

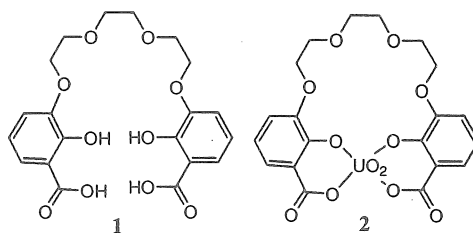
Design of the self-organized hosts as a specific sensor of alkaline or alkaline earth metal ions

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Summary

Development of the strategy for molecular design of self-organized hosts for alkaline or alkaline earth metal ions has been established. Prehost molecule **1** has been prepared according to the strategy. Prehost **1** has two salicylic acid groups at the both ends of tri(ethylene glycol). Prehost **1** has been self-organized in the presence of uranyl ion to give the real host molecule **2**. Binding properties of **2** were studied for alkaline metal or alkaline earth metal ions by ¹H-NMR in DMSO-d₆. Relative equilibrium constants of **2** with Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Na⁺, or K⁺ were summarized in Table 1.

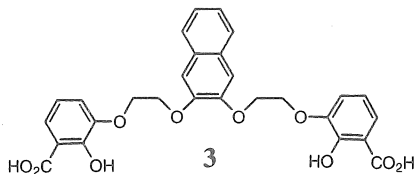


Self-organized host **2** showed the maximum equilibrium constant for Sr²⁺ (ionic radius: 1.18 Å). For smaller alkaline earth metal ions, such as Mg²⁺ and Ca²⁺, the relative equilibrium constants K_{rel} were

Table 1. Relative equilibrium constants of **2** with alkali and alkaline earth metal ions.

M ²⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Na ⁺	K ⁺
ionic radius (Å)	0.72	1.00	1.18	1.35	1.02	1.38
K _{rel}	1/900	1/4	1	1/20	1/13	1/33

decreased dramatically. In the case of larger alkaline earth metal ion, Ba²⁺, K_{rel} were decreased also. These results indicate that self-organized host **2** provides hole size suitable for Sr²⁺. Equilibrium constant of **2** with Sr²⁺ was measured with cryptand [2.2.1], which has a very strong affinity for Sr²⁺ (log K = 6.1). By the competition experiment, affinity of **2** for Sr²⁺ is 50 times larger than that of cryptand [2.2.1]. In order to obtain ion sensing ability, prehost **3** was synthesized with a fluorescent probe in the spacer.



In fluorescence experiment, uranyl **3** self-organized host showed 10 times larger affinity with Sr²⁺ than K⁺. Based on these results, it is indicated that a specific sensor of Sr²⁺ has been developed.