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## Novel squaraine signalling Zn(II) ions: three-state fluorescence response to a single input

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### Abstract

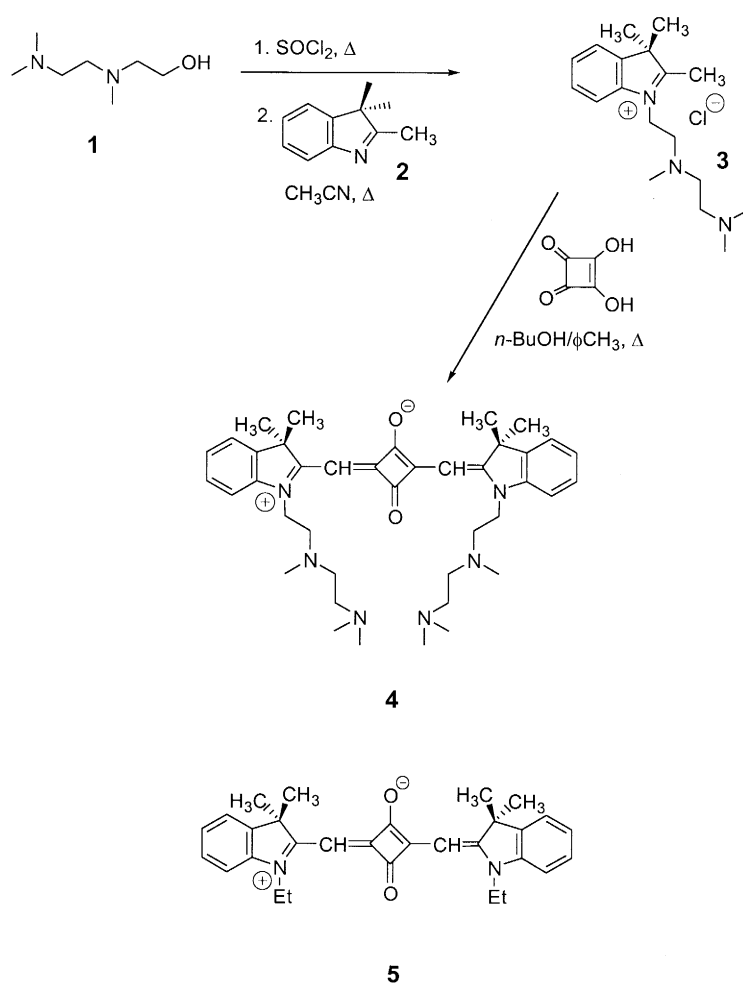
A novel metal ion sensitive 2,3,3-trimethyl-3*H*-indole-derived squaraine dye showing different fluorescence responses depending on the complexation stoichiometry has been synthesized. Thus, three levels of signals are attainable by varying the Zn(II) ion concentration. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** fluorescence; dyes; indolines/indolinones; molecular devices.

En route to a perhaps not so distant goal of information processing at the molecular level, there is intense activity in the design, synthesis and characterization of molecular switches and logic gates. Controllable fluorescence signals mostly resulting from PET activity<sup>1</sup> are at the center of current activity in the field. In recent years, carrying the notions of solid-state silicon-based computing to the molecular world, molecular analogs of AND,<sup>2</sup> OR,<sup>3</sup> NOR,<sup>4</sup> XOR<sup>5</sup> and INHIBIT<sup>4</sup> logic gates have been proposed. The potential is tremendous, but molecular computing, as suggested previously,<sup>6</sup> does not need to be limited to the two states (off–on) of the binary logic. In principle at least, one kind of input (chemical, light or otherwise) can address more than two states. The advantage to be gained in the speed of processing, memory density and power consumption is enormous.<sup>7</sup> In addition, much simpler construction with fewer gate elements seems to be possible. We now report a molecular system that can be considered to respond in ternary logic.

As a part of our study of squaraine-based ion sensing molecular devices,<sup>8</sup> we have targeted *N*-(3,6-dimethyl-3,6-diazaheptyl)indolenine-squaraine (**4**) in order to investigate the participation of groups attached to the indolenine system and the squaryl oxygen in metal ion coordination. Squaraines have very promising spectral properties for molecular sensors, including high quantum yield and long wavelength excitation and emission. According to CNDO calculations,<sup>9</sup> the charge transfer in these molecules is mostly confined to the squaryl moiety, making the squaryl oxygens the primary electron donors in the fluorophore structure. Thus, targeting that part of the molecule is a promising way of generating a stronger signal on metal ion binding. The squaraine **4** was synthesized in three steps from commercially

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Scheme 1.

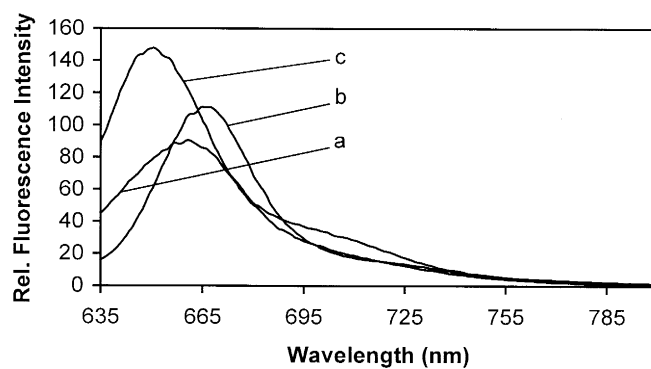


Fig. 1. Changes in the emission spectrum of 1.0  $\mu\text{M}$  squaraine **4** with indicated concentrations of Zn(II). Intermediate concentrations were omitted for clarity, but a significant shift in emission to shorter wavelengths was observable at 1 mM Zn(II). (a) Zn(II)=0; (b) Zn(II)=1.0  $\mu\text{M}$ , Zn(II)/ligand=1; (c) Zn(II)=0.025 M, Zn(II)/ligand=25 000. Excitation is at 600 nm

available materials (Scheme 1). *N*-(*N'*,*N'*-Dimethylaminoethyl)-*N*-methylaminoethanol was converted to the corresponding halide by refluxing in  $\text{SOCl}_2$ . Quaternization of the 2,3,3-trimethylindolenine proceeds smoothly to give **3**. Squaraine forming condensation was carried out in an *n*-BuOH/ $\text{PhCH}_3$  solvent mixture using a Dean–Stark trap for the azeotropic removal of the water. Compound **4** was obtained in good yield (85%) and purified by precipitation of a chloroform solution by the addition of hexane. The material obtained in this way was analytically pure.<sup>10</sup> The squaraine as expected had a sharp absorption peak around 640 nm. To serve as a reference for the parent squaraine response, the well-known squaraine dye **5** ( $\text{R}=\text{CH}_2\text{CH}_3$ ) was also synthesized. This squaraine, as expected, showed no response to  $\text{Zn(II)}$  at any concentration up to 0.2 M, either in absorption or emission spectra, demonstrating that the squaryl oxygens alone are unable to chelate  $\text{Zn(II)}$ . However, the response of compound **4** to different concentrations of  $\text{Zn(II)}$  in a solvent system of 50% acetonitrile–50% *n*-butanol is highly interesting (Fig. 1). When excited at 600 nm, the emission maximum at 660 nm shifts to 665 nm increasing in intensity at that wavelength up to 1.0  $\mu\text{M}$   $\text{Zn(II)}$  which corresponds to a ligand to  $\text{Zn(II)}$  ratio of 1:1; further increase in the ion concentration decreases the emission intensity at 665 nm, and as the  $\text{Zn(II)}$  concentration reaches 0.025 M ( $\text{Zn(II)}$  to ligand ratio: 25 000), the emission peak is shifted to 650 nm. When followed at 640 nm, the fluorescence emission intensity first decreases three-fold at low concentrations and increases two-fold at high concentrations compared to the free squaraine ligand. Thus, the molecule offers three  $\text{Zn(II)}$  addressable states, providing an example of a molecular ternary logic: state 0=0  $\text{Zn(II)}$  medium fluorescence, state 1=1.0  $\mu\text{M}$  low fluorescence, and state 2= $2.5 \times 10^{-2}$  M high fluorescence. The apparent increase in the emission intensity at shorter wavelengths is not likely to be due to medium effects, because the spectral shift is already present at 1 mM  $\text{Zn(II)}$  concentration. This multi-state response is a reflection of two complexes of different stoichiometries becoming the dominant species at different concentrations (1:1 versus 2:1) Thus, we demonstrate that in the design of logic elements for molecular information processing ternary and perhaps higher order logic functions can be useful. Our work along these lines is in progress.

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9. Bigelow, R. W.; Freund, H. J. *Chem. Phys.* **1986**, *107*, 159.
10. <sup>1</sup>H NMR, (DMSO-*d*<sub>6</sub>, 400 MHz) δ 1.49 (s, 12H), 3.48–3.78 (m, 34H), 5.98 (s, 2H), 7.20 (t, 2H), 7.27–7.43 (m, 4H), 7.58 (d, 2H); <sup>13</sup>C NMR, (DMSO-*d*<sub>6</sub>, 100 MHz) δ 24.8, 25.0, 38.3, 41.2, 53.1, 53.9, 55.2, 58.0, 112.9, 120.2, 122.3, 126.5, 133.6, 140.8, 150.5, 151.4, 165.5; MS (FAB) 652 (M<sup>+</sup>); elemental analysis: found: C, 73.23; H, 6.77; N, 12.51. C<sub>40</sub>H<sub>56</sub>N<sub>6</sub>O<sub>2</sub> requires: C, 73.58; H, 8.64; N, 12.87.