Determination of Mercury(II) in Aquatic Plants Using Quinoline-Thiourea Conjugates as a Fluorescent Probe

Guodong FENG, Yuanyuan DING, Zhiyong GONG, Yanna DAI, and Qiang FEI[†]

Department of Analytical Chemistry, College of Chemistry, Jilin University, Changchun 130021, P. R. China

In this study, a quinoline-thiourea conjugate (1-phenyl-3-(quinoline-8-yl) thiourea, PQT) was synthesized and used as a fluorescence sensor to detect mercury ion. The observation is coincident with the well-documented phenomenon that a thiocarbonyl-containing group on a fluorochrome quenches the fluorescence due to the heavy atom effect of the S atom. The large fluorescence enhancement of PQT in the buffered MeCN-water mixture (1/1 v/v; HEPES 100 mM; pH 8.0) was caused by the Hg²⁺ induced transformation of the thiourea function into a urea group. As such, protic solvents can be ascribed to hydrogen bond formation on the carbonyl oxygen to reduce the internal conversion rate. The fluorescence intensity of PQT was enhanced quantitatively with an increase in the concentration of mercury ion. The limit of detection of Hg²⁺ was 7.5 nM. The coexistence of other metal ions with mercury had no obvious influence on the detection of mercury. A quinolone-thiourea conjugate was used as a fluorescent probe to detect Hg²⁺ in aquatic plants and the experimental results were satisfactory.

Keywords Fluorescent probe, PQT, mercury, aquatic plants

(Received April 6, 2013; Accepted May 16, 2013; Published July 10, 2013)

Introduction

Today, aquatic food is an important component of the human diet. Besides being a good source of minerals (phosphorus, iron, zinc, and potassium), vitamins (A, B6, and B12) and proteins, aquatic food products are low in saturated fat and rich in unsaturated fat.¹ However, aquatic food contamination is frequently a subject of public debate and concern. This possible hazard is closely related to the fact that aquatic ecosystems act as the ultimate repository for all classes of contaminants.² Mercury, a ubiquitous metal in water systems with both natural and anthropogenic sources, deserves special scrutiny due to its high toxicity. Mercury can be transferred from aquatic plants to aquatic food webs.^{3,4} Therefore, the determination of mercury in aquatic plants is very important.

Many techniques such as atomic absorption/emission spectroscopy,⁵⁻¹¹ inductively coupled plasma mass spectrometry (ICP-MS)¹² and electrochemical methods^{13,14} have been used to detect Hg²⁺ in environmental samples. Nevertheless, they require expensive and sophisticated instrumentation.^{15,16} In recent years, many efforts have been made to design various specialty chemosensors for Hg²⁺ ion detection.¹⁷⁻³² A very attractive approach focuses on the research of fluorescent Hg²⁺ ion sensors,³³⁻⁴⁰ which is highly effective for discriminating the presence of a target over the spectrally complex background inherent in real-world samples. Fluorescent probes for Hg²⁺ have been designed based on a reversible or irreversible fluorescence reaction. Although receptor-type probes are useful for reversible detection of Hg²⁺, dissociation constants (*K_d*)

toward Hg²⁺ are determinant for their working concentration ranges, and this point is likely to limit their general and practical use.⁴¹ Thus, it is accepted that the detection of Hg²⁺ at ppb levels with high selectivity can be achieved by fluorescent probes based on irreversible fluorescence reactions rather than receptor-type probes.⁴¹⁻⁵⁷ For the design of the irreversible fluorescent probes for Hg²⁺ detection, oxymercuration reaction has been recently explored.^{56,57} The design principle is quite interesting, but the technique requires high temperatures or long reaction times, especially for detecting Hg²⁺ at ppb levels. Although it is challenging to propose a totally new irreversible reaction such as oxymercuration, it seems difficult to find a more useful irreversible reaction than desulfurization, which has dominated as the most reliable irreversible reaction for the design of a fluorescent probe for Hg²⁺ detection. On the design principle by recourse of desulfurization, thiourea has played the most important role among thiocarbonyl containing groups.⁵⁸⁻⁶⁵

Herein, we have synthesized a quinolone-thiourea conjugate (1-phenyl-3-(quinoline-8-yl) thiourea, PQT)^{66,67} for desulfurization by Hg²⁺. The fluorescent probe has high sensitivity and selectivity for Hg²⁺ over other metal ions. We detected mercury in aquatic plants using the quinolone-thiourea conjugate as a fluorescent probe. In this study, an experimental approach based on incubation in indoor microcosms was tested to investigate the possible accumulation effect of the presence of mercury on aquatic plants in constructed freshwater ecosystems.

Experimental

Reagents and chemicals

Dichloromethane, acetonitrile and acetic ether were purchased from Tianjin Tiantai Fine Chemical Co., Ltd. (Tianjin, China).

[†] To whom correspondence should be addressed.
E-mail: crdcai@jlu.edu.cn

Scheme 1 Synthetic route of PQT. Reagents and conditions: (I) dried CH_2Cl_2 , stirred for 48 h.

A supply of 8-aminoquinoline was purchased from Matrix Scientific (Columbia, SC). Phenyl isothiocyanate was purchased from Acros Organics (Fair Lawn, NJ). $\text{Hg}(\text{NO}_3)_2 \cdot 1/2 \text{H}_2\text{O}$ was purchased from Taixing Chemical Co., Ltd. (Nanjing, China). EDTA was purchased from Beijing Chemical Works (Beijing, China). HEPES was purchased from Beijing Dingguo Changsheng Biotechnology Co., Ltd. (Beijing, China). Twice-distilled water was used throughout all experiments. Thin layer chromatography (TLC) was carried out using silica gel 60 F254, and column chromatography was conducted over silica gel (300–400 mesh), both of which were obtained from the Qingdao Ocean Chemicals (Qingdao, China). All metal ion solutions were diluted from stock solutions.

Apparatus

The structures of compounds were identified by ^1H NMR and ^{13}C NMR (Varian Mercury 300 NMR spectrometer), using TMS as an internal standard. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in hertz. High resolution mass spectra were measured with the Agilent 1290-micro TOF Q II mass spectrometer. Other mass spectra were measured with the Applied Biosystems api2000 Q-trap mass spectrometer. All fluorescence intensity and spectra were obtained using an RF-5301PC spectrofluorometer (Shimadzu, Japan) with excitation slit set at 5.0 nm and emission at 5.0 nm. The pH measurements were carried out on a Sartorius PB-10 pH meter.

Synthesis of PQT

A solution of phenyl isothiocyanate (1.35 g, 10 mM) and 8-aminoquinoline (1.29 g, 10 mM) in CH_2Cl_2 (30 mL) was stirred at room temperature for 48 h. The white crystals were precipitated in the solvent. The crystals were filtered out then washed with CH_2Cl_2 . The reaction product was dried. The yield was 39% (Scheme 1). HRMS (ESI⁺-TOF) m/z 280.0905 ($[\text{M}+\text{H}]^+$ calcd. for 280.0903). ^1H NMR (CDCl_3 , 300 MHz) δ 10.80 (s, 1H), 9.46 (dd, $J = 9$ Hz, $J = 1.8$ Hz, 1H), 8.57 (q, $J = 4.2$ Hz, $J = 1.8$, 1H), 8.14 (m, 2H), 7.60–7.37 (m, 8H). ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 177.43, 147.95, 139.24, 136.37, 134.79, 129.96, 127.87, 127.19, 126.81, 125.17, 122.24, 121.57, 117.34.

Preparation of 1-phenyl-3-(quinolin-8-yl) urea (PQU)

PQT (0.128 g, 0.46 mM) and $\text{Hg}(\text{NO}_3)_2 \cdot 1/2 \text{H}_2\text{O}$ (0.162 g, 0.5 mM) in acetonitrile (15 mL) were stirred at room temperature for 60 min. The red HgS was precipitated in the solution then the red precipitate was filtered out. The filtrate was concentrated in vacuo and then purified by flash column chromatography using dichloromethane and ethyl acetate (2:1, v/v) as eluent to provide PQU as a white solid. ^1H NMR (DMSO , 300 MHz) δ 9.04 (s, 1H), 7.95–7.97 (m, 2H), 7.33–7.36 (m, 3H), 6.89–7.00 (m, 3H), 6.83–6.85 (dd, 2H), 6.66–6.69 (m, 1H), 6.03–6.07 (m, 1H); MS (ESI): m/z 262.1 $[\text{M}-\text{H}]^+$.

Fig. 1 (A) Excitation (1) and emission (2) spectra of PQT in a buffered MeCN–water mixture, emission (3) spectra of PQT solution with Hg^{2+} . (B) The proposed mechanism for increasing fluorescence intensity of PQT upon Hg^{2+} addition, and fluorescence color change of the solution. Concentration of PQT, 10 μM ; Hg^{2+} , 10 μM ; $\lambda_{\text{ex}} = 309$ nm; $\lambda_{\text{em}} = 406$ nm.

Digestion procedure of the aquatic plant

The aquatic plants were triple-rinsed in deionized water, then oven-dried at 80°C to a constant weight. The sample was then reduced to a fineground. About 0.5 g of the sample was weighed into a dry, clean round-bottom flask. Next, 6 mL of HCl and 2 mL of HNO_3 were added and the mixture was heated with a heating jacket. The temperature was gradually increased until heavy evolution of fumes ceased. If carbonization appeared, the vessel was removed from the hot plate, cooled and about 1 mL of HNO_3 was added. The mixture was then heated again until complete digestion was achieved. The final residue was diluted to 10 mL with double deionized water.

Results and Discussion

Fluorescence property of PQT

In a pH 8.0 HEPES buffer (100 mM) containing 50% MeCN, fluorescence excitation and emission spectra of PQT were recorded and the results are shown in Fig. 1(A). The compound PQT exhibited weak fluorescence; the fluorescence emission peak was at 406 nm with an excitation wavelength of 309 nm. This observation is coincident with the well-documented phenomenon that a thiocarbonyl-containing group on a fluorochrome quenches the fluorescence due to the heavy atom effect of the S atom.^{65–68} To our surprise, it was interesting to find that Hg^{2+} had an effect on the fluorescence emission of PQT. PQT also gave a shorter response time with Hg^{2+} , and the enhanced response time^{69,70} was 2.5 s. Within 2 min, the

Fig. 2 Effect of water content on the fluorescence intensity of PQT measured without (■) and with (●) Hg^{2+} in an aqueous MeCN solution (HEPES 100 μM). Concentration of PQT, 10 μM ; Hg^{2+} , 10 μM ; λ_{ex} = 309 nm; λ_{em} = 406 nm.

fluorescence intensity of PQT after the addition of Hg^{2+} reached a constant value, which was about 10 times larger than the blank intensity (Fig. S9, Supporting Information). Mercury ion induced transformation of the thiourea function into a urea group of PQT is as depicted in Fig. 1(B). In the present case, the conversion was effective, occurring exclusively with Hg^{2+} ions in the HEPES buffer. The product of the reaction of PQT with Hg^{2+} was isolated, and identified as PQU.

Effect of water content on the fluorescence response of PQT

The fluorescence measurements of PQU pure acetonitrile solution were taken every 10 min for 60 min; there was no change in the fluorescence characteristics. However, an unexpectedly dramatic enhancement of PQU fluorescence emission was observed when 0.1 M HEPES (pH = 8.0) was added to the solution of PQU in acetonitrile. A substantial red shift was also observed in the PQU fluorescence emission, from 357 to 406 nm (Fig. S10, Supporting Information). The remarkable fluorescence enhancement induced by protic solvents can be ascribed to hydrogen bond formation on the carbonyl oxygen of PQU; in polar protic solvents, the S_1 (π, π^*) state is subject to solvent stabilization, whereas the S_2 (n, π^*) state is destabilized by hydrogen bonding interactions with protic solvents, increasing the S_1 - S_2 energy gap and thus reducing the internal conversion rate.⁷¹

In this part, the effects of water content on the fluorescence response of PQT to Hg^{2+} were investigated. Experimental results are shown in Fig. 2. The fluorescence (excited at 309 nm) characteristic of PQT showed no obvious change in the water content range from 10 to 70%. However, in the presence of the Hg^{2+} ion, there was a remarkable fluorescence enhancement of PQT under the water content from 10 to 50%. From 50 to 70%, the fluorescence change of PQT was unobscure. The white crystals were precipitated in the solvent when the water content was 80%. Therefore, the water content of 50% was chosen as an optimum experimental condition.

Effect of pH on the fluorescence response of PQT

The effect of different pH levels of the PQT solution on sensing Hg^{2+} was also explored. As depicted in Fig. 3, the

Fig. 3 Change in fluorescence intensity of PQT in a MeCN-water mixture measured with (●) and without (×) Hg^{2+} as a function of pH. Concentration of PQT, 10 μM ; Hg^{2+} , 10 μM ; λ_{ex} = 309 nm; λ_{em} = 406 nm; MeCN-water mixture (1/1 v/v).

fluorescence intensity (excited at 309 nm) of PQT did not show significant change in the pH range from 1.0 to 13.0. However, in the presence of Hg^{2+} , there was an obvious fluorescence off-on change of PQT with different fluorescence enhancement efficiency in the pH range from 2.0 to 6.0. The fluorescence intensity reached the maximum at pH 6.0 and remained almost constant until pH 10.0, as shown in Fig. 3. Therefore, pH 8.0 was chosen as the optimum experimental condition.

Interference of large amount of common anions in Hg^{2+} determination

An important feature of the sensor is its high selectivity toward mercury ions over other competitive species. The interference of a number of common anions for the detection of Hg^{2+} with PQT was carried out with excitation fixed at 309 nm and emission at 406 nm. No significant fluorescence intensity changes were observed with common interference anions, such as NO_3^- , Cl^- , CO_3^{2-} , F^- , SO_4^{2-} , SCN^- and Ac^- . In the competition experiments, the same concentration of the above-mentioned anions (10 μM) were added to 10 μM of Hg^{2+} in a buffered MeCN-water mixture (1/1 v/v; HEPES 100 mM; pH 8.0), and the fluorescence response of the chemosensor was detected and then compared with that of buffered MeCN-water mixture (1/1 v/v; HEPES 100 mM; pH 8.0) containing only 10 μM of Hg^{2+} (Fig. S11, Supporting Information). These experimental results showed that the response of the sensor to Hg^{2+} was unaffected by the presence of the other potentially contaminating anions.

Selectivity of PQT for Hg^{2+}

In addition, the interference of common metal ions for the detection of Hg^{2+} with PQT was carried out with excitation fixed at 309 nm and emission at 406 nm. Figure 4 (the gray bar portion) illustrates the fluorescence response of PQT to different metal ions of interest; no significant fluorescence intensity changes were observed with common interferences such as alkali, alkaline earth, and transitional metal ions, indicating that other metal ions did not induce transformation of the thiourea function of PQT into a urea group and our proposed sensor exhibits high selectivity to Hg^{2+} over other metal ions. To test

Fig. 4 Fluorescence response of PQT in a buffered MeCN-water mixture to 10 μM of Hg^{2+} or 10 μM of other metal ions (the gray bar portion) and to the mixture of 10 μM of other metal ions with 10 μM of Hg^{2+} (the red bar portion). Concentration of PQT, 30 μM ; buffered MeCN-water mixture (1/1 v/v; HEPES 100 mM; pH 8.0).

practical applicability of our fluorescence chemosensor for Hg^{2+} , competition experiments were also carried out. The same concentration of the above-mentioned metal ions (10 μM) were added to 10 μM of Hg^{2+} in a buffered MeCN-water mixture (1/1 v/v; HEPES 100 mM; pH 8.0), and the fluorescence response of the chemosensor was detected and then compared with that of buffered MeCN-water mixture (1/1 v/v; HEPES 100 mM; pH 8.0) containing only 10 μM of Hg^{2+} . The results are also shown in Fig. 4 (the red bar portion). Figure 4 shows that Ba^{2+} , Be^{2+} , Ca^{2+} and Li^{+} have a fluorescence quenching effect of 10% and Cu^{2+} has an interference quenching effect of 20%. This indicates that these metal ions form a complex with PQT. When the fluorescence response of PQT for Hg^{2+} was detected with these coexisting ions, these ions would consume a certain concentration of PQT. So, the fluorescence response of PQT to Hg^{2+} with these coexisting ions is lower than PQT containing only Hg^{2+} . In this part, EDTA was chosen as a masking agent to eliminate the interference of these ions. The effect of EDTA content on the fluorescence response of PQT to Hg^{2+} was investigated. The fluorescence characteristic of PQT showed no obvious change with the addition of EDTA content ranging from 1 to 30 equiv. of Hg^{2+} . The fluorescence quenching effect of PQT to Hg^{2+} was less than 15% with EDTA content range from 40 to 100 equiv. (Fig. S13, Supporting Information). EDTA as a masking agent was examined for Ba^{2+} , Be^{2+} , Ca^{2+} , Cu^{2+} and Li^{+} at concentrations not affecting the determination of Hg^{2+} . A 10-fold excess of Cu^{2+} could be masked with EDTA and equal amounts of Ba^{2+} , Be^{2+} , Ca^{2+} and Li^{+} could be eliminated with EDTA (Fig. S14, Supporting Information).

These experimental results showed that the response of the sensor to Hg^{2+} was unaffected by the presence of the other potentially contaminating metal ions. These results implied that the selectivity of PQT toward Hg^{2+} was remarkable, suggesting PQT is a viable selective chromogenic sensor for Hg^{2+} .

Fluorescence response of PQT to Hg^{2+}

Under conditions of pH 8.0 HEPES buffer (100 mM) containing 50% MeCN and with the excitation and emission slits set to a 5-nm band-pass, we observed that the fluorescence response of PQT increased upon increasing the Hg^{2+}

Table 1 Results of the sample analysis and recovery of added Hg^{2+} in aquatic plants

Sample	Found/ μmol	Hg added ^a / μmol	Hg found ^b / μmol	Recovery, %
<i>Microsorium pteropus</i>	3.68	1.00	1.01	101
<i>Anubias nana</i>	3.11	1.00	0.98	98
		2.00	2.04	102
<i>Bacopa caroliniana</i>	3.07	1.00	0.97	97
		2.00	1.96	98
<i>Echinodorus uruguayensis</i>	5.16	1.00	0.97	97
		2.00	2.07	103.5

a. Amount of Hg^{2+} added to each sample.

b. Amount of Hg^{2+} detected in each sample.

concentration over the range of 1 – 40 μM (Fig. S15A, Supporting Information). As shown in the inset of Fig. S15A, we found that the fluorescence intensity of PQT increased with an increase of the concentration of Hg^{2+} from 1 to 10 μM . When the concentration of Hg^{2+} exceeded 10 μM , the fluorescence intensity of PQT showed no apparent change. After the slits were set to 10 nm for both excitation and emission, the fluorescence spectra of PQT with Hg^{2+} concentration from 0 to 900 nM was measured (Fig. S15B, Supporting Information). The inset of Fig. S15B shows the line curve of fluorescence intensity of PQT titrated with Hg^{2+} concentration. The limit of detection of PQT to Hg^{2+} was 7.5 nM. Thus, our present approach provides a highly sensitive fluorescence probe for detecting Hg^{2+} in the water or biological samples.

Detection of Hg^{2+} in aquatic plants

The practical application of the designed chemosensor was evaluated by using it to detect Hg^{2+} in four kinds of aquatic plants. Aquatic plants were put in a glass culture cylinder measuring in 16 cm of diameter with 4 L of deionized water with 800 μM Hg^{2+} . After a week, the aquatic plants were rinsed in deionized water, and dried at 80°C to a constant weight. The samples (0.5 g) were wet digested and diluted to 10 mL with double deionized water. In order to reduce the pH influence in the detection, 4 mL of HEPES buffered water/MeCN containing PQT was added to 1 mL of the sample to keep the pH value at 8.0, and then its fluorescence intensity change was measured. The Hg concentrations of the samples were determined by the optimized fluorometric procedure, and the results obtained are summarized in Table 1. The concentrations of Hg^{2+} in *Bacopa caroliniana* was the lowest. Therefore, we surmise aquatic plants with large leaves like *Echinodorus uruguayensis* have greater ability to accumulate the Hg^{2+} in freshwater ecosystems. Recovery experiments for varying added amounts of Hg^{2+} were carried out, and the experimental results are also shown in Table 1. These results confirmed the validity of the proposed method.

Conclusions

In conclusion, we have demonstrated that PQT as a fluorescent probe for the detection of Hg^{2+} shows high sensitivity and the fluorescence intensity increases quantitatively with an increase in the Hg^{2+} , with a limit of detection of 7.5 nM. PQT has higher selectivity for Hg^{2+} than other metal ions. When the other metal

ions coexist with Hg, there is no obvious influence on the detection of mercury. The lowest test concentration of Hg²⁺ in this assay was 20 nM (0.004 mg/L). This study suggests that the determination of mercury in aquatic plants using the quinolone-thiourea conjugate as a fluorescent probe is viable.

Acknowledgements

The authors are grateful for the financial support from the Basic Research Foundation of Jilin University (Nos. 201103096 and 201103102) and the Science-Technology Development Project of Jilin Province of China (No. 201105008).

Supporting Information

Characterization Data of obtained compounds, fluorometric analysis and supplementary figures. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

- J. Lloret, *Mar. Pollut. Bull.*, **2010**, *60*, 1640.
- I. Ahmad, J. P. Coelho, I. Mohmood, N. A. Anjum, M. Pacheco, M. A. Santos, A. C. Duarte, and E. Pereira, *Food Chem.*, **2012**, *133*, 665.
- R. Correia, D. Oliveira, and J. Guimarães, *Aquat. Geochem.*, **2012**, *18*, 421.
- N. Regier, F. Larras, A. G. Bravo, V. G. Ungureanu, D. Amouroux, and C. Cosio, *Chemosphere*, **2013**, *90*, 595.
- D. Karunasagar, J. Arunachalam, and S. Gangadharan, *J. Anal. At. Spectrom.*, **1998**, *13*, 679.
- Y. Yamini, N. Alizadeha, and M. Shamsipur, *Anal. Chim. Acta*, **1997**, *355*, 69.
- E. Kopysc, K. Pyrzynska, S. Garbos, and E. Bulska, *Anal. Sci.*, **2000**, *16*, 1309.
- T. Duan, X. Song, J. Xu, P. Guo, H. Chen, and H. Li, *Spectrochim. Acta, Part B*, **2006**, *61*, 1069.
- J. V. Cizdziel and S. Gerstenberger, *Talanta*, **2004**, *64*, 918.
- Z. L. Zhu, G. C. Y. Chan, S. J. Ray, X. R. Zhang, and G. M. Hieftje, *Anal. Chem.*, **2008**, *80*, 7043.
- Z. L. Zhu, G. C. Y. Chan, S. J. Ray, X. R. Zhang, and G. M. Hieftje, *Anal. Chem.*, **2008**, *80*, 8622.
- L. Jian, W. Goessler, and K. J. Irgolic, *Fresenius J. Anal. Chem.*, **2000**, *366*, 48.
- X. C. Fu, X. Chen, Z. Guo, L. T. Kong, J. Wang, J. H. Liu, and X. J. Huang, *Electrochim. Acta*, **2010**, *56*, 463.
- T. Alizadeh, M. R. Ganjali, and M. Zare, *Anal. Chim. Acta*, **2011**, *689*, 52.
- S. Young, *Spectrochim. Acta, Part A*, **2007**, *68*, 705.
- Y. Long, D. Jiang, X. Zhu, J. Wang, and F. Zhou, *Anal. Chem.*, **2009**, *81*, 2652.
- A. Coskun, M. D. Yilmaz, and E. U. Akkaya, *Org. Lett.*, **2007**, *9*, 607.
- M. H. Lee, J. S. Wu, J. W. Lee, J. H. Jung, and J. S. Kim, *Org. Lett.*, **2007**, *9*, 2501.
- J. Wang and X. Qian, *Org. Lett.*, **2006**, *8*, 3721.
- S. Yoon, A. E. Albers, A. Wong, and C. J. Chang, *J. Am. Chem. Soc.*, **2005**, *127*, 16030.
- X. Guo, X. Qian, and L. Jia, *J. Am. Chem. Soc.*, **2004**, *126*, 2272.
- E. M. Nolan and S. J. Lippard, *J. Am. Chem. Soc.*, **2003**, *125*, 14270.
- X. Zhu, S. Fu, W. Wong, J. Guo, and W. Wong, *Angew. Chem., Int. Ed.*, **2006**, *45*, 3150.
- E. M. Nolan and S. Lippard, *J. Chem. Rev.*, **2008**, *108*, 3443.
- J. Manimala and E. V. Anslyn, *Eur. J. Org. Chem.*, **2002**, 3909.
- K. S. Kim and L. Qian, *Tetrahedron Lett.*, **1993**, *34*, 7677.
- R. A. Batey and D. A. Powell, *Org. Lett.*, **2000**, *2*, 3237.
- D. Boeglin, S. Cantel, A. Heitz, J. Martinez, and J. A. Fehrentz, *Org. Lett.*, **2003**, *5*, 4465.
- M. Y. Chae and A. W. Czarnik, *J. Am. Chem. Soc.*, **1992**, *114*, 9704.
- G. Hennrich, W. Walther, U. Resch-Genger, and H. Sonnenschein, *Inorg. Chem.*, **2001**, *40*, 641.
- K. C. Song, J. S. Kim, S. M. Park, K. C. Chung, S. Ahn, and S. K. Chang, *Org. Lett.*, **2006**, *8*, 3413.
- S. K. Ko, Y. K. Yang, J. Tae, and I. Shin, *J. Am. Chem. Soc.*, **2006**, *128*, 14150.
- H. Zheng, X. J. Zhang, X. Cai, Q. N. Bian, M. Yan, G. H. Wu, X. W. Lai, and Y. B. Jiang, *Org. Lett.*, **2012**, *14*, 1986.
- L. H. Wu, L. F. Han, Y. B. Ruan, and Y. B. Jiang, *Chin. J. Anal. Chem.*, **2010**, *38*, 121.
- X. Q. Liu, X. Shu, X. Zhou, X. Zhang, and J. Zhu, *J. Phys. Chem. A*, **2010**, *114*, 13370.
- M. G. Choi, D. H. Ryu, H. L. Jeon, S. Cha, J. Cho, H. H. Joo, K. S. Hong, C. Lee, S. Ahn, and S. K. Chang, *Org. Lett.*, **2008**, *10*, 3717.
- K. N. Kim, M. G. Choi, J. H. Noh, S. Ahn, and S. K. Chang, *Bull. Korean Chem. Soc.*, **2008**, *29*, 571.
- Y. Xia and C. Zhu, *Talanta*, **2008**, *75*, 215.
- S. Y. Moon, N. J. Youn, S. M. Park, and S. K. Chang, *J. Org. Chem.*, **2005**, *70*, 2394.
- R. Martinez, A. Espinosa, A. Tarraga, and P. Molina, *Org. Lett.*, **2005**, *7*, 5869.
- E. M. Nolan and S. J. Lippard, *Chem. Rev.*, **2008**, *108*, 3443.
- H. Zheng, Z. H. Qian, L. Xu, F. F. Yuan, L. D. Lan, and J. G. Xu, *Org. Lett.*, **2006**, *8*, 859.
- S. Voutsadaki, G. K. Tsikalas, E. Klontzas, G. E. Froudakis, and H. E. Katerinopoulos, *Chem. Commun.*, **2010**, *46*, 3292.
- Z. Q. Hu, C. S. Lin, X. M. Wang, L. Ding, C. L. Cui, S. F. Liu, and H. Y. Lu, *Chem. Commun.*, **2010**, *46*, 3765.
- W. Lin, X. Cao, Y. Ding, L. Yuan, and Q. Yu, *Org. Biomol. Chem.*, **2010**, *8*, 3618.
- Y. Zhou, X. Y. You, Y. Fang, J. Y. Li, K. Liu, and C. Yao, *Org. Biomol. Chem.*, **2010**, *8*, 4819.
- G. Zhang, D. Zhang, S. Yin, X. Yang, Z. Shuai, and D. Zhu, *Chem. Commun.*, **2005**, 2161.
- B. Liu and H. Tian, *Chem. Commun.*, **2005**, 3156.
- Y. K. Yang, K. J. Yook, and J. Tae, *J. Am. Chem. Soc.*, **2005**, *127*, 16760.
- X. Zhang, Y. Xiao, and X. Qian, *Angew. Chem., Int. Ed.*, **2008**, *47*, 8025.
- W. Shi and H. Ma, *Chem. Commun.*, **2008**, 1856.
- M. G. Choi, Y. H. Kim, J. E. Namgoong, and S. K. Chang, *Chem. Commun.*, **2009**, 3560.
- W. Jiang and W. Wang, *Chem. Commun.*, **2009**, 3913.
- M. H. Lee, S. W. Lee, S. H. Kim, C. Kang, and J. S. Kim, *Org. Lett.*, **2009**, *11*, 2101.
- F. Song, S. Watanabe, P. E. Floreancig, and K. Koide, *J. Am. Chem. Soc.*, **2008**, *130*, 16460.
- M. Santra, D. Ryu, A. Chatterjee, S. K. Ko, I. Shin, and K. H. Ahn, *Chem. Commun.*, **2009**, 2115.
- Y. S. Cho and K. H. Ahn, *Tetrahedron Lett.*, **2010**, *51*,

- 3852.
58. P. Z. Qin, C. G. Niu, G. M. Zeng, J. H. Zhu, and L. Yue, *Anal. Sci.*, **2008**, *24*, 1205.
59. L. Zhou, Y. Wang, Z. Liu, and Q. Huang, *J. Hazard. Mater.*, **2009**, *161*, 995.
60. Y. Shiraishi, S. Sumiya, and T. Hirai, *Org. Biomol. Chem.*, **2010**, *8*, 1310.
61. K. Tsukamoto, Y. Shinohara, S. Iwasaki, and H. Maeda, *Chem. Commun.*, **2011**, *47*, 5073.
62. S. Sumiya, T. Sugii, Y. Shiraishi, and T. Hirai, *J. Photochem. Photobiol., A*, **2011**, *219*, 154.
63. H. Li and H. Yan, *J. Phys. Chem. C*, **2009**, *113*, 7526.
64. C. Y. Wu, C. C. Lin, T. M. Fu, C. R. Yang, and Y. P. Yen, *J. Chem.*, **2010**, *63*, 329.
65. W. C. Lin, C. Y. Wu, Z. H. Liu, C. Y. Lin, and Y. P. Yen, *Talanta*, **2010**, *81*, 1209.
66. H. Poradowska, K. Nowak, and W. Czuba, *Pol. J. Chem.*, **1979**, *53*, 1895.
67. D. M. Wiles and T. Suprunchuk, *J. Chem. Eng. Data*, **1969**, *14*, 506.
68. N. J. Turro, V. Ramamurthy, and J. C. Scaiano, "Principles of Molecular Photochemistry: An Introduction", **2009**, University Science Books, California, 311.
69. X. L. Liu, X. F. Zhang, R. Lu, P. C. Xue, D. F. Xu, and H. P. Zhou, *J. Mater. Chem.*, **2011**, *21*, 8756.
70. P. C. Xue, R. Lu, J. H. Jia, M. Takafuji, and H. Ihara, *Chem. Eur. J.*, **2012**, *18*, 3549.
71. A. Kobayashi, K. Takehira, T. Yoshihara, S. Uchiyama, and S. Tobita, *Photochem. Photobiol. Sci.*, **2012**, *11*, 1368.
-