Cu(II)- and Hg(II)-Induced Modulation of the Fluorescence Behavior of a Redox-Active Sensor Molecule

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Here, we report on a fluorescent 1,2,4-thiadiazole derivative (oxidized form) and its reduced form, the corresponding iminoyl thiourea. The thiadiazole displays a strong modulation of its fluorescence behavior, selectively upon addition of Cu(II), while the iminoyl thiourea functions as a chemodosimeter for Hg(II). Additionally, the Cu(II)–thiadiazole complex is characterized by HRMS, and the Hg(II)-induced desulfurization of the iminoyl thiourea is monitored by mass spectrometry.

Introduction

While the design of fluorogenic receptors for metal cations such as alkaline and alkaline earth metal cations as well as, more recently, for the d^{10} metal cation Zn(II) is a well-established field in supramolecular chemistry,[1] still a great deal of effort is invested in the construction of devices that are able to signal the presence of heavy and transition metal cations.[2] Considering the growing interest in molecules capable of performing logic operations, special attention has to be focused on the importance of heavy and transition metal cations in such devices serving as molecular switches.[3]

Most of the known molecular systems that monitor these cations selectively, especially strongly quenching paramagnetic Cu(II) or the heavy metal cation Hg(II), exploit the mechanism of complexation-induced fluorescence quenching (CHEQ).[4] Only a very few systems have been reported in which complexation of Cu(II) or Hg(II) results in an enhancement of the fluorescence. In most cases, to suppress the interaction of the quenching metal ions and the fluorophore, considerable synthetic effort had to be made to obtain chemically demanding supramolecular assemblies,[5] usually with a structurally well developed receptor unit being part of a fluoroionophore system.[6] Recently, we reported on a redox-switchable fluoroionophore combining a high selectivity for Hg(II) with a high signal output, i.e., fluorescence enhancement.[7] In this system a simple 1,2,4-thiadiazole was attached via a methylene spacer to an anthracene fluorophore in a way that allowed photoinduced electron transfer (PET) from the receptor to the fluorophore unit to occur. It is known from the literature that selective binding of heavy metal and transition metal cations is achieved by receptors containing sulfur or nitrogen heteroatoms.[8,9] Previously, we have shown the complexation behavior of redox-switchable 1,2,4-thiadiazole/iminoyl thiourea ionophores.[10]

Following this modular approach, a structurally more simple 1,2,4-thiadiazole/iminoyl thiourea redox system with a naphthyl fluorophore was synthesized (Figure 1). Both forms, the heterocyclic thiadiazole **1** (oxidized form) and the ring-opened

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(1) *Chemosensors of Ion and Molecule Recognition*; Desvergne, J. P., Czarnik, A. W., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997; pp 75–90. de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1567. Koike, T. *Chem. Soc. Rev.* **1998**, *27*, 179–184. Kubo, K.; Ishige, R.; Kubo, J.; Sakurai, T. *Talanta* **1999**, *48*, 181–187.

(2) Kido, H.; Szurdoki, F.; Gustin, M. S.; Hammock, B. D. In *Metals and Genetics*; Sarkar, A., Ed.; Kluwer Academic/Plenum Publishers: New York, 1999; pp 101–115. Alfimov, M. V.; Gromov, S. P.; Fedorov, Y. V.; Fedorova, O. A.; Vedernikov, A. I.; Churakov, A. I.; Kuz'mina, L. G.; Howard, J. A. K.; Bossmann, S.; Braun, A.; Woerner, M.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1999**, *121*, 4992–5000.Wang, F.; Schwabacher, A. W. *J. Org. Chem.* **1999**, *64*, 8922–8928. Bergonzi, R.; Fabbrizzi, L.; Licchelli, M.; Mangano, C. *Coord. Chem. Rev.* **1998**, *70*, 31–46.

(3) Beer, P. D.; Gale, P. A.; Cheng, G. Z. *Cood. Chem. Rev.* **1999**, *185–186*, 3–36. Amendola, V.; Fabbrizzi, L.; Linati, L.; Mangano, C.; Pallavinci, P.; Zema, M. *Chem. Eur. J.* **1999**, *12*, 3679–3688. Fabbrizzi, L.; Licchelli, M.; Pallavinci, P. *Acc. Chem. Res.* **1999**, *32*, 846–853. de Silva, A. P.; Dixon, I. M.; Gunaratne, H. Q. N.; Gunnlaugsson, J. T.; Maxwell, P. R. S.; Rice, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 1393–1394.

(4) Krämer, R. *Angew. Chem.* **1998**, *110*, 804–806; *Angew. Chem., Int. Ed.* **1998**, *37*, 772–773. Yoon, J.; Ohler, N. E.; Vance, D. H.; Aumiller, W. D.; Czarnik, A. W. *Tetrahedron Lett.* **1997**, *38*, 3845–3848. Torrado, A.; Walkup, G. K.; Imperiali, B. *J. Am. Chem. Soc.* **1998**, *120*, 609–610. Bernardo, M. A.; Pina, F.; Escuder, B.; Garcia-España, E.; Godino-Salido, M. L.; LaTorre, J.; Luis, S. V.; Ramirez, J. A.; Soriano, C. *J. Chem. Soc., Dalton Trans.* **1999**, 915–921.

(5) Inuoe, M. B.; Medrano, F.; Inoue, M.; Raitsimring, A.; Fernando, Q. *Inorg. Chem.* **1997**, *36*, 2335–2340. Grandini, P.; Mancin, F.; Tecilla, P.; Scrimin, P.; Tonellato, U. *Angew. Chem.* **1999**, *111*, 3247–3250.

(6) Gosh, P.; Bharadwaj, P. K.; Roy, J.; Gosh, S. *J. Am. Chem. Soc.* **1997**, *119*, 11903–11909. Talanova, G. G.; Elkarim, N. S. A.; Talanov, V. S.; Bartsch, R. A. *Anal. Chem.* **1999**, *71*, 3106–3109. Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968–969.

(7) Hennrich, G.; Sonnenschein, H.; Resch-Genger, U. *J. Am. Chem. Soc.* **1999**, *121*, 5073–5074.

(8) Chae, M. Y.; Czarnik, A. W. *J. Am. Chem. Soc.* **1992**, *114*, 9704–9705. Dujols, V.; Ford, F.; Czarnik, A. W. *J. Am. Chem. Soc.* **1997**, *119*, 7386–7387.

(9) Guillon, E.; Dechamps-Olivier, I.; Mohamadou, A.; Barbier, J.-P. *Inorg. Chim. Acta* **1998**, *268*, 13–19. Sandor, M.; Geistmann, F.; Schuster, M. *Anal. Chim. Acta* **1999**, *388*, 19–26. Cattrall, R. W.; Gregorio, C. C.; Webster, R. D. *Anal. Chem.* **1997**, *69*, 3353–3359. Bernardo, M. A.; Pina, F.; Garcia-España, E.; LaTorre, J.; Luis, S. V.; Llinares, J. M.; Ramirez, J. A.; Soriano, C. *Inorg. Chem.* **1998**, *37*, 3935–3942.

(10) Hennrich, G.; Sonnenschein, H.; Resch-Genger, U. *Eur. J. Org. Chem.* **2000**, *3*, 539–542.

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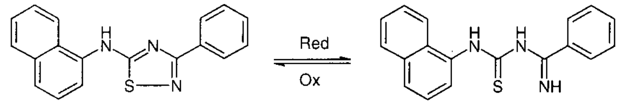


1 **2**

Figure 1. Oxidized form **1**: 3-phenyl-5-(1-aminonaphthyl)-1,2,4-thiadiazole. Reduced form **2**: *N*-iminobenzyl-*N*′-(α-naphthyl)-thiourea.

Table 1. Spectroscopic Data of the Free Compounds **1**, **2**, and **3** (ϵ, Extinction Coefficient; Ex, Excitation Wavelength in nm; Φ_f, Fluorescence Quantum Yield)[a]

	absorption λ_{ex}/nm ($\log_{10} \epsilon$)	fluorescence λ_{em}/nm (ex)	Φ_f
1	220 (4.66), 243 (4.48), 319 (3.95)	405 (350)	1.9×10^{-3}
2	217 (4.74), 305 (4.22)	334, 412* (290)	5.1×10^{-3}
3	223 (4.81), 309 (4.29)	368 (290)	5.9×10^{-3}

[a] (*) Broad shoulder, weakly fluorescent.

iminoyl thiourea **2** (reduced form), can be converted into each other by chemical oxidation or reduction, respectively. Therefore, the system presented can be considered as a two-faced molecule containing binding sites that differ in geometry and electron-donating capacity, depending on the redox state.

In this paper, we study the influence of different heavy metal and transition metal cations on the fluorescence behavior of **1** and **2** by optical spectroscopy accompanied by mass spectroscopic measurements. Mass spectroscopy has proved to be a powerful tool in the study of host−guest interactions.[11] Here, it offers the opportunity to monitor the chemical processes occurring in solution in a concentration range similar to that used for the fluorometric studies. Furthermore, all the metal-cation-containing solutions investigated are accessible by this method, whereas with NMR spectroscopy the paramagnetism of Cu(II) would lead to severe problems. Due to the relatively low association constants expected[12] and the difficulties in obtaining suitable crystals for X-ray analysis, we used high-resolution mass (HRMS) and IR spectroscopy for complex characterization.

Results and Discussion

Synthesis. Compound **2** was prepared under mild conditions in 56% yield by reacting benzamidinium hydrochloride with 1-naphthylisothiocyanate in the presence of sodium hydrogen carbonate. Using 1-naphthylisocyanate in the presence of triethylamine, the urea **3** as a reference compound for **2** was obtained in the same manner. **2** can be easily converted into the 1,2,4-thiadiazole **1** by oxidation with iodine. The back-reduction of **1**, leading to the thiourea **2**, can be achieved with zinc in glacial acetic acid.[13]

Spectroscopic Studies. The absorption and fluorescence properties of free **1**, **2**, and **3** are listed in Table 1. The spectra in acetonitrile were recorded in the concentration range between 1.1×10^{-5} and 3.9×10^{-5} for **1**, **2**, and **3**.

Addition of various bivalent cations (Ca(II), Hg(II), Mg(II), Ni(II), and Pb(II)) in a 1−100-fold excess (complete complexation) has only minor effects on the fluorescence behavior of the 1,2,4-thiadiazole **1**. The emission of weakly fluorescent compound **1** is quenched by Ni(II) and Pb(II), while addition of Ca(II) gives a slightly enhanced (2-fold) fluorescence intensity. No spectral shifts are observed. The cation-induced changes in the UV/vis spectrum of **1** are negligible.

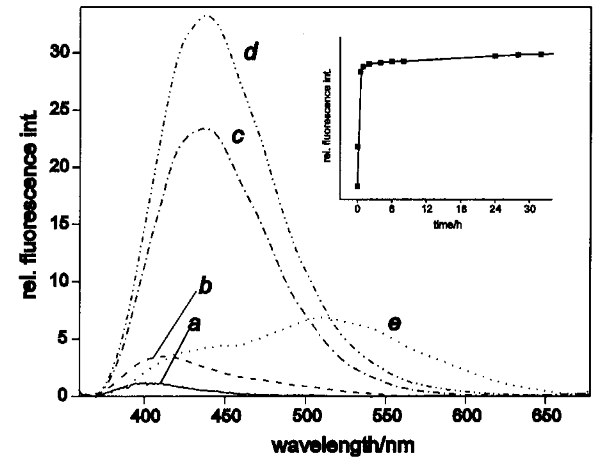


Figure 2. Fluorescence behavior of **1** ($c = 3.65 \times 10^{-5}$ M in acetonitrile, excitation at 350 nm) upon addition of $Cu(ClO_4)_2$; measurement after 48 h: (a) free **1**; (b) 0.1 equiv of Cu(II); (c) 0.3 equiv of Cu(II); (d) 0.5 equiv of Cu(II); (e) 2 equiv of Cu(II). Inset: ■, **1** + 0.5 equiv of Cu(II), time-dependent fluorescence enhancement.

Remarkably, a drastic Cu(II)-induced modulation of the fluorescence of **1** is found (Figure 2). Upon addition of Cu(II) in the sub-parts per billion concentration region, i.e., 0.05−0.5 equiv (0.18−1.8 μM) of **1**, the probe's fluorescence is switched on immediately, accompanied by a red shift of the emission maximum from 405 nm for the free thiadiazole derivative **1** to 442 nm in the presence of 0.5 equiv Cu(II), successively.

The strongest fluorescence enhancement (FE) is observed for a metal-to-ligand concentration ratio (Cu(II):**1**) of 1:2. The increase of the emission intensity is time dependent, varying additionally with the concentration of **1**. Immediately after addition of 0.5 equiv of Cu(II), a 4-fold fluorescence enhancement is obtained, and an approximately constant signal is reached after 6 h (inset, Figure 2). The final FE is 46-fold, the fluorescence quantum yield of the Cu(II)−**1** complex being 0.088.

Increasing the concentration of Cu(II) results in the occurrence of a new broad and structureless band with a global maximum located at 531 nm. This behavior is also dependent on the concentration of **1** and is consistent with the formation of intermolecular excimers.[14] The excimer complex displays an enhanced fluorescence compared to the fluorescence of the free monomeric compound **1**. Upon a further increase of the metal ion concentration, gradual dynamic fluorescence quenching is observed.

Mass spectrometry proved the formation of a 1:2 Cu(II) complex by its characteristic isotopic pattern and high resolution of the mass signal at *m*/*z* 667, using samples with concentrations of the same order of magnitude as those employed for the spectroscopic studies. For both metal-to-ligand ratios investigated, i.e., 1:1 and 1:2, the same 1:2 Cu(II)−**1** complex was found as the only complex species. Also in mass spectroscopy, time-dependent complex formation can be observed from a time-dependent variation of the peak intensities of **1** and the complex. Hence, also the complex displaying excimer emission exists in a 1:2 stoichiometry. The different fluorescence behavior is

(11) Vincenti, M. *J. Mass Spectrom.* **1995**, *30*, 925−939.
(12) da Silva, A. S.; de Silva, M. A. A.; Carvalho, C. E. M.; Antunes, O. A. C.; Herrera, J. O. M.; Brinn, I. M.; Mangrich, A. S. *Inorg. Chim. Acta* **1999**, *292*, 1−6. Maekawa, M.; Munakata, M.; Kuroda-Sowa, T.; Suenaga, Y.; Sugimoto, K. *Inorg. Chim. Acta* **1999**, *290*, 153−158.
(13) See ref 10 and citations therein.
(14) Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans.* **1995**, 1305−1314. Beeby, A.; Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans.* **1996**, 1565−1579.

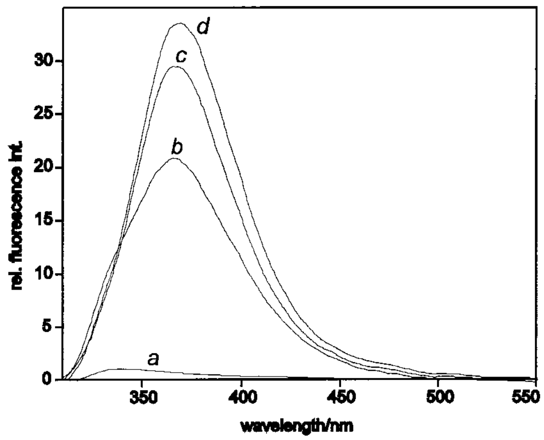
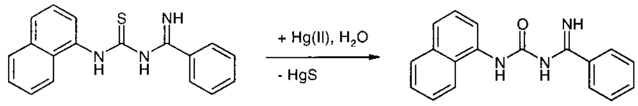


Figure 3. Fluorescence enhancement of **2** ($c = 1.94 \times 10^{-5}$ M in acetonitrile, excitation at 290 nm) upon addition of $Hg(ClO_4)_2$; measurement after 48 h: (a) free **2**; (b) 0.1 equiv of Hg(II); (c) 10 equiv of Hg(II); (d) 1 equiv of Hg(II).



2 **3**

Figure 4. Desulfurization of the iminoylthiourea **2** by Hg(II) leading to the corresponding urea **3**.

therefore attributed to different coordination modes within the complex due to various possible binding sites and conformers.

To reveal more details about the exact mode of the Cu(II) coordination, IR spectroscopic measurements were performed in addition to the UV/vis and MS studies. By comparison of the spectral position and shape of the vibrational bands of the free ligand **1** with those of the Cu(II) complex, obtained as an amorphous solid, it can be seen that Cu(II) coordination by **1** takes place to the NH group and additionally to the thiadiazole ring, most likely to the N_4-nitrogen.[15]

Upon addition of Hg(II) to a solution of **2**, a red shift and an increase in the naphthalene emission are observed immediately, after 48 h finally yielding a band at 368 nm with a 34-fold enhanced fluorescence intensity while the emission band at initially 334 nm has disappeared almost completely (Figure 3). Simultaneously, the absorption maximum of **2** at 305 nm is shifted to 295 nm. This time-dependent effect, reaching constant signal intensities after 48 h, is significant with amounts of Hg(II) exceeding 0.1 equiv (1.9 μmol). An excess of Hg(II) (>1 equiv) leads to an initial fluorescence enhancement, followed by a subsequent bimolecular quenching. The fluorescence of **2** is quenched completely after 48 h upon addition of a 100-fold excess (1.9 mmol) of Hg(II).

This behavior is due to the desulfurization of the thiocarbonyl function by the thiophilic Hg(II) cation, leading to the *N*-iminobenzyl-*N′*-(α-naphthyl)-urea **3** (Table 1 and Figure 4). Free **3** displays strongly enhanced fluorescence upon addition of Hg(II). The enhancement of the emission intensity proceeds slowly and is accompanied by a hypsochromic shift of the absorption band from 309 to 291 nm. After 48 h the fluorescence quantum yield has increased from 5.9×10^{-3} for free **3** to 1.7×10^{-1}.

Although a slow complexation of Hg(II) by urea **3** can be assumed,[16] the formation of a complex species could not be confirmed by mass spectrometry. Upon addition of Hg(II) (2 equiv) to **2** in acetonitrile solution, a signal at *m/z* 290 appears rapidly, attributed to the molecular ion $[\mathbf{3} + H]^+$, while the peak at *m/z* 304 (molecular ion $[\mathbf{2} - H]^+$) decreases. At higher values, various ion peaks with weak intensities are found which are attributed to the presence of cluster ions only; i.e., there is no evidence for the formation of a Hg(II) complex.

Also for the iminoyl thiourea **2**, the fluorometric response upon addition of various cations proved to be very selective for Hg(II).[17] A 100-fold excess (complete complexation) of Ca(II) and Ni(II) results in a modest enhancement (40% and 20% respectively) of the emission intensity at 334 nm. Addition of 100 equiv of Cu(II) yields a weakly fluorescent excimer band at 519 nm. Again, the effects observed in the absorption spectra are negligible.

Conclusion

We synthesized a structurally simple redox-switchable molecular sensing system which exists in two structurally different forms. Each form is capable of signaling selectively the strongly fluorescence quenching cations Cu(II) respectively Hg(II) by drastic fluorescence enhancement. A fluorescent 1:2 Cu(II)−**1** complex is obtained, displaying a FE factor of 46. Switching on the fluorescence is achieved immediately after addition of the respective metal cation, although gaining a full, constant signal requires a long period of time, making the system less attractive for analytical applications. The iminoylthiourea **2** functions as a chemodosimeter, reporting selectively the presence of Hg(II) by a 34-fold fluorescence enhancement. The signaling mechanism for both forms, i.e., the Cu(II)−**1** complex formation or the chemical reaction of **2**, is revealed in solution by means of mass spectroscopy.

Experimental Section

General Methods. All the reagents and solvents, which were of the highest purity commercially available, were obtained from Aldrich and Merck, respectively. The reaction progress was monitored by analytical thin-layer chromatography (TLC), performed with plastic silica gel plates 60 F_{254} (5735, Merck). Column chromatography was carried out with silica gel 60 (7731, Merck). The purity of **1** and **2** was checked by HPLC. Nuclear magnetic resonance data were recorded on a UNITY plus-500 spectrometer with chemical shifts reported in parts per million (Me_4Si as internal standard, *J* in hertz, coupling constants taken directly from the obtained spectra). IR spectra were determined in KBr with a Perkin-Elmer model 1600 instrument. Melting points were determined using a Boetius apparatus and are uncorrected.

Fluorescence and UV/Vis Spectroscopy. Absorption spectra were recorded on a Carl Zeiss SPECORD M400 spectrometer. A Spectronic Instruments Inc. 8100 fluorescence spectrometer was employed for the fluorescence studies. Emission measurements were performed in a four-sided 1 cm quartz cell at room temperature in a right angle geometry and are corrected for the spectral response of the detection system. Standard solutions (10^{-2}−10^{-3} M) for titration experiments were prepared using spectroscopic grade acetonitrile and dried metal perchlorates. Appropriate dilution was carried out using volumetric pipets. The spectra in acetonitrile were recorded at concentrations of 3.9×10^{-5} M for **1**, 1.51×10^{-5} M for **2**, and 1.10×10^{-5} M for **3**. The fluorescence quantum yields were determined using quinine sulfate as standard ($\Phi_f = 0.55$)[18] with absorbances of the solutions of **1**, **2**, and **3** adjusted to 0.1−0.2 at the excitation wavelength.

(15) Due to the difficulties of making an unequivocal assignment of the various peaks in the region between 1600 and 1200 cm^{-1} to the respective vibrational transitions, we restrict ourselves to only noting the significant differences in the spectra of free **1** and the Cu(II) complex in this area. See also: Kurzer, F. *J. Chem. Soc., Perkin Trans. 1* **1985**, 311−314.

(16) Richter, R.; Sieler, J.; Beyer, L.; Lindqvist, O.; Andersen, L. *Z. Anorg. Allg. Chem.* **1986**, *522*, 171−183.

(17) Desulfurization of **2** occurs also with Ag(I), leading to a 30-fold fluorescence enhancement.

Mass Spectrometry. All the mass spectra were acquired on a MAT 95 (Finnigan MAT, Bremen) high-resolution sector field mass spectrometer with electrospray ionization (API-II). Typical, optimized values for some parameters were the following: capillary voltage, 2.8 kV; capillary temperature, 230 °C; capillary/skimmer voltage, 50 V; sheath/auxiliary gas, 4/0.2 L/min air. The acetonitrile dissolved samples were flow-injected by using a 20 μL sample loop with methanol as the mobile phase at a flow rate of 200 μL/min. The exact masses of the ions were determined by peak matching with polypropylene glycols at a resolution of 5000−6000.

Materials. ***N*-Iminobenzyl-*N'*-(α-naphthyl)-thiourea (2).** A mixture of 1-naphthylisothiocyanate (185 mg, 1.0 mmol), benzamidine hydrochloride (156 mg, 1.0 mmol), and sodium hydrogen carbonate (140 mg) was stirred overnight in dioxane (20 mL) at room temperature. The resulting solid was filtered off and washed with dioxane. The filtrate was concentrated in vacuo. The remaining yellow oil was treated with diethyl ether and *n*-hexane to give a yellow solid. Recrystallization from acetonitrile−ethanol (4:1 v/v) gave pale yellow crystals. Yield 171 mg (56%), mp 160−164 °C. Anal. Calcd for $C_{18}H_{15}N_3S$: C, 70.82; H, 4.92; N, 13.77. Found: C, 70.82; H, 4.86; N, 13.54. NMR: δ_H ($CDCl_3$) 11.6 (1 H, br s, N*H*), 10.8 (1 H, br s, N*H*), 8.05−7.25 (12 H, m, Ph-*H*, Naph-*H*), 6.5 (1H, br s, N*H*); δ_C (DMSO-d_6) 186.71 (−*C*═S), 162.30 (−*C*═N−), 139.49, 134.64, 131.82, 128.96, 128.44, 128.21, 128.06, 127.61, 124.66, 123.86, 123.53, 122.48 (Ph−*C*, Naph−*C*);. MS (ESI): *m*/*z* (relative intensity) 304 ($[M - H]^+$, 100), 256, 240, 228. TLC: $R_f = 0.16$ *n*-Hex−EE (4:1 v/v).

3-Phenyl-5-(1-aminonaphthyl)-1,2,4-thiadiazole (1). To a suspension of **2** (146 mg, 0.5 mmol) in chloroform (20 mL) was added a saturated chloroformic iodine solution dropwise until no further decolorization was observed. NaOH (1 N, 20 mL) was added, the suspension was stirred for 10 min, and the phases were separated. The organic layer was dried ($MgSO_4$), and the solvent was evaporated to give a yellow solid. Recrystallization from 2-propanol yielded pure **1** as colorless crystals. Yield 126 mg (83%), mp 152 °C. NMR: δ_H ($CDCl_3$) 8.8 (1 H, br s, N*H*), 8.13−7.25 (12 H, m, Ph−*H*, Naph−*H*); δ_C ($CDCl_3$) 183.85 (−*C*−S), 169.76 (−N−*C*═N−), 135.23, 134.56, 132.91, 129.97, 128.75, 128.39, 127.84, 127.54, 127.07, 126.98, 126.91, 125.78, 121.08, 119.07 (Ph−*C*, Naph−*C*). IR: ν_{max} 3157s (NH), 1630w (C═N). HRMS: calculated for $[C_{18}H_{13}N_4S-H]^-$, 302.0752; found, 302.0748; error 1.5 ppm. TLC: $R_f = 0.63$ *n*-Hex−EE (4:1 v/v).

Bis-(3-phenyl-5-(1-aminonaphthyl)-1,2,4-thiadiazole)−Cu(II) Complex. **(a) In Solution.** A solution of **1** ($c = 3.65 \times 10^{-4}$ M) in acetonitrile was treated with 2 equiv of $Cu(ClO_4)_2$ and left for 48 h before the measurement. HRMS: calculated for $[C_{36}H_{24}N_6S_2Cu]$, 667.0700; found, 667.0700; error −0.6 ppm.

(**b**) **As a Solid.** To a solution of **1** (100 mg, 0.33 mmol) in ethyl acetate (8 mL) was added copper(II) triflate (58 mg, 0.16 mmol). Slow evaporation of the solvent afforded the Cu(II) complex after 6 d as a brown, amorphous solid. IR: ν_{max} 3164br (NH), 1611s (C═N). HRMS: calculated for $[C_{36}H_{26}N_6S_2Cu]$, 669.0956; found, 669.0945; error 1.5 ppm.

***N*-Iminobenzyl-*N'*-(α-naphthyl)-urea (3).** Benzamidinium hydrochloride (1.0 g, 6.4 mmol) and 1-naphthylisocyanate (1.1 g, 6.4 mmol) were refluxed in dioxane (50 mL) and triethylamine (5 mL) for 2.5 h. The resulting solid was filtered off, and the filtrate was concentrated in vacuo. Treating the remaining yellow oil with chloroform−petroleum ether (4 mL, 1:1 v/v) and leaving it overnight in the refrigerator led to the precipitation of colorless crystals which were filtered off and recrystallized from acetonitrile. Yield 380 mg (41%), mp 138 °C. Anal. Calcd for $C_{18}H_{15}N_3O$: C, 70.74; H, 5.19; N, 14.53. Found: C, 70.64; H, 5.07; N, 14.23. NMR: δ_H ($CDCl_3$) 9.96 (1 H, br s, Naph−N*H*), 8.04−7.47 (13 H, m, Ph−*H*, Naph−*H*, −N*H*), 6.21 (1 H, br s, N*H*); δ_C ($CDCl_3$) 165.90 (−*C*═O), 164.11 (−*C*═N−), 135.43, 134.14, 133.42, 131.82, 128.80, 128.62, 126.97, 125.97, 125.83, 124.66, 121.03, 119.16 (Ph−*C*, Naph−*C*). MS (FAB): *m*/*z* (relative intensity) 290 ($[M + H]^+$, 100), 169, 144, 121. TLC: $R_f = 0.15$ *n*-Hex−EE (4:1 v/v).

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(18) Testa, A. C. *Fluorescence News* **1969**, *4*, 1−3. Olmsted, J., III. *J. Phys. Chem.* **1979**, *83*, 2581−2584.