

Supporting Information Available for

**Design and Synthesis of A Caged Zn²⁺ Probe,
8-Benzenesulfonyloxy-5-*N,N*-dimethylaminosulfonylquinolin-2-ylmethyl-pendant
1,4,7,10-Tetraazacyclododecane, and Its Hydrolytic Uncaging upon Complexation
with Zn²⁺.**

**Shin Aoki,^{*,†,‡} Kazusa Sakurama,[§] Ryosuke Ohshima,[†] Nanako Matsuo,[†] Yasuyuki
Yamada,^{†,‡} Ryoko Takasawa,[†] Sei-ichi Tanuma,[†] Kei Takeda,[§] and Eiichi Kimura[#]**

Faculty of Pharmaceutical Sciences, Tokyo University of Science,

2641 Yamazaki, Noda 278-8510 Japan,

Center for Drug Delivery Research, Tokyo University of Science,

2641 Yamazaki, Noda 278-8510 Japan,

Division of Medicinal Chemistry, Graduate School of Biomedical Sciences,

Hiroshima University, 1-2-3 Kasumi, Minami-ku, Hiroshima, 734-8551 Japan,

And Department of Chemistry, Shizuoka University

836 Ohya, Suruga-ku, Shizuoka, 422-8529 Japan

[†] Faculty of Pharmaceutical Sciences, Tokyo University of Science

[‡] Center for Drug Delivery Research, Tokyo University of Science

[§] Graduate School of Biomedical Sciences, Hiroshima University

[#] Department of Chemistry, Shizuoka University

^{*} To whom correspondence should be addressed.

Shin Aoki : shinaoki@rs.noda.tus.ac.jp

Figure S1. Formation of a Zn^{2+} complex of **8** ($50\ \mu\text{M}$) followed by ε at 274 nm upon addition of $50\ \mu\text{M}\ \text{Zn}^{2+}$ (a), $250\ \mu\text{M}\ \text{Zn}^{2+}$ (b), and $500\ \mu\text{M}\ \text{Zn}^{2+}$ (c) at pH 7.4 (10 mM HEPES with $I = 0.1$ (NaNO_3)) and $25\ ^\circ\text{C}$.

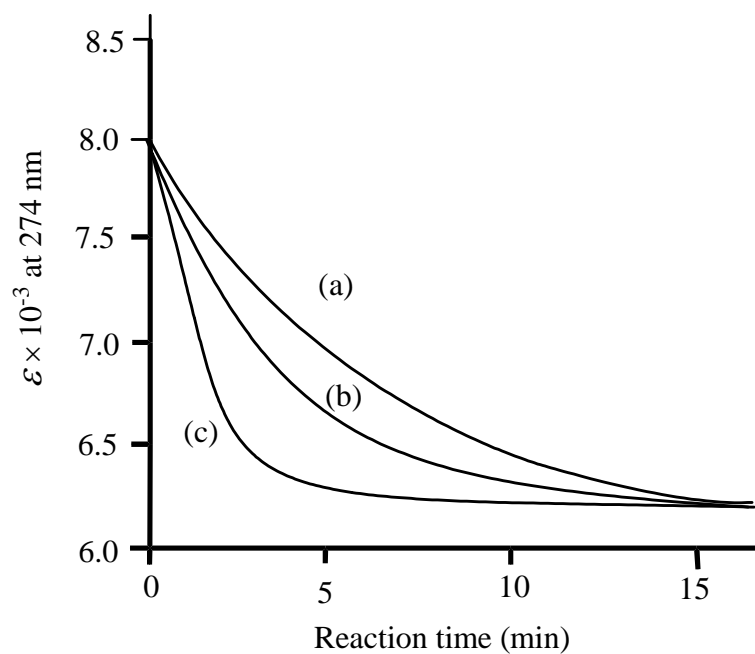


Figure S2. Hydrolysis of 4-nitrophenyl acetate (100 μM) in the presence of 100 μM **1** (ZnL^1) (plain curve) and 100 μM **2** (CdL^1) (dashed curve) in 10/90 $\text{CH}_3\text{CN}/10\text{ mM TAPS}$ (pH 8.4 with $I = 0.1$ (NaNO_3)) at 25 $^\circ\text{C}$. C_0 = initial concentration of 4NPA C_X = concentration of formed 4-nitrophenolate. The $\log \varepsilon$ value of 4-nitrophenolate at 400 nm is 4.24 at pH 8.4 (ref. 33 in the text).

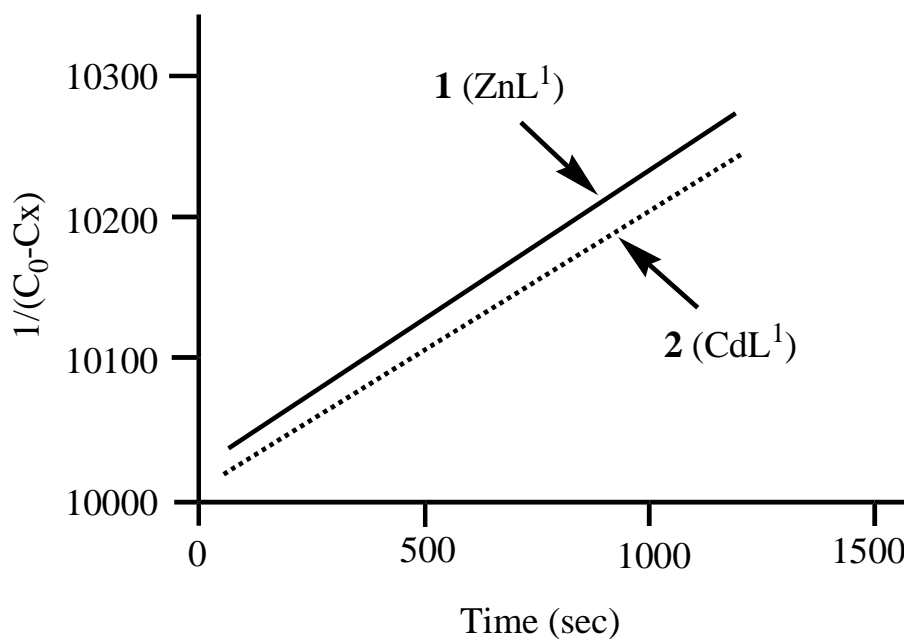


Figure S3. The $1/T$ - $\ln(k_2/T)$ -profile for the hydrolysis of 4NPA (50 μM) catalyzed by 100 μM **1** (ZnL^1) (closed circles) and 100 μM **2** (CdL^1) (closed squares) in 10/90 $\text{CH}_3\text{CN}/10$ mM TAPS (pH 8.4) with $I = 0.1$ (NaNO_3).

