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SYNTHESIS OF 1,3-DI(2-THIAZOLYL)AZULENE AND ITS SELECTIVE CHROMOGENIC RESPONSE TO MERCURY(II) ION

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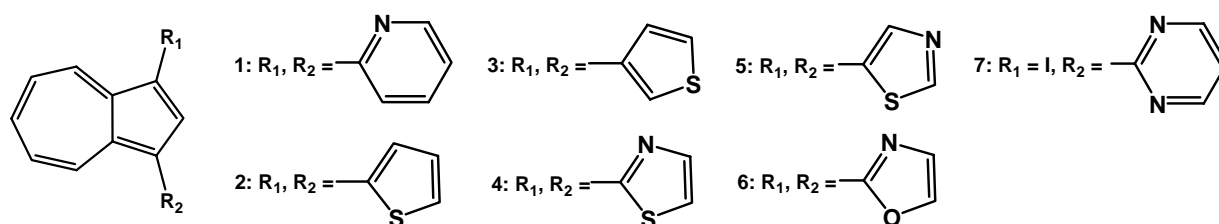
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Abstract – Azulene derivatives bearing heteroaryl groups in the 1,3-positions were synthesized, and the color and spectral changes occurring upon the addition of metal ions were examined. Of the compounds tested, title compound **4** appears to exhibit the most selective chromogenic behavior toward Hg²⁺ ion.

INTRODUCTION

Although it is well known that adding protic acid or metal ions to azulene derivatives results in a color change,¹ the preparation of much simpler azulene derivatives which undergo a color change would be significant for furthering our understanding of azulenic chromophores. Recently, we reported the synthesis of pyridylazulenes (for example, **1**), and the color and spectral changes occurring upon the addition of acid or metal ions were investigated in detail.² The color changed from blue to red upon the addition of trifluoroacetic acid or soft heavy metal ions such as Hg²⁺ and Pb²⁺, depending on the substitution patterns of the pyridyl group on the azulene skeleton.

The selective recognition of heavy metal ions or the colorimetric sensing of Hg²⁺ ion is currently a very important topic, as exemplified by interest in azacrown ethers, azocalix[4]arene, etc.³ To direct our efforts toward achieving Hg²⁺-selectivity in azulene chemistry, compounds **2–7** bearing thienyl, thiazolyl, oxazolyl, or pyrimidinyl groups at the 1,3-positions of the azulene skeleton were prepared. Here we describe the protocol for their synthesis, and their color and UV/vis spectral changes upon the addition of metal salts. The selective chromogenic behavior of these compounds towards heavy metal ions, and structural studies of the products, are also presented.



RESULTS AND DISCUSSION

Compound **2** was prepared according to the procedure reported by Oda, et al.^{4b} Compounds **3–6** could be synthesized by a similar methodology based on the Stille coupling of 1,3-diiodoazulene⁵ and 2–3 equiv of the corresponding stannyl reagents in the presence of tetrakis(triphenylphosphine)palladium (0.1 eq), cesium fluoride (3.5 eq) and copper iodide(I) (0.5 eq).⁶ Use of 3-(trimethylstannyl)thiophene,⁷ 2-(tri-*n*-butylstannyl)thiazole, 5-(trimethylstannyl)thiazole,⁸ and 2-(tri-*n*-butylstannyl)oxazole as stannyl reagents afforded **3** (yield 50%, green crystals, mp 109–110 °C), **4** (yield 70%, green crystals, mp 186–188 °C), **5** (yield 79%, green crystals, mp 185–187 °C), and **6** (yield 83%, greenish blue crystals, mp >200 °C), respectively. Compound **7** (blue crystals, mp 118–119 °C) could be prepared by the reaction of 1,3-diiodoazulene and 2-(tri-*n*-butylstannyl)pyrimidine⁹ using tris(dibenzylidene)acetone dipalladium instead of tetrakis(triphenylphosphine)palladium as the palladium catalyst in 33% yield. The expected structures of **2–7** were fully supported by spectral data and elemental analysis; in addition, **2** had been previously identified.⁴ All these compounds were stable and showed no sign of degradation after storage for 1 year at –30 °C.

We studied changes in the spectral properties and colors of **2–7** upon addition of metal ions. The coordination of soft heavy metal ions onto the heteroaromatic moiety was expected to enhance its electron-withdrawing ability and influence the π -conjugate system of azulene. Little color change for **2** and **3** was effected by the addition of the nitrate or perchlorate salt of metal ions (Li⁺, Na⁺, Ca²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Ag⁺, Pb²⁺, Cu²⁺, Cr³⁺) in aqueous acetone or acetone, even if a large excess of metal ions was added to the compounds. Furthermore, for **4–7**, the individual addition of Li⁺, Na⁺, Ca²⁺, Zn²⁺, and Cd²⁺ also produced negligible color changes.

In contrast, the individual addition of heavy metal ions (Hg²⁺, Ag⁺, Pb²⁺, Cu²⁺, Cr³⁺) to **4–7** produced red or reddish brown color changes as well as almost no color change. Interestingly, **4** was a deep red color only upon the addition of Hg²⁺ ion, and the absorption spectrum of **4** showed a substantial blue shift (73 nm) upon the addition of 1 equiv of Hg(ClO₄)₂ (Figure 1). Compound **5** was a reddish brown color in acetone only upon the addition of Cu²⁺ ion as the perchlorate, whereas **6** (blue) turned red in acetone when a small amount of Hg²⁺ or Ag⁺ ions were added. In acetone, **7** (blue) turned red or reddish brown when a small amount of Hg²⁺ or Cr³⁺ ions were added as perchlorates, respectively.

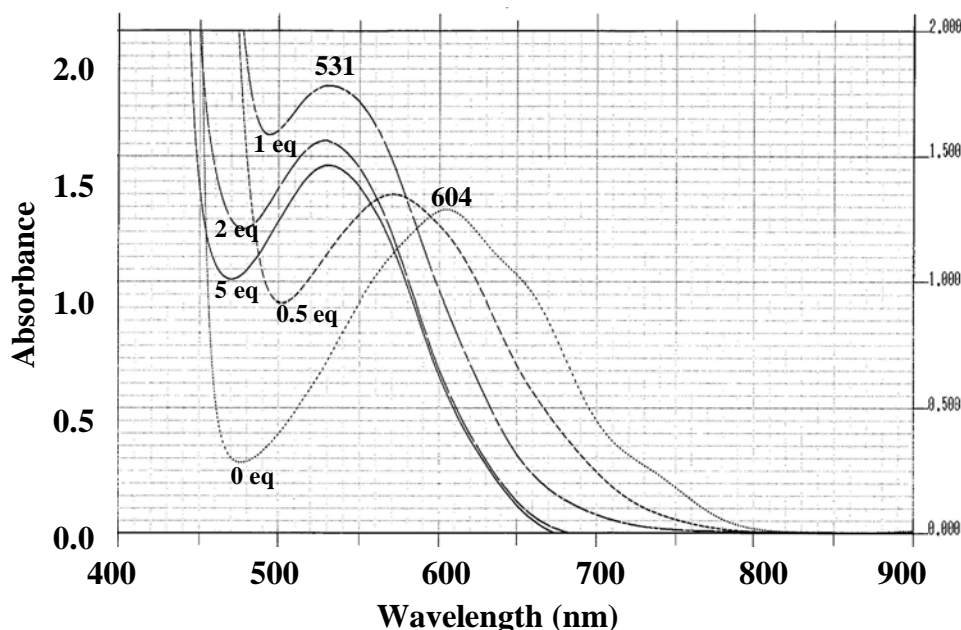


Figure 1. Spectral changes of **4** (0.0023 M) upon the addition of $\text{Hg}(\text{ClO}_4)_2$ in acetone, where the amount of $\text{Hg}(\text{ClO}_4)_2$ varies from 0.5 to 5 equiv.

To obtain information regarding the interaction of these heteroarylazulenes with Hg^{2+} ion, ^1H NMR and ESI-TOF-MS analyses were performed. In the ^1H NMR spectrum of the complex formed by the reaction of **4** and 1 equiv of $\text{Hg}(\text{ClO}_4)_2$ in acetone, the aromatic protons were shifted downfield (0.4–0.5 ppm for H-4, H-5, H-6 of azulene skeleton, 0.5–0.6 ppm for thiazolyl moiety) compared with **4**, except for the upfield shift by ca. 0.5 ppm for H-4 of the azulene skeleton.¹⁰ ESI-TOF-MS measurement of the complex in acetone provided a charged peak at m/z 553.0, which is assignable to $[\text{Hg} \cdot \mathbf{4} \cdot \text{acetone-H}]^+$ (Figure 2). The observed isotopic and theoretical distributions were in close agreement. These data suggest that **4** strongly interacts with Hg^{2+} ion in acetone. Similar behaviors were found upon complexation of **6** or **7** with Hg^{2+} ion.¹¹ Thus, the observed color changes in **4**, **6**, and **7** with Hg^{2+} ion can be explained by stabilization of the HOMO of the azulene skeleton, caused by the enhanced electron-withdrawing ability of the 2-thiazolyl, 2-oxazolyl, and 2-pyrimidinyl group, respectively, as demonstrated by Liu, et al. in the protonation of azulene derivatives.¹¹

No ^1H NMR chemical shift changes were observed by adding Hg^{2+} ion to **2** or **3** (bearing the thienyl group) in acetone. In addition, no mass peak due to the Hg^{2+} complex with **2** or **3** was observed, revealing the absence of complexation between **2** or **3** and Hg^{2+} ion; this was unexpected¹² since the sulfur donor atom of the thiophene ring should coordinate to Hg^{2+} ion.^{3h} In contrast, **5** (bearing the 5-thiazolyl group) provided a mass peak at m/z 553.1 assignable to $[\text{Hg} \cdot \mathbf{5} \cdot \text{acetone-H}]^+$ and significant ^1H NMR downfield chemical shifts, suggesting the complexation of **5** with Hg^{2+} ion. However, the absorption spectrum of **5** showed a small blue shift of ca. 30 nm and the color change was also small: blue to yellowish green upon the addition of 1 equiv of $\text{Hg}(\text{ClO}_4)_2$. Therefore, C=N double bond in the heteroaromatic moiety at the 1-position or 1,3-positions of the azulene skeleton is necessary for the blue

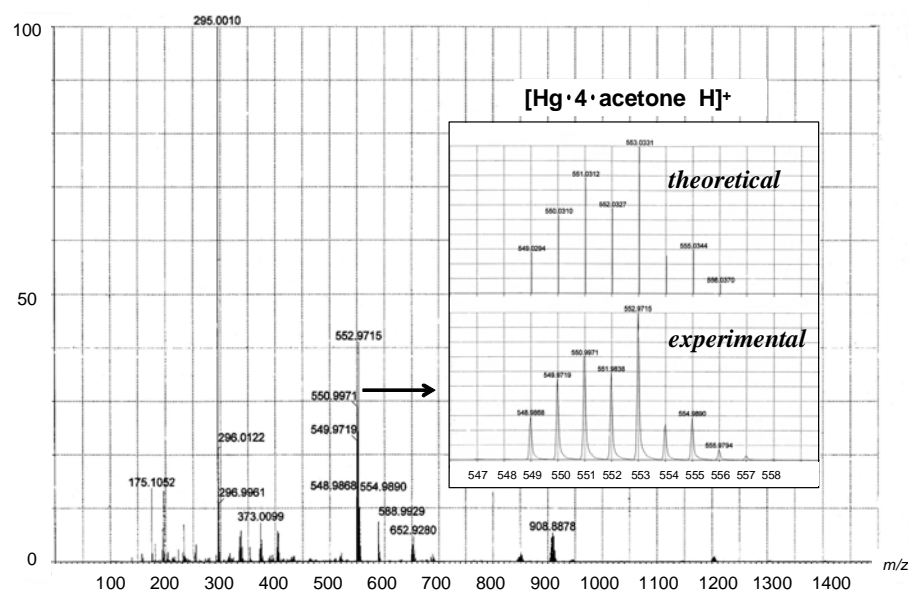


Figure 2. ESI-TOF-MS spectra of **4** with 1 equiv of Hg(ClO₄)₂ in acetone.

azulenic chromophore to turn red upon the addition of Hg²⁺ ion. Furthermore, the above experimental data suggest that, among the compounds investigated in this work, title compound **4** exhibits the most highly selective chromogenic behavior toward Hg²⁺ ion.

EXPERIMENTAL

Melting points were determined on a Shibata MEL-270 melting point apparatus and are uncorrected. Infrared spectra were measured with a Shimadzu FT IR-8100 Fourier transform infrared spectrophotometer. Ultraviolet spectra were obtained on Shimadzu UV-2200 spectrometer. ¹H and ¹³C NMR spectra in CDCl₃ were recorded on a Jeol JNM-AL300 or JNM-A400. The chemical shifts are described as values in ppm relative to a Si(Me)₄ standard for ¹H NMR. Electron impact and high resolution mass spectra were measured at a voltage of 70 eV on a Jeol JMS-600H or JMS-700. Electrospray ionization-time-of-flight mass spectra were recorded on a Micromass LCT-TOF-MS. Elemental analysis was achieved using a LECO CHNS-932. Analytical thin-layer chromatography was conducted on a plate coated with Merck Kieselgel 60 F₂₅₄ (0.25 mm thickness). Most reactions were carried out in serum-capped, oven-dried, and argon-purged flasks. 2-(Tri-*n*-butylstannyl)thiazole and 2-(tri-*n*-butylstannyl)oxazole were commercially available from Frontier Scientific, Inc. Other stannyl reagents were prepared according to the literature method.⁷⁻⁹

Cross-Coupling Reactions: Typical Procedure A. 1,3-Di(2-thiazolyl)azulene (**4**)

To the mixture of 1,3-diiodoazulene (194 mg, 0.511 mmol), Pd(PPh₃)₄ (58 mg, 0.050 mmol), CuI (47 mg, 0.247 mmol), and CsF (252 mg, 1.658 mmol) was added a solution of 2-(tri-*n*-butylstannyl)thiazole (454 mg, 1.213 mmol) in DMF (5 mL). The mixture was stirred at 55 °C for 1 h. The reaction mixture was

poured into water (10 mL) and extracted with EtOAc (50 mL). The organic layer was washed with brine (2 x 10 mL), dried over MgSO₄, and concentrated. The crude product was subjected to silica gel column chromatography using silica gel (6 g) and a 1:3 mixture of benzene and hexane to benzene as eluent to afford 282 mg of greenish blue solid, which was further purified by silica gel (5 g) and a 1:20 to 1:1 mixture of EtOAc and hexane, then EtOAc to a 30:1 mixture of EtOAc and MeOH as eluent to give **4** (105 mg, 70%) as greenish blue crystals. mp 186–188 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, 1H, *J* = 3.4 Hz), 7.51 (t, 1H, *J* = 10.0 Hz), 7.80 (t, 1H, *J* = 9.9 Hz), 7.94 (d, 2H, *J* = 3.4 Hz), 8.59 (s, 1H), 9.79 (d, 2H, *J* = 9.5 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 117.2, 121.4, 128.0, 137.3, 138.4, 139.2, 141.0, 143.4, 164.7. IR (KBr) 3073, 1570, 1534, 1487, 1401, 1113, 851, 725 cm⁻¹. EIMS *m/z* 294 (M⁺, 100%). HRMS (EI) *m/z* calcd for C₁₆H₁₀N₂S₂. 294.0285. found. 294.0275. Anal. Calcd for C₁₆H₁₀N₂S₂: C, 65.28; H, 3.42; N, 9.52; S, 21.78. Found: C, 65.74; H, 3.57; N, 9.30; S, 21.39. UV/VIS (acetone): λ_{max} (ε) = 209 (15950), 330 (41667), 410 (12500), 605 (540).

1,3-Di(3-thienyl)azulene (3)

Yield: 50%; green crystals; mp 109–110 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.10 (t, 2H, *J* = 9.9 Hz), 7.42 (s, 2H), 7.43 (dd, 2H, *J* = 1.5, 3.2 Hz), 7.48 (dd, 2H, *J* = 2.9, 4.9 Hz), 7.56 (t, 1H, *J* = 9.8 Hz), 8.09 (s, 1H), 8.56 (d, 2H, *J* = 9.5 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 121.3, 123.4, 125.1, 125.7, 128.3, 129.0, 136.0, 136.7, 137.5, 139.0. IR (KBr) 1570, 1393, 785, 739, 664 cm⁻¹. EIMS *m/z* 292 (M⁺, 100%). HRMS (EI) *m/z* calcd for C₁₈H₁₂S₂. 292.0380. found. 292.0394. UV/VIS (acetone): λ_{max} (ε) = 210 (20940), 326 (15470), 385 (6880), 632 (290). Anal. Calcd for C₁₈H₁₂S₂: C, 73.93; H, 4.14; S, 21.93. Found: C, 74.08; H, 4.43; S, 22.17.

1,3-Di(5-thiazolyl)azulene (5)

Yield: 79%; green crystals; mp 185–187 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, 2H, *J* = 9.8 Hz), 7.71 (t, 1H, *J* = 9.8 Hz), 8.08 (s, 2H), 8.12 (s, 1H), 8.63 (d, 2H, *J* = 9.5 Hz), 8.88 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 119.0, 125.4, 136.4, 137.8, 138.0, 140.2, 140.4, 141.3, 152.2. IR (KBr) 1576, 1531, 1393, 1279, 1111, 874, 845, 795, 741 cm⁻¹. EIMS *m/z* 294 (M⁺, 100%). HRMS (EI) *m/z* calcd for C₁₆H₁₀N₂S₂. 294.0285. found 294.0335. Anal. Calcd for C₁₆H₁₀N₂S₂: C, 65.28; H, 3.42; N, 9.52; S, 21.78. Found: C, 65.72; H, 3.69; N, 9.23; S, 21.46. UV/VIS (MeCN): λ_{max} (ε) = 195 (18750), 225 (16670), 310 (27500), 390 (7080) 618 (250).

1,3-Di(2-oxazolyl)azulene (6)

Yield: 83%; greenish blue crystals; mp > 200 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 2H), 7.58 (t, 2H, *J* = 10.0 Hz), 7.76 (s, 2H), 7.86 (t, 1H, *J* = 9.8 Hz), 8.91 (s, 1H), 9.77 (d, 2H, *J* = 9.5 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 115.0, 128.1, 128.2, 136.2, 137.1, 138.9, 139.0, 140.7, 160.1. IR (KBr) 1572, 1435, 741

cm⁻¹. EIMS *m/z* 262 (M⁺, 100%). HRMS (EI) *m/z* calcd for C₁₆H₁₀O₂N₂. 262.0742. found. 262.0753. UV/VIS (acetone): λ_{max} (ε) = 327 (18750), 398 (10110), 592 (490), 420 (sh).

Cross-Coupling Reaction: Procedure B. 1-Iodo-3-(2-pyrimidinyl)azulene (7)

To the mixture of 1,3-diiodoazulene (308 mg, 0.811 mmol), Pd₂dba₃ (53 mg, 0.058 mmol), CuI (44 mg, 0.231 mmol), and AsPh₃ (75 mg, 0.245 mmol) was added a solution of 2-(tri-*n*-butylstannyl)pyrimidine (448 mg, 1.215 mmol) in DMF (10 mL). The mixture was stirred at 50 °C for 4 h. The reaction mixture was poured into water (20 mL) and extracted with EtOAc (70 mL). The organic layer was washed with 1M KF aq (10 mL), brine (2 x 10 mL), dried over MgSO₄, and concentrated. The crude product was subjected to silica gel column chromatography using silica gel (11 g) and a 1:20 to 1:8 mixture of EtOAc and hexane as eluent to afford 107 mg of blue oil, which was further purified by silica gel (3.5 g) and a 1:20 to 1:8 mixture of EtOAc and hexane as eluent to give **7** (88 mg, 33%) as blue crystals. mp 118–119 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.03 (t, 1H, *J* = 4.8 Hz), 7.41 (t, 1H, *J* = 9.7 Hz), 7.47 (t, 1H, *J* = 10.1 Hz), 7.74 (t, 1H, *J* = 9.8 Hz), 8.33 (d, 1H, *J* = 9.7 Hz), 8.77 (d, 2H, 4.8 Hz), 8.87 (s, 1H), 10.04 (d, 1H, *J* = 9.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 117.1, 126.1, 127.19, 127.22, 138.2, 138.6, 139.5, 139.8, 143.6, 146.5, 156.8, 163.7. IR (KBr) 1566, 1547, 1497, 1460, 1443, 1370, 1289, 808, 743 cm⁻¹. EIMS *m/z* 332 (M⁺, 30%), 234 (40%), 205 (M⁺-I, 100%). HRMS (EI) *m/z* calcd for C₁₄H₉N₂I. 331.9811. found. 331.9836. Anal. Calcd for C₁₄H₉IN₂: C, 50.63; H, 2.73; N, 8.43. Found: C, 50.76; H, 2.82; N, 8.05. UV/VIS (acetone): λ_{max} (ε) = 325 (18630), 385 (12570), 398 (12130), 580 (450), 700 (sh), 620 (sh).

General Procedures for the Titration Experiments by UV/vis.

Screw-capped quartz cells were used in order to prevent the volatilization of solvent and to mix up the samples. To a solution of azulene derivative in acetone (2.3 x 10⁻³ M, 3 mL) was added a 0.87 M solution of Hg(ClO₄)₂ in acetone using a pipet at ambient temperature. After mixing, the changes of color were checked by the naked eye and UV/vis spectra were measured.

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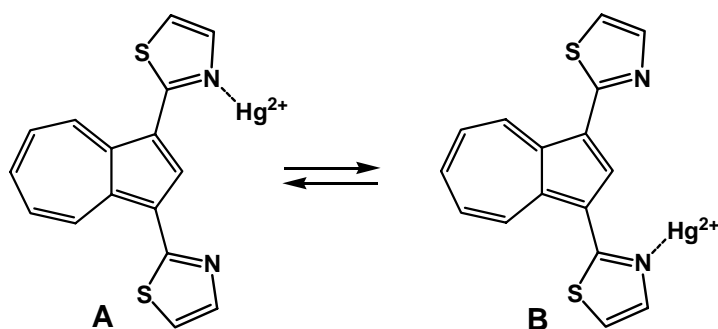
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 - The **4** · Hg²⁺ complex, displayed the symmetrical ¹H NMR signals in spite of two thiazolyl groups,

Hg²⁺-complexed and free thiazolyl group. ¹H NMR (600 MHz, acetone-*d*₆) δ 8.12 (t, 2H, *J* = 10.2 Hz), 8.25 (d, 2H, *J* = 3.6 Hz), 8.41 (t, 1H, *J* = 9.6 Hz), 8.45 (d, 2H, *J* = 3.6 Hz), 9.14 (s, 1H), 9.54 (d, 2H, *J* = 10.2 Hz). Although the proton signals were not split into unsymmetrical pattern upon cooling to –80 °C, signal broadening was observed, suggesting that the Hg²⁺-complex **A** is in fast equilibrium with **B** at ambient temperature on the NMR time scale as shown below.



11. Upon complexation with Hg²⁺ ion, compound **6** showed the downfield shifts (ca. 0.5 ppm for H-2, H-5, H-6 of azulene skeleton, 0.6–0.7 ppm for oxazolyl moiety) or upfield shift (0.2 ppm for H-4 of azulene skeleton) in ¹H NMR spectrum, and blue shift of 73 nm in acetone in UV/vis spectrum. ESI-TOF-MS spectrum of the **6** · Hg²⁺ complex displayed the signal at *m/z* 520.8 assignable to [Hg · **6** · acetone–H]⁺. Compound **7** showed the downfield shifts (ca. 0.3 ppm for H-5, H-6, H-8 of azulene skeleton, 0.5–0.7 ppm for pyrimidinyl moiety) or upfield shift (0.4 ppm for H-4 of azulene skeleton) in ¹H NMR spectrum, and blue shift of 50 nm in acetone in UV/vis spectrum upon complexation with Hg²⁺ ion. ESI-TOF-MS spectrum of the **7** · Hg²⁺ complex showed the signal at *m/z* 591.0 assignable to [Hg · **7** · acetone–H]⁺.
12. The absence of Hg²⁺–S complexation might be due to the low nucleophilicity of the sulfur atom of thiophene ring or the high stability of thiophene. To induce the interaction between a sulfide such as thiophene and Hg²⁺ ion, it seems to be necessary that an organic ligand containing sulfur has the active multi-sites of coordination with Hg²⁺ ion.