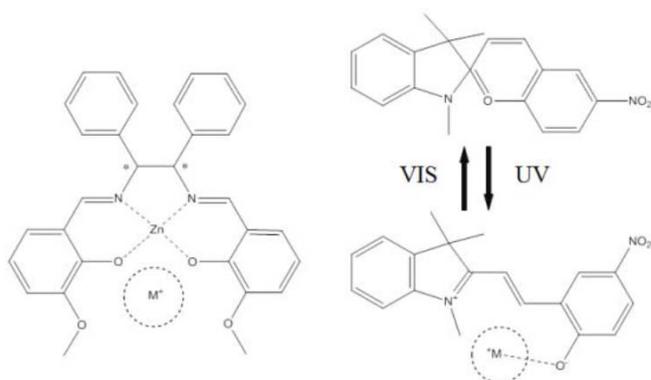


Figure 3: System 3: Salen-type chiral Schiff base Zn(II) complex (left) and Sp(Mc) (right).

As depicted in Figure 1, system 1 is composed of trans-type chiral Schiff base Zn(II) complexes [25], as a fluorescence probe with blue emission, and spiropyran (Sp) or merocyanine (Mc) [27-30]. It is well known that colorless closed-ring Sp occurs photoisomerization to purple open-ring Mc form, which is possible to coordinate metal ions, after UV irradiation. The reverse photoisomerization can occur after visible light irradiation. Among divalent ions of the first transition metals and trivalent ions of lanthanide metals, screening for coordination to Mc has also been investigated. Only Zn^{2+} , Cu^{2+} , and Gd^{3+} ions could indicate high quantitativities in methanol solutions. However, as increasing concentration of Zn^{2+} ions, fluorescence intensity of Zn(II) complexes is enhanced, while opposite tendency could be observed for Cu^{2+} and Gd^{3+} ions.

As depicted in Figure 2, system 2 is composed of salen-type chiral Schiff base Zn(II) complexes [26]. In order for comparison of qualitative coordination of Zn^{2+} , Cu^{2+} , and Gd^{3+} ions, salen-type chiral Schiff base Zn(II) complexes are employed for this system. The salen-type ones can act as fluorescence probes as well as direct coordination sites for metal ions to be analyzed.

Not only Zn^{2+} , Cu^{2+} , and Gd^{3+} ions but also alkali and alkali earth ions were investigated for screening. Consequently, Ba^{2+} , Ca^{2+} , and Sr^{2+} ions could also exhibit fairly quantitative behavior and detection of CD spectra as well as fluorescence spectra is proved to be useful for metal ion sensing.

As depicted in Figure 3, system 3 is hybrid systems composed of spiropyran (Sp) or merocyanine (Mc) and salen-type chiral Schiff base Zn(II) complexes [26]. It may be straightforwardly expected specific coordination of Zn^{2+} , Cu^{2+} , and Gd^{3+} ions, fluorescence quenching by Mc as well as CD detection of Zn(II) complexes, in addition, competition coordination of metal ions to be analyzed between two potential sites. However, the merit of this complicated system is elucidating mechanism of intermolecular interactions and spectroscopic features by means of metal coordination.

2. METHODS

2.1. Materials

Analytical pure Sp (Mc), 1', 3'-Dihydro-1', 3', 3'-trimethyl-6-nitrospiro [2H-1-benzopyran- 2, 2'-(2H)-indole], (Aldrich) and methanol (Kanto) were used as received without further purification. Trans-type [25] and salen-type [26] chiral Schiff base Zn(II) complexes were prepared according to the literature procedures.

2.2. Experimental Conditions

System 1: Screening of metal ions was carried out as follows: Hybrid system of 0.005 mM ($M = \text{mol}/\text{dm}^3$) trans-type Zn(II) complex, 0.1 mM Sp (Mc), and transition metal (II) ions of Cu^{2+} and Zn^{2+} or lanthanide (III) ions of La^{3+} , Ce^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Er^{3+} , Yb^{3+} , and Lu^{3+} (0.04, 0.06, and 0.08 mM) in a methanol solution. Then, we have measured fluorescence intensities of system 1 after UV irradiation ($\lambda_{\text{ex}} = 280 \text{ nm}$).

System 2: Screening of metal ions was carried out as follows: Hybrid system of 0.01 mM salen-type Zn(II) complex and Zn^{2+} , Cu^{2+} , Gd^{3+} ions, all alkali and alkali earth metal ions (0.0125, 0.0500, and 0.1000 mM) in a methanol solution for comparison with system 1. Then, we have measured fluorescence intensities of system 2 ($\lambda_{\text{ex}} = 360 \text{ nm}$).

System 3: Testing Zn^{2+} , Cu^{2+} , and Gd^{3+} ions in a methanol solution under three conditions was carried out as follows: <1> Hybrid systems of 0.02 mM Zn(II) complex, 0.1 mM Sp (Mc), and Gd^{3+} ion (0.0125,

0.0250, 0.0375, 0.0500, 0.0625, 0.0750, 0.0875, and 0.1000 mM). <2> Hybrid systems of 0.02 mM Zn(II) complex, 0.05 mM Sp (Mc), and Cu²⁺ ion (0.0025, 0.0050, 0.0075, 0.0100, 0.0125, 0.0150, 0.0175, and 0.0200 mM). <3> Hybrid systems of 0.01 mM Zn(II) complex, 0.1 mM Sp(Mc), and Zn²⁺ ion (0.0125, 0.0250, 0.0375, 0.0500, 0.0625, 0.0750, 0.0875, and 0.1000 mM). Then, we have measured fluorescence intensities ($\lambda_{\text{ex}} = 360$ and 533 nm), and UV-vis and CD spectra for system 3 after UV irradiation for comparison with systems 1 and 2.

2.3. Physical Measurements

Electronic spectra have been measured on a JASCO V-570 UV/VIS/NIR spectrophotometer in the range of 800-200 nm at 298 K. Circular Dichroism (CD) spectra have been measured on a JASCO J-820 spectropolarimeter in the range of 800-200 nm at 298 K. Fluorescence spectra have been recorded on a JASCO FP-6200 spectrophotometer at 298K. UV light irradiation (for opening Sp to form Mc) has been carried out using a Hayashi UV lamp (1.0 mW/cm²).

3. RESULTS AND DISCUSSION

3.1. System 1

As mentioned in METHODS, we have measured fluorescence intensity of system 1 with Zn²⁺ and Gd³⁺ ions after UV irradiation ($\lambda_{\text{ex}} = 280$ nm). As shown in Figure 4, the fluorescence intensity ($\lambda_{\text{em}} = 460$ nm) indicated linear correlation to the concentration of Zn²⁺ and Gd³⁺ ions.

As shown Figure 4, increasing of concentration of Zn²⁺ ion results in quantitatively increasing fluorescence intensity of a Zn(II) complex, while increasing of concentration of Gd³⁺ ion results in quantitatively decreasing fluorescence intensity of a Zn(II) complex. Partially unclear behavior of ions concentration dependence of intensity may be attributed to incomplete association of metal ions. Because slight deviation from perfectly linear correlation was observed (probably concerning coordination to Mc) [27-30], data of Cu²⁺ was excluded from Figure 4. However, the tendency of Cu²⁺ ion is exactly similar to that of Gd³⁺ ion.

The reason of different tendency of Zn²⁺ ion and Cu²⁺ and Gd³⁺ ions may be elucidated by excitation energy of Zn(II) complex transfers to Mc-metal complex and intermolecular interaction between Zn(II) complex and Mc. Zn²⁺ ion coordinated to Mc also plays a similar

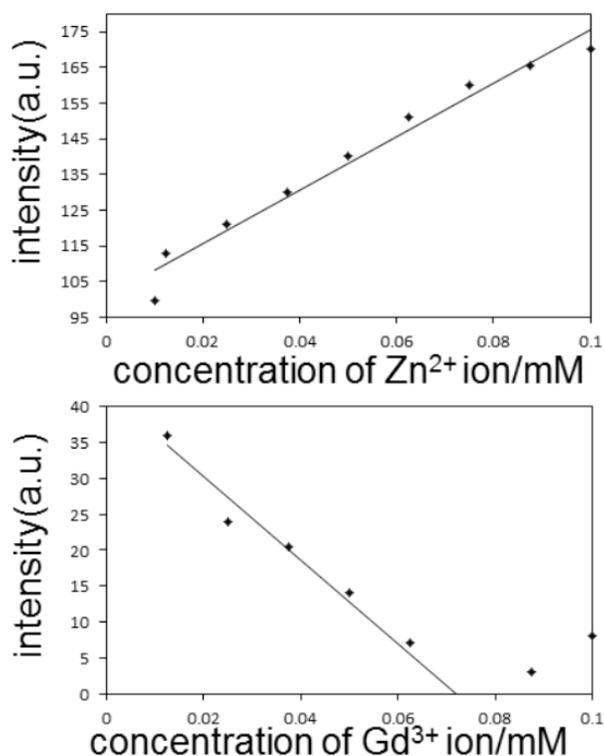


Figure 4: Calibration curves of fluorescence intensity ($\lambda_{\text{ex}} = 280$ nm) of a trans-type Zn(II) complex for system 1 as a function of concentration of analyzed Zn²⁺ (upper) and Gd³⁺ (lower) ions.

role as emissive complexes and it leads to enhance fluorescence intensity of a trans-type Zn(II) complex. On the other hand, paramagnetic Cu²⁺ and Gd³⁺ ions coordinated to Mc act as a good quencher which cause energy transfer enable to continue emission.

3.2. System 2

As for system 2, we have measured fluorescence intensity with Cu²⁺, Zn²⁺, and Gd³⁺ ions. As shown in Figure 5, the fluorescence intensity ($\lambda_{\text{em}} = c.a. 480$ nm) indicated similarly linear correlation to the concentration of Zn²⁺, Cu²⁺, Gd³⁺ ions, whose increasing/decreasing intensity as a function of ion concentration is different from system 1. For comparison of system 1, more well-coordinated but unreliable calibration curves for Ba²⁺, Ca²⁺, and Sr²⁺ ions are neglected (not shown).

Uniform decreasing of fluorescence intensity is explained that coordination of metal ions to be analyzed to the salen-type Zn(II) complex makes differences in electronic structures as binuclear metal complexes similarly, which do not indicate intense emission. Deviation from linearity for Gd³⁺ is ascribed to coordination.

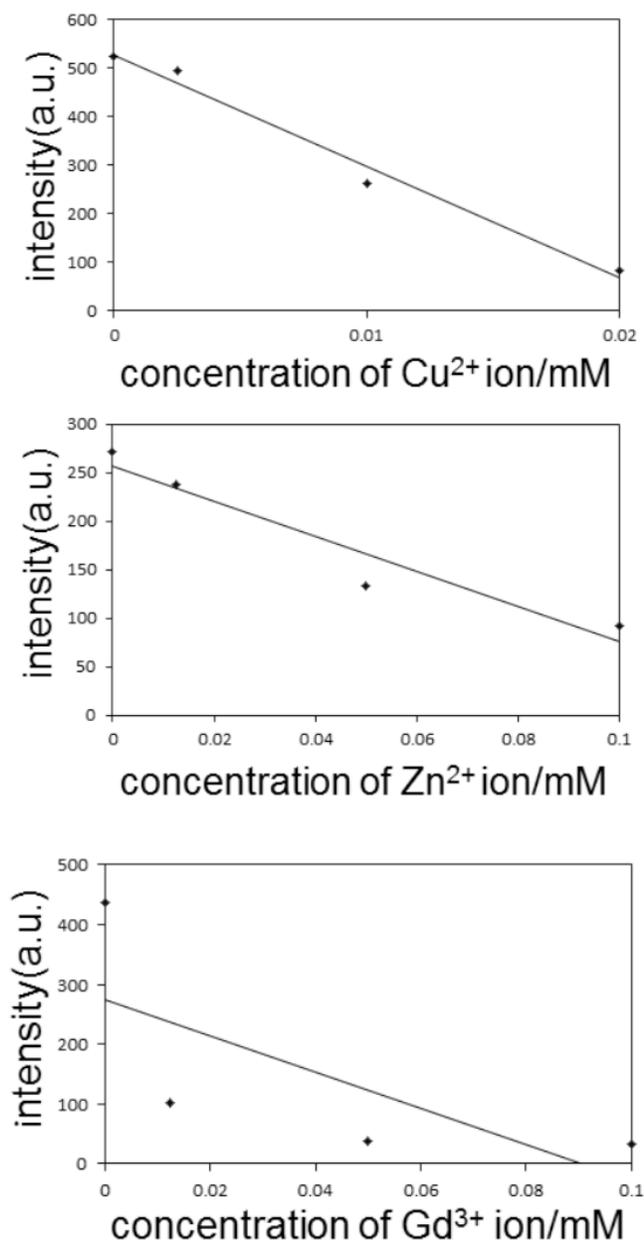


Figure 5: Calibration curves of fluorescence intensity ($\lambda_{\text{ex}} = 360 \text{ nm}$) of a salen-type Zn(II) complex for system 2 as a function of with concentration of analyzed Cu^{2+} (upper), Zn^{2+} (middle), and Gd^{3+} (lower) ions.

3.3. System 3

As for system 3, we have measured UV-vis spectra with the corresponding CD spectra (Figures 6, 8, 10) and fluorescence intensity (Figures 7, 9, 11) with Gd^{3+} (Figures 6, 7), Cu^{2+} (Figures 8, 9), Zn^{2+} (Figures 10, 11) ions before and after UV irradiation. Although these are hybrid systems, the CD spectra provide selective information of chiral species (chiral salen-type Zn(II) complexes). Because only system 3 indicated clear spectral changes detectable with CD spectra. Additionally, selective information based on

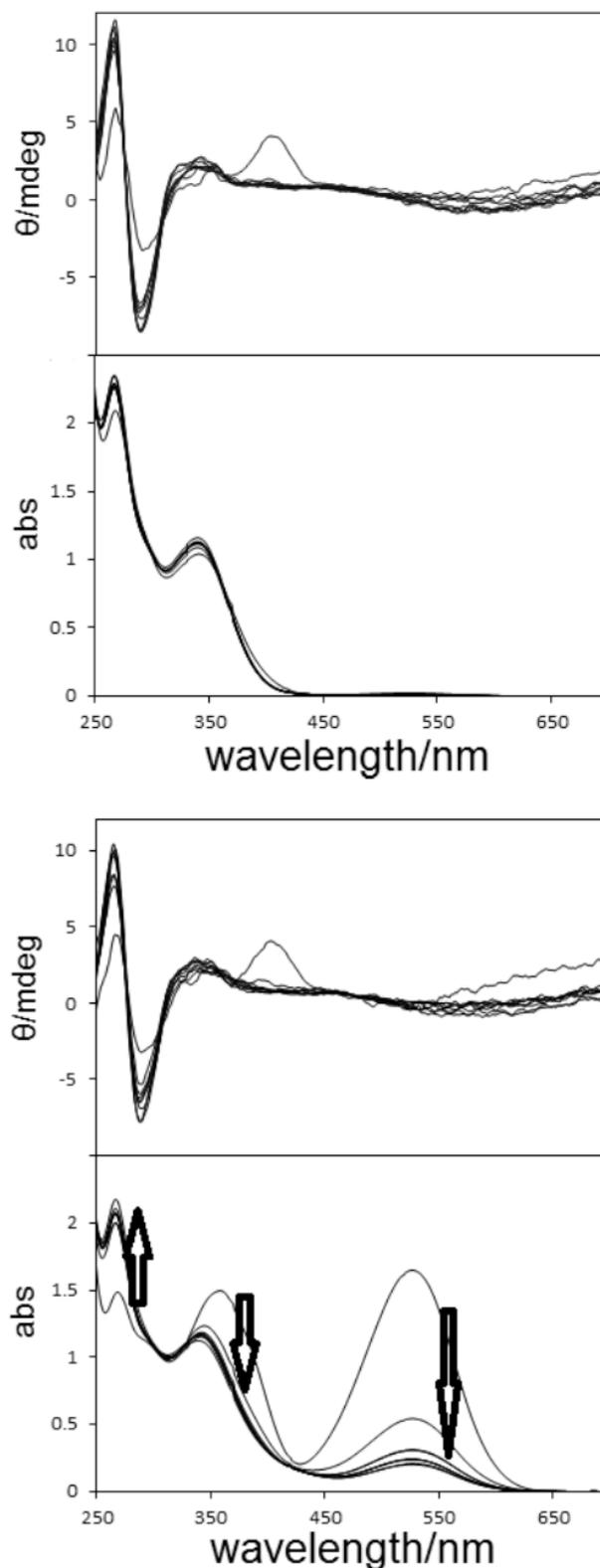


Figure 6: Comparison of CD and UV-vis spectra of system 3 with Gd^{3+} ion before (upper) and after (lower) irradiation of UV light. Arrows emphasize spectral changes due to formation of Mc after UV light irradiation.

fluorescence spectra of a salen-type Zn(II) complex ($\lambda_{\text{em}} = \text{c.a. } 480 \text{ nm}$) and Mc ($\lambda_{\text{em}} = 620 \text{ nm}$) can be

obtained by changing excitation wavelengths. Moreover, these spectral changes before and after irradiation of UV light are in agreement with Sp (only sites of a salen-type Zn(II) complex can coordinate metal ions to be analyzed) and Mc (both sites of Mc and a salen-type Zn(II) complex can coordinate metal ions to be analyzed) to investigate competition coordination.

In Figures 7, 9, 11, obviously common CD peaks for system 3 at 260 and 280 nm or 410 nm are assigned to $\pi-\pi^*$ band of phenyl groups or salicylaldehyde moiety, respectively. Obviously common absorption peaks for system 3 at 260 nm, 340 nm, and 530 nm are assigned to $\pi-\pi^*$ band of phenyl groups or salicylaldehyde moiety, and Mc, respectively.

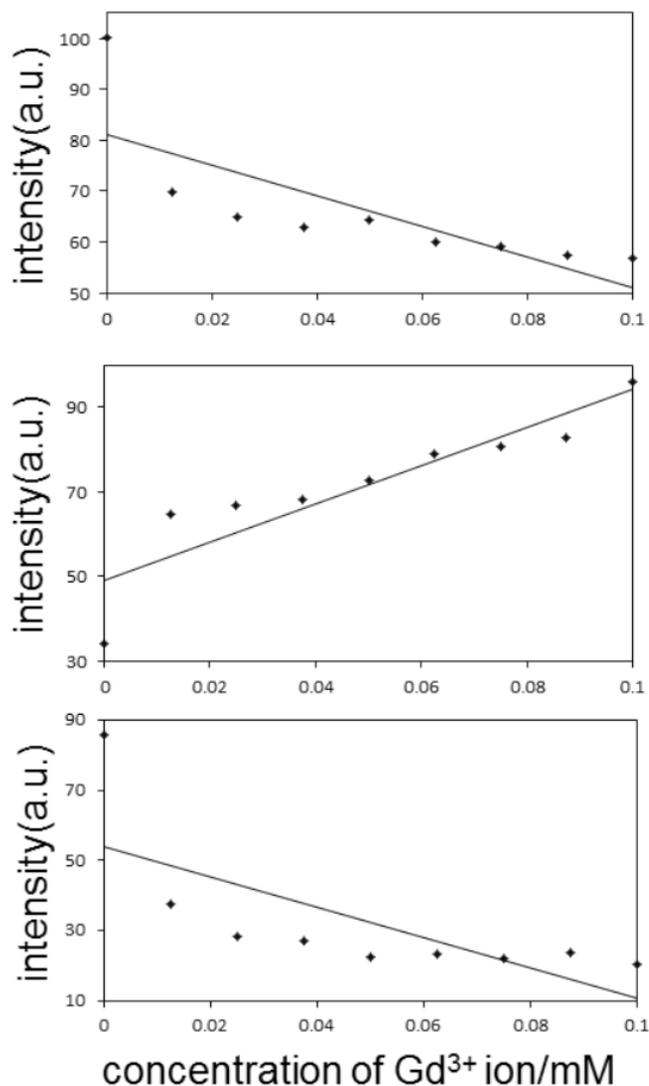


Figure 7: comparison of calibration curves of fluorescence intensity spectra of system 3 with Gd^{3+} ion ($\lambda_{ex} = 360$ nm: before UV irradiation (upper) and after UV irradiation (middle) and $\lambda_{ex} = 533$ nm (lower)).

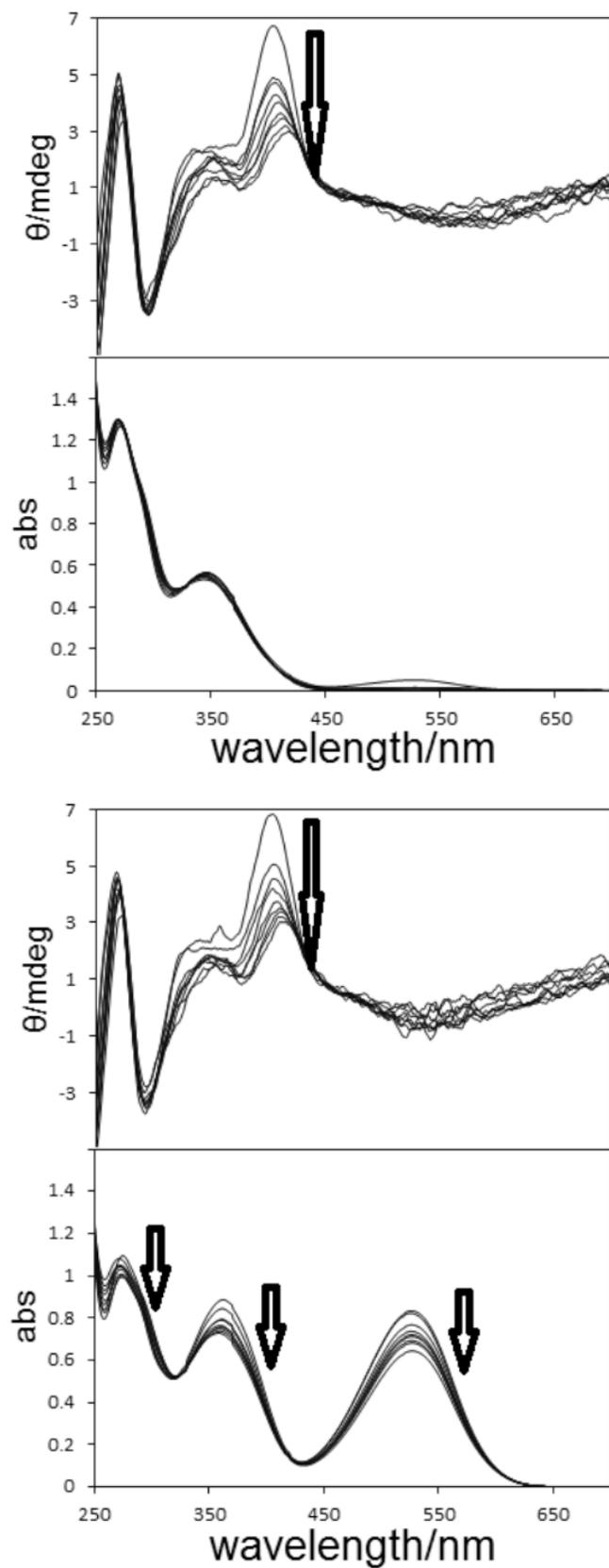


Figure 8: Comparison of CD and UV-vis spectra of system 3 with Cu^{2+} ion before (upper) and after (lower) irradiation of UV light. Arrows emphasize spectral changes due to formation of Mc after UV light irradiation.

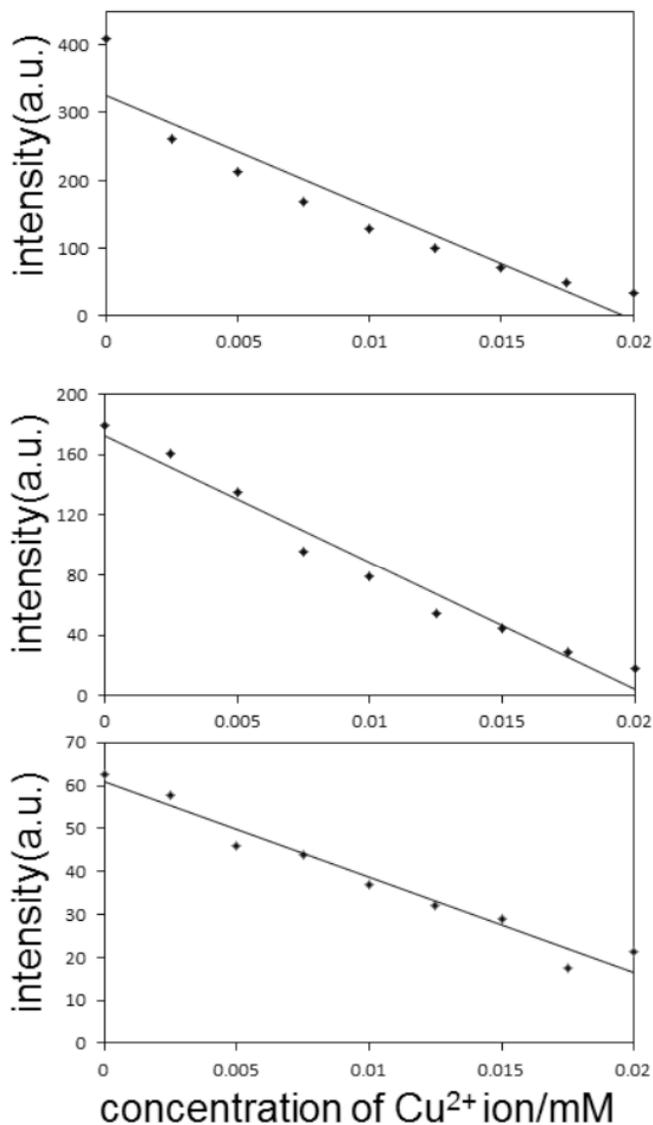


Figure 9: comparison of calibration curves of fluorescence intensity spectra of system 3 with Cu²⁺ ion ($\lambda_{\text{ex}} = 360$ nm: before UV irradiation (upper) and after UV irradiation (middle) and $\lambda_{\text{ex}} = 533$ nm (lower)).

In the case of Gd³⁺ ion, after irradiation of UV light, CD peaks at 280 nm indicated definite changes, while those at 410 nm indicated little changes. Absorption peaks at 260 nm increased, while the peaks at 360 and 530 nm decreased. Fluorescence intensity increased for Zn(II) complex ($\lambda_{\text{ex}} = 360$ nm) and decrease for Mc ($\lambda_{\text{ex}} = 533$ nm) after UV irradiation.

In the case of Cu²⁺ ion, after irradiation of UV light, CD peaks at 260, 280, and 410 nm decreased quantitatively. UV-vis peaks at 260 nm increased, while the peaks at 360 and 530 nm decreased. The magnitude of decrease of the peak at 530 nm of Cu²⁺ ion is much smaller than that of Gd³⁺ ion. Fluorescence intensity decreased for Zn(II) complex ($\lambda_{\text{ex}} = 360$ nm)

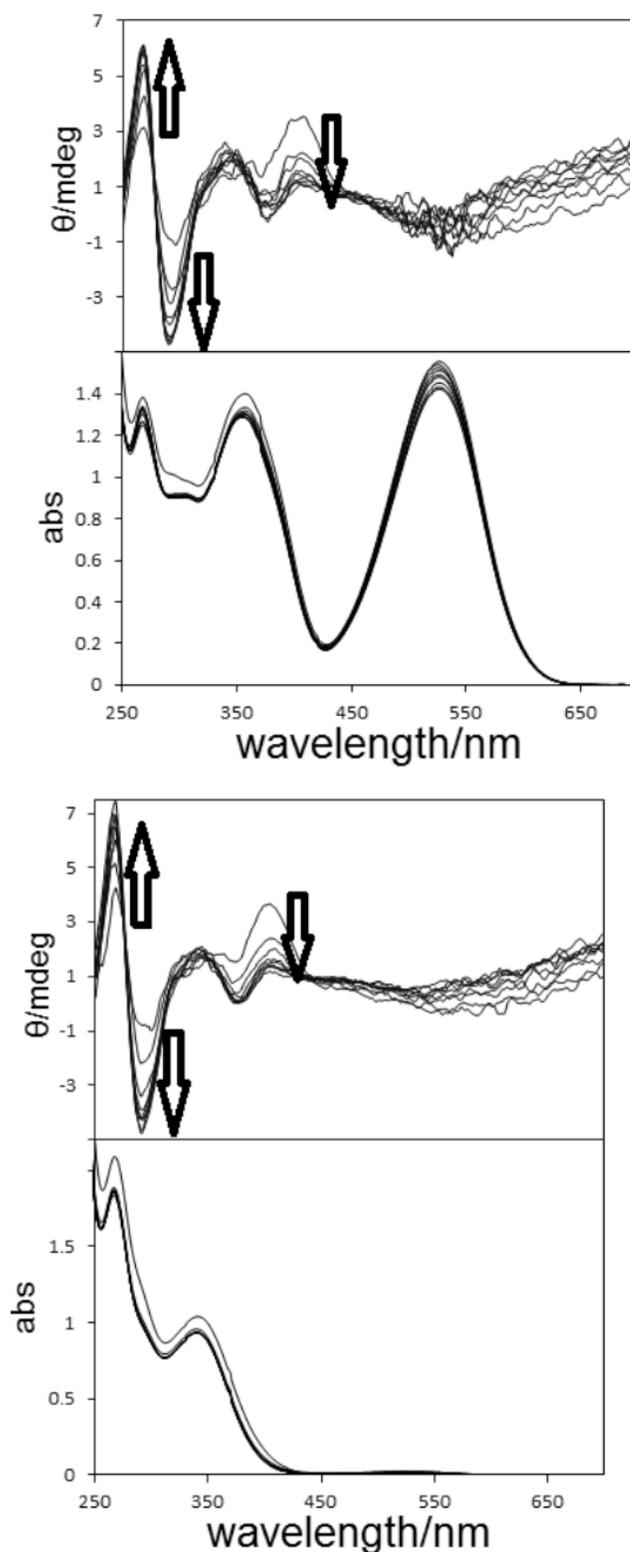


Figure 10: Comparison of CD and UV-vis spectra of system 3 with Zn²⁺ ion before (upper) and after (lower) irradiation of UV light. Arrows emphasize spectral changes due to formation of Mc after UV irradiation

after UV irradiation. However, the peaks of Mc ($\lambda_{\text{ex}} = 533$ nm) is not reproducible.

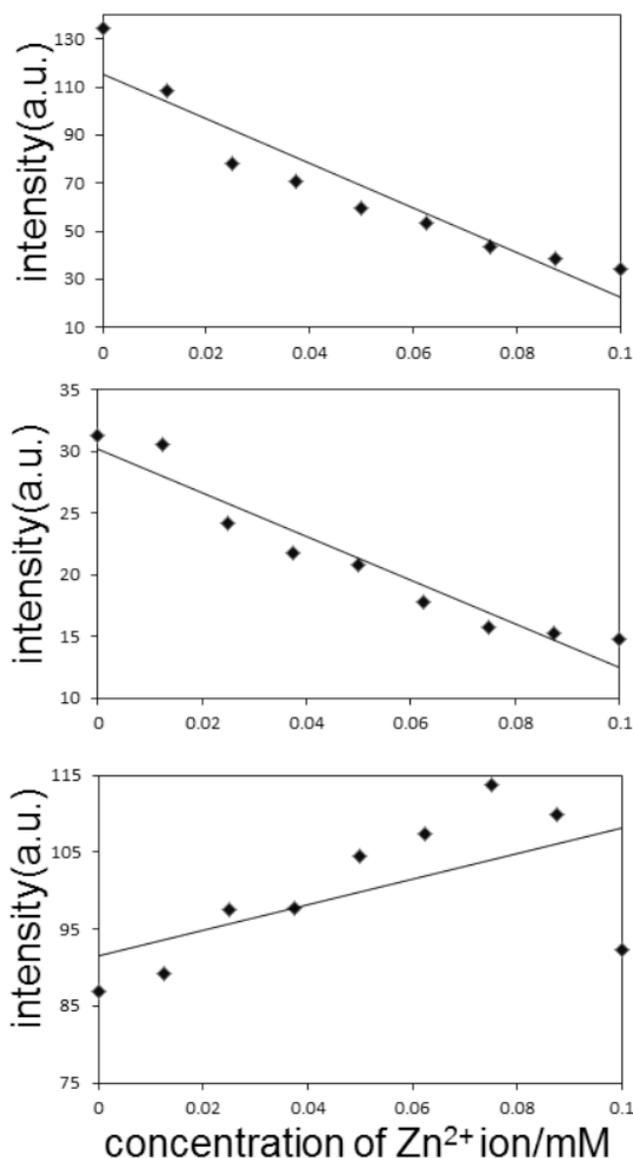


Figure 11: comparison of calibration curves of fluorescence intensity spectra of system 3 with Zn²⁺ ion ($\lambda_{\text{ex}} = 360$ nm: before UV irradiation (upper) and after UV irradiation (middle) and $\lambda_{\text{ex}} = 533$ nm (lower)).

In the case of Zn²⁺ ion, quantitative spectral changes could be observed for CD bands at 260, 280, and 410 nm and little spectral changes also could be observed for UV-vis bands at 530 nm in contrast to Cu²⁺ or Gd³⁺ ion. However, fluorescence intensity linearly decreased for Zn(II) complex ($\lambda_{\text{ex}} = 360$ nm) and almost linearly increased for Mc ($\lambda_{\text{ex}} = 533$ nm) as a function of concentration of doped Zn²⁺ ion. Partially unclear behavior of ions concentration dependence of intensity may be attributed to incomplete association of metal ions.

Accordingly, competitive coordination and changes after UV irradiation for system 3 may be summarized

as follows: It seems that Gd³⁺ ion transferred to from Zn(II) complex to Mc. Competitive coordination of Cu²⁺ ion to Zn(II) complex (major) and Mc (minor) seem to occur. It appears Zn²⁺ ion coordinates to Zn(II) complex consistently.

Furthermore, according to UV-vis, CD and fluorescence spectra, coordination affinity to salen chiral Zn(II) complex in system 3 are found to be Zn²⁺ > Cu²⁺ > Gd³⁺ and that to Mc is in reverse order. This result doesn't contradict that in system 1. Making use of these properties, we can remove these metals selectively in soil and water, including heavy metals and also apply those to a chromatography, an ion exchange resin and detoxification effects.

4. CONCLUSION

In summary, it should be noted that excitation and fluorescence wavelengths are $\lambda_{\text{ex}} = 260$ nm and $\lambda_{\text{em}} = 460$ nm for a trans-type Zn(II) complex, $\lambda_{\text{ex}} = 360$ nm and $\lambda_{\text{em}} = 480$ nm for a salen-type Zn(II) complex, and $\lambda_{\text{ex}} = 533$ nm and $\lambda_{\text{em}} = 620$ nm for Mc. By using the results, we have constructed and tested three (hybrid) systems for metal ion sensing for the first time. System 1 elucidates that only Zn²⁺, Cu²⁺, and Gd³⁺ ions exhibit quantitative changes of fluorescence intensities of (not directly coordinating Mc but) trans-type Zn(II) complexes as functions of concentration of ions to be analyzed. System 2 elucidates that Zn²⁺, Cu²⁺, and Gd³⁺ ions (as well as Ba²⁺, Ca²⁺, and Sr²⁺ ions more fairly) exhibit quantitative decrease of fluorescence intensities of salen-type Zn(II) complexes as a function of directly coordinated metal ions. System 3 elucidates not only experimentally confirming facts of the quantitative changes of fluorescence intensities but also competitive coordination mechanism between salen-type Zn(II) complexes and Mc of Zn²⁺, Cu²⁺, and Gd³⁺ ions in methanol solutions. Development of application to ion sensing with supramolecular systems can be also expected.

REFERENCES

- [1] Shi S, Zhang Y, Chen X, Peng M. Investigation of Flavonoids Bearing Different Substituents on Ring C and Their Cu²⁺ Complex Binding with Bovine Serum Albumin: Structure Affinity Relationship Aspects. *J Agric Food Chem* 2011; 59: 10761-69. <http://dx.doi.org/10.1021/jf2027523>
- [2] Chiu Y-C, Okajima T, Murakawa T, Uchida M, Taki M, Hirota S, *et al.* Kinetic and Structural Studies on the Catalytic Role of the Aspartic Acid Residue Conserved in Copper Amine Oxidase. *Biochemistry* 2006; 45: 4105-120. <http://dx.doi.org/10.1021/bi052464i>

- [3] Coughtrey PJ, Martin MH. The uptake of lead, zinc, cadmium, and copper by the pulmonate mollusc, *Helix aspersa muller*, and its relevance to the monitoring of heavy metal contamination of the environment. *Oecologia* 1977; 27: 65-74.
<http://dx.doi.org/10.1007/BF00345685>
- [4] VanZile ML, Cosper NJ, Scott RA, Giedroc DP. The Zinc Metalloregulatory Protein *Synechococcus* PCC7942 SmtB Binds a Single Zinc Ion per Monomer with High Affinity in a Tetrahedral Coordination Geometry. *Biochemistry* 2000; 39: 11818-29.
<http://dx.doi.org/10.1021/bi001140o>
- [5] Major DT, Gao J. A Combined Quantum Mechanical and Molecular Mechanical Study of the Reaction Mechanism and α -Amino Acidity in Alanine Racemase. *J Am Chem Soc* 2006; 128: 16345-57.
<http://dx.doi.org/10.1021/ja066334r>
- [6] McClung JP, Scrimgeour AG. Zinc: an essential trace element with potential benefits to soldiers. *Mil Med* 2005; 170: 1048-52.
- [7] Smith Jr. JC, McDaniel EG, Fan FF, Halsted JA. Zinc: A Trace Element Essential in Vitamin A Metabolism. *Science* 1973; 181: 954-55.
<http://dx.doi.org/10.1126/science.181.4103.954>
- [8] Jeejeebhoy K. Zinc: an essential trace element for parenteral nutrition. *Gastroenterology* 2009; 137: S7-12.
<http://dx.doi.org/10.1053/j.gastro.2009.08.014>
- [9] Ojida A, Takashima I, Kohira T, Nonaka H, Hamachi I. Turn-On Fluorescence Sensing of Nucleoside Polyphosphates Using a Xanthene-Based Zn(II) Complex Chemosensor. *J Am Chem Soc* 2008; 130: 12095-101.
<http://dx.doi.org/10.1021/ja803262w>
- [10] Hou J, Song F, Wang L, Wei G, Cheng Y, Zhu C. In Situ Generated 1:1 Zn(II)-Containing Polymer Complex Sensor for Highly Enantioselective Recognition of N-Boc-Protected Alanine. *Macromolecules* 2012; 45: 7835-42.
<http://dx.doi.org/10.1021/ma301553y>
- [11] Pandey R, Kumar P, Singh AK, Shahid M, Li P-Z, Singh SK, et al. Fluorescent Zinc(II) Complex Exhibiting "On-Off-On" Switching Toward Cu^{2+} and Ag^+ Ions. *Inorg Chem* 2011; 50: 3089-97.
<http://dx.doi.org/10.1021/ic1018086>
- [12] Germain ME, Vargo TR, McClure BA, Rack JJ, van Patten PG, Odoi M, et al. Quenching Mechanism of Zn(Salicylaldehyde) by Nitroaromatics. *Inorg Chem* 2008; 47: 6203-11.
<http://dx.doi.org/10.1021/ic702469g>
- [13] Crivat G, Kikuchi K, Nagano T, Priel T, Hershinkel M, Sekler I, et al. Fluorescence-Based Zinc Ion Sensor for Zinc Ion Release from Pancreatic Cells. *Anal Chem* 2006; 78: 5799-804.
<http://dx.doi.org/10.1021/ac060764j>
- [14] Khatua S, Choi SH, Lee J, Kim K, Do Y, Churchill DG. Aqueous Fluorometric and Colorimetric Sensing of Phosphate Ions by a Fluorescent Dinuclear Zinc Complex. *Inorg Chem* 2009; 48: 2993-99.
<http://dx.doi.org/10.1021/ic8022387>
- [15] Lin H-Y, Cheng P-Y, Wan C-F, Wu A-T. A turn-on and reversible fluorescence sensor for zinc ion. *Analyst* 2012; 137: 4415-17.
<http://dx.doi.org/10.1039/c2an35752f>
- [16] Byrne RJ, Stitzel SE, Diamond D. Photo-regenerable surface with potential for optical sensing. *J Mater Chem* 2006; 16: 1332-37.
<http://dx.doi.org/10.1039/b516400a>
- [17] Sumalekshmy S, Fahrni CJ. Metal-Ion-Responsive Fluorescent Probes for Two-Photon Excitation Microscopy. *Chem Mater* 2011; 23: 483-500.
<http://dx.doi.org/10.1021/cm1021905>
- [18] Yuasa J, Fukuzumi S. OFF-OFF-ON Switching of Fluorescence and Electron Transfer Depending on Stepwise Complex Formation of a Host Ligand with Guest Metal Ions. *J Am Chem Soc* 2008; 130: 566-75.
<http://dx.doi.org/10.1021/ja0748480>
- [19] Germain ME, Knapp MJ. Turn-on Fluorescence Detection of H_2O_2 and TATP. *Inorg Chem* 2008; 47: 9748-50.
<http://dx.doi.org/10.1021/ic801317x>
- [20] Rosell FI, Mauk MR, Mauk AG. pH- and Metal Ion-Linked Stability of the Hemopexin-Heme Complex. *Biochemistry* 2005; 44: 1872-79. <http://www.ncbi.nlm.nih.gov/pubmed/15697213>
<http://dx.doi.org/10.1021/bi0480077>
- [21] Dean NE, Hancock RD, Cahill CL, Frisch M. Affinity of the Highly Preorganized Ligand PDA (1,10-Phenanthroline-2,9-dicarboxylic acid) for Large Metal Ions of Higher Charge. A Crystallographic and Thermodynamic Study of PDA Complexes of Thorium(IV) and the Uranyl(VI) ion. *Inorg Chem* 2008; 47: 2000-10.
<http://dx.doi.org/10.1021/ic701574j>
- [22] Lo H-S, Yip S-K, Wong KM-C, Zhu N, Yam VW-W. Selective Luminescence Chemosensing of Potassium Ions Based on a Novel Platinum(II) Alkynylcalix[4]crown-5 Complex. *Organometallics* 2006; 25: 3537-40.
<http://dx.doi.org/10.1021/om060218f>
- [23] Zhao Q, Li F, Liu S, Yu M, Liu Z, Yi T, Huang C. Highly Selective Phosphorescent Chemosensor for Fluoride Based on an Iridium(III) Complex Containing Arylborane Units. *Inorg Chem* 2008; 47: 9256-64.
<http://dx.doi.org/10.1021/ic800500c>
- [24] Männel-Croisé C, Zelder F. Complex Samples Cyanide Detection with Immobilized Corrinoids. *Appl Mater Interfaces* 2012; 4: 725-29.
<http://dx.doi.org/10.1021/am201357u>
- [25] Akitsu T. Photofunctional supramolecular solution systems of Chiral Schiff Base Nickel(II), Copper(II), and Zinc(II) complexes and photochromic azobenzenes. *Polyhedron* 2007; 26: 2527-35.
<http://dx.doi.org/10.1016/j.poly.2006.12.031>
- [26] Hiratsuka T, Shibata H, Akitsu T. Structures and Properties of 3d-4f and 3d Chiral Schiff base Complexes. *Crystallography* 2010; 3: 45-64. https://www.novapublishers.com/catalog/product_info.php?products_id=36359&osCsid=168c08748e890891d8335a0f23b338ea
- [27] Arai K, Shitara Y, Ohyama T. Preparation of photochromic spiropyran linked to methyl cellulose and photoregulation of their properties. *J Mater Chem* 1996; 6: 11-14.
<http://dx.doi.org/10.1039/jm9960600011>
- [28] Wojtyk JTC, Kazmaier PM, Buncel E. Effects of metal ion complexation on the spiropyran-merocyanine interconversion: development of a thermally stable photo-switch. *Chem Commun* 1998; 16: 1703-704.
<http://dx.doi.org/10.1039/a804908d>
- [29] Shao N, Wang H, Gao X-D, Yang R-H, Chan W-H. Spiropyran-Based Fluorescent Anion Probe and its Application for Urinary Pyrophosphate Detection. *Anal Chem* 2010; 82: 4628-36.
<http://dx.doi.org/10.1021/ac1008089>
- [30] Xie X, Mistlberger G, Bakker E. Reversible Photodynamic Chloride-Selective Sensor Based on Photochromic Spiropyran. *J Am Chem Soc* 2012; 134: 16929-32.
<http://dx.doi.org/10.1021/ja307037z>
- [31] Shepherd GB, Papadakis N, Hammes GG. Fluorescence Energy-Transfer Measurements between Coenzyme A and Flavin Adenine Dinucleotide Binding Sites of the *Escherichia coli* Pyruvate Dehydrogenase Multienzyme Complex. *Biochemistry* 1976; 15: 2888-93.
<http://dx.doi.org/10.1021/bi00658a029>

- [32] Takashi R. Fluorescence Energy Transfer between Subfragment- 1 and Actin Points in the Rigor Complex of Actosubfragment- I. *Biochemistry* 1979; 18: 5164-69.
<http://dx.doi.org/10.1021/bi00590a021>
- [33] Shepherd GB, Hammes GG. Fluorescence Energy Transfer Measurements in the Pyruvate Dehydrogenase Multienzyme Complex from *Escherichia coli* with Chemically Modified Lipoic Acid. *Biochemistry* 1977; 16: 5234-41.
<http://dx.doi.org/10.1021/bi00643a012>
- [34] Liu H, Fu Z, Xu K, Cai H, Liu X, Chen M. Structure-Property Relationship of Highly π -Conjugated Schiff-Base Moiety in Liquid Crystal Diepoxide Polymerization and Mesophases Stabilization. *J Phys Chem B* 2011; 115: 7568-77.
<http://dx.doi.org/10.1021/jp202998x>

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