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Cerium-based metal–organic tetrahedron for selective sensing of ribonucleosides through the cooperation of hydrogen bonding interaction

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ABSTRACT

By incorporating triamine-triazines as hydrogen bonding sites into the fragment of the ligand, cerium-based metal–organic tetrahedron Ce-TBMN has been used as an artificial chemosensor for selective recognition of guanosine over other ribonucleosides. With the size constraint of the tetrahedron, Ce-TBMN showed the selective fluorescent response of GMP among the twelve ribonucleotides.

Supramolecular assembly of pre-designed organic and inorganic building blocks is an excellent tool of constructing well-defined nano-sized molecular cavities which can encapsulate and stabilize special guest substrates [1–5]. By incorporating hydrogen bonding sites for efficient guest interactions and aromatic groups for π stacking interactions, such metal–organic polyhedra have been considered as an efficient candidate to achieve excellent nucleoside recognition [6,7].

The recognition of nucleoside derivatives is essential for biologically significant functions such as genome duplication, protein synthesis, and signal transduction [8,9]. It is difficult to detect special nucleoside with high selectivity because of the subtle variation of the nucleoside structures. Generally, the complementary hydrogen bonding and π stacking interactions play important roles in the molecular recognition of nucleoside [10–13]. Inspired by the hydrogen bonding interaction of protein with other biochemical species in living systems [14–17], we have reported several Werner-type capsules having amide groups as multiple hydrogen bonding sites for the recognition of nucleoside derivatives [6,7] and saccharides [18–20].

Herein we expanded our Werner-type capsules to a well-defined Ce-based tetrahedron supramolecular nanocage Ce-TBMN, which has been proved to be an efficient molecular flask to prompt the Knoevenagel condensation reactions of salicylaldehyde derivatives and cyanosilylation reactions of aromatic aldehydes, [21] for selective sensing of nucleoside derivatives through the cooperation of hydrogen bonding interactions, π stacking interactions and the well-defined cavity of the capsule (Fig. 1). The triamine-triazine groups within the tetrahedron Ce-TBMN might work as multiple hydrogen bonding sites for the selective recognition of glucosamine [22]. The edge Ce···Ce separations of Ce-TBMN were about 18.0 Å and the inner volume of the tetrahedron was about 630 $Å^3$ with the opening size of the windows on the edges being about 18.0 × 7.6 $Å^2$, allowing the guest molecule with suitable size to ingress or egress the cavity to interact with the tetrahedron. It is anticipated that the complementary hydrogen bonding and the potential π stacking interaction, in cooperation with the spatial affect of the tetrahedron nanocage would benefit the selective recognition of nucleoside molecule. At the same time, the efficient electronic communication between the multiple hydrogen bonding site and the 2-hydroxy-1-naphthalene would convert the recognition information into the generation of fluorescent signal.

The electrospray ionization mass spectrometry data demonstrated that the compound Ce-TBMN was substantially stable in solution. The compound Ce-TBMN exhibited an intense peak at m/z 1136.46, a moderate peak at m/z 1515.59 (Fig. 2). These signals could be assigned to the negative charged species $[(Ce\text{-}TBMN\text{-}5H) + K]^{4-}$ and $[(Ce\text{-}TBMN\text{-}4H) + K]^{3-}$. In the presence of 10 times amount of guanosine (Fig. 3), exact comparison of those interesting experimental peaks with the simulative ones obtained on the basis of natural isotopic abundance revealed that the negative peak at m/z 1268.97 could be reasonably assigned to $[(Ce\text{-}TBMN\text{-}4H) + 2G]^{4-}$, providing evidence of a 1:2 stoichiometric host–guest complexation. Upon the addition of other ribonucleosides, no host–guest complex species was detected in the

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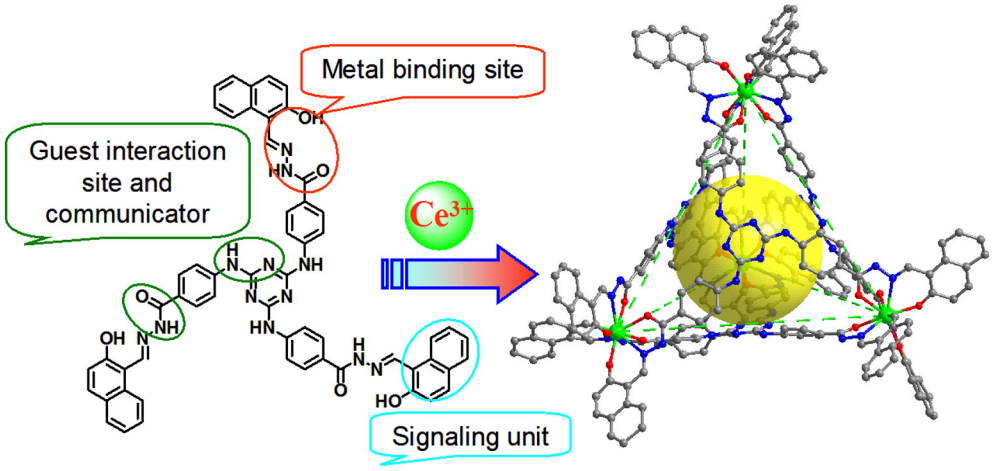

Fig. 1. Molecular design of the H_6TBMN and the constructional fragment of the Ce-based tetrahedron Ce-TBMN.

ESI-MS under the same experimental condition. It suggested a selective recognition of the compound Ce-TBMN toward guanosine in solution.

Such a recognition phenomenon was further characterized by fluorescence spectra. The compound Ce-TBMN exhibited an emission band at about 486 nm in DMF solution (1×10^{-5} M) when excited at 385 nm. The emission intensity exhibited about 3.10 times enhancement when guanosine (G) (2×10^{-3} M) was added into the solution (Fig. 4). The Hill-plot profile of the fluorescence titration curve at 486 nm demonstrated the 1:2 stoichiometric host–guest complex with the association constant ($\log K_{ass}$) being calculated as 5.26 ± 0.20. The addition of ribonucleotide adenosine (A) (2×10^{-3} M) to the solution of the compound Ce-TBMN (1×10^{-5} M) caused 1.41 times fluorescence enhancement, while the addition of nucleotides cytidine (C) (2×10^{-3} M) or uridine (U) (2×10^{-3} M) led to 0.76 times fluorescence enhancement of the solution respectively suggesting the selective recognition of the compound Ce-TBMN toward guanosine.

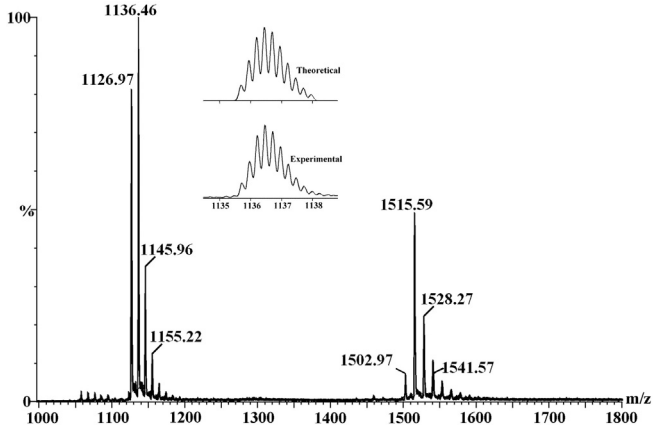

Fig. 2. ESI-MS of the nanocage Ce-TBMN formed in DMF solution in the absence of guanosine. The insert exhibited the measured and simulated isotopic patterns at 1136.46.

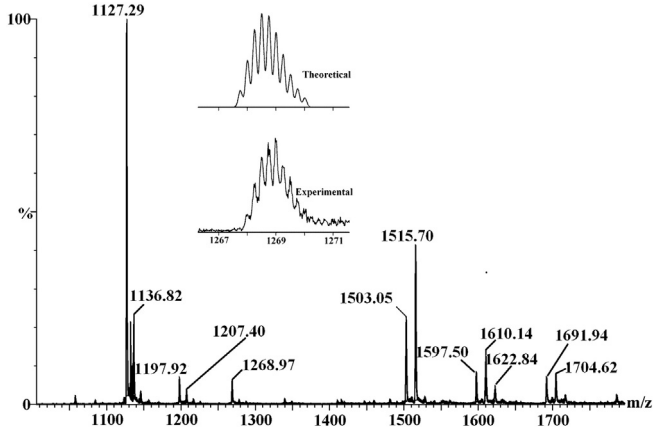

Fig. 3. ESI-MS of the nanocage Ce-TBMN formed in DMF solution in the presence of 10 times amount of guanosine. The insert exhibited the measured and simulated isotopic patterns 1268.97.

Exact comparison of those interesting selective sensing of Ce-TBMN to the four ribonucleosides revealed that the steric effect and hydrogen bonding interaction played important role in the selective sensing process. The nucleotide guanosine (G) is relatively larger matching with the cavity of the cage well. Moreover, it has the potential to form four pairs of hydrogen bonding interaction (Fig. 5) with the multiple hydrogen bonding sites of the compound Ce-TBMN. For the nucleotide adenosine (A), although it matches with the nanocage well, it can form only three pairs of hydrogen bonding interaction with the multiple hydrogen bonding sites of the Ce-TBMN. Therefore, the fluorescence enhancement of the cage in response to nucleoside adenosine (A) is weaker than that of nucleotide guanosine (G). The nucleotides cytidine (C) and uridine (U) could not match with the nanocage Ce-TBMN well

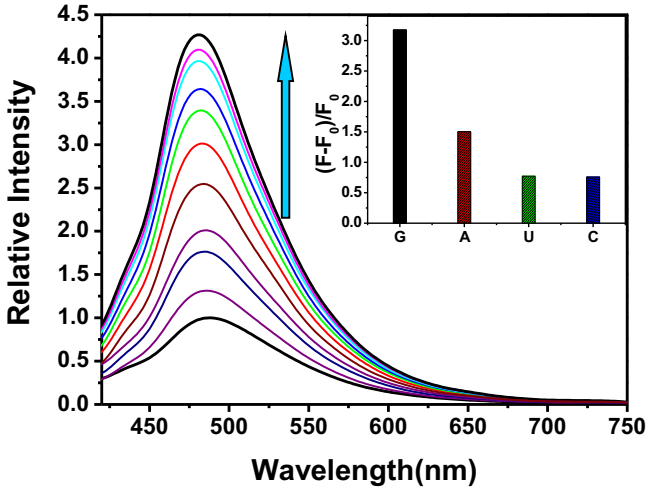

Fig. 4. The family of fluorescence spectra of the compound Ce-TBMN (1×10^{-5} M) in DMF solution upon the addition of a standard solution of guanosine (G). The insert exhibited the respective response of Ce-TBMN (1×10^{-5} M) to the four RNA-based nucleosides (2×10^{-3} M) (nucleotide guanosine, black; nucleotide adenosine, red; nucleotides uridine, green; nucleotides cytidine, blue). The samples were excited at 385 nm, the emission intensities were recorded at 486 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)