

Communication

Cavity-directed nitroaromatics sensing within a carbazole-based luminescent supramolecular M_2L_3 cage

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ABSTRACT

The design and preparation of luminescent M_2L_3 metal-organic cage *via* the coordination-driven self-assembly of carbazole-based ligand with a V-shaped geometry is described. The cage Zn-L1 with an open cavity which equipped aromatic rich ligands shows the highest emission quenching efficiency towards picric acid than other nitroaromatic explosives. The quenching ability depended on whether there formed the host-guest molecules are well explored by electrospray ionization mass spectrometry (ESI-MS), and isothermal titration microcalorimetry (ITC).

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Coordination-driven self-assembly of discrete supramolecular metal-organic cages with a hollow cavity environment have attracted a great deal of attention in recent years [1–3]. The abundant structural configurations and fruitful functionalities could be successfully achieved by rational selection of different metal centers and well-designed ligands [4–6], which offers them with the unique abilities on catalysis [7], sensing [8,9], enantio-selective recognition [10] and other important fields [11–13]. Specifically, the confined cavity microenvironment must be designed elaborately to provide a good size and shape match for targeted guests. And the other key issues include how to subtly fabricate strong host-guest interactions by turning the multiple weak interactions, such as hydrogen bonding, π -stacking, and hydrophilic/lipophilic interactions of the cage when a suitable guest was selected [14]. Furthermore, desirable photophysical properties such as light-harvesting and emission tuning are also desired by integrating emissive ligands and/or coordination complexes into the supramolecular architectures [15].

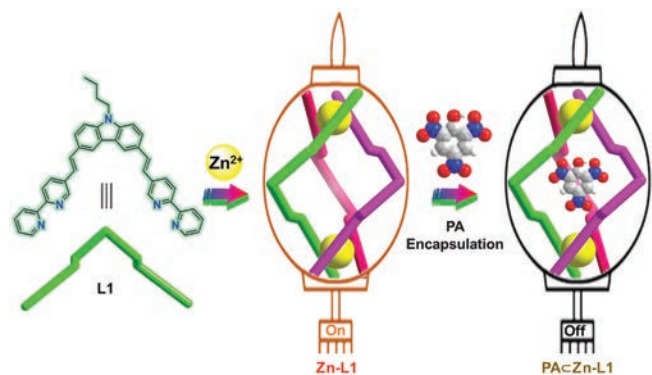
On the other hand, rapid and effective monitoring of nitroaromatic explosives, such as picric acid (PA), trinitrotoluene (TNT), and dinitrotoluene (DNT) has become an area of concern, especially in many crowded public places [16]. Currently, a wide range of instrumental techniques like metal detection, surface-enhanced Raman spectroscopy, gas chromatography-mass spectrometry are available for nitroaromatic compounds detection [17]. However, these methods are very difficult in practice because

of their lack of portability and tedious operation. Chemical fluorescence identification [18,19] is gradually known for its high selectivity and sensitivity in the field of explosive detection [20,21]. Among various transduction methods used for explosive detection, the fluorescence quenching, in particular, is considered to be the most effective tool for sensing nitroaromatic explosives in recent years owing to its high sensitivity, easy visualization, and short response time for detection [22]. In order to achieve the detection of a nitroaromatic explosive in a selective and sensitive manner, it is of great significance that the matching between the size of the cavity and the guest nitroaromatic molecules in a host-guest manner [23].

In search of luminescent cages for nitroaromatic compounds detection selectively and sensitively, herein, we reported a luminescent metal-organic cage based on carbazole ligands with a 'V' shape conformation. The preferred carbazole ligands and its derivatives are a kind of important electron-rich heterocyclic compounds with a large steric rigid plane and many excellent photoelectric properties [24,25]. We thought that combining NN chelating sites with C=C double bond connection in the organized carbazole architectures may result in effective host receptors, which may provide the steric, geometric, and luminescent functional requirements for the recognition of nitroaromatic compounds. The cage Zn-L1 with an open cavity size was achieved controllably through careful structural design, and showed good fluorescence emission property. Impressively, the emission of Zn-L1 can be quenched more efficiently by PA than other explosives. Nevertheless, free carbazole ligands showed no obvious quenching phenomenon towards PA which demonstrated that the supramolecular species formation between the cage host and the

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Scheme 1. Schematic representation of the fragments of the luminescent cage Zn-L1 and cavity-directed nitroaromatics sensing based on host-guest complexation species formation.

encapsulated nitroaromatic guests is crucial for effective detection (Scheme 1).

The carbazole core-containing ligand **L1** decorated with two *N,N*-bidentate chelators on the 3,6-positions by C=C double bond connection was synthesized in four steps from commercially available starting materials *via* a Pd-catalyzed Suzuki-Miyaura cross-coupling, as described in the Supporting information (Fig. S1 in Supporting information) [26,27]. Ligand **L1** was fully characterized by nuclear magnetic resonance (NMR) and atmospheric pressure chemical ionization mass spectrometry (APCI-MS). Such a V-shaped conformation was considered well preserved during the assembly process, enabling the resulted assemblies with an internal hollow cavity that capable of encapsulating guest molecules [28]. Noted that **L1** exhibited a high emissive band at $\lambda_{em} = 474$ nm at when excited at 400 nm (Fig. S8 in Supporting information).

Combined with **L1** (3.0 equiv.) and $Zn(NTf_2)_2$ (2.0 equiv., $NTf_2 =$ bis(trifluoromethanesulfonyl)imide) in CH_3CN at 70 °C for 2 h yielded Zn-L1. ESI-MS analyses confirmed the formation of a [2 + 3] supramolecular metal-organic cage with the formula $Zn_2(L1)_3(NTf_2)_4$. The peaks at m/z 470.42, 720.53, and 1220.75 were safely assigned to the species $[Zn_2(L1)_3]^{4+}$, $[Zn_2(L1)_3(NTf_2)]^{3+}$, and $[Zn_2(L1)_3(NTf_2)_2]^{2+}$, respectively, when comparison of the experimental peaks with these simulated results obtained on the basis of natural isotopic abundance (Fig. 1). These results showed the successfully assembly of Zn-based architecture with high stability in solution.

To further confirm the formation of [2 + 3] metal-organic cage, the UV-vis titration was well-conducted. The ligand **L1** exhibited a broad band at about $\lambda = 356$ –394 nm, assignable to the π - π^* and n - π^* charge transfer band. Upon the addition Zn^{2+} ions, this band was decreased gradually and new peaks at about $\lambda = 302$ nm, and $\lambda = 407$ –500 nm that attributed to the metal-ligand charge transfer increased significantly (Fig. 2). These bands remained constant after adding approximately 0.67 equiv. of Zn^{2+} . The almost linear

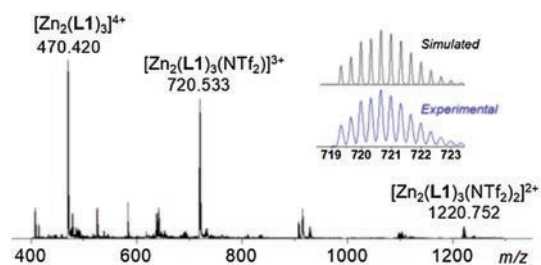


Fig. 1. ESI mass spectra of Zn-L1 in CH_3CN , the inset shows the simulated and experimental isotopic patterns at m/z 720.53.

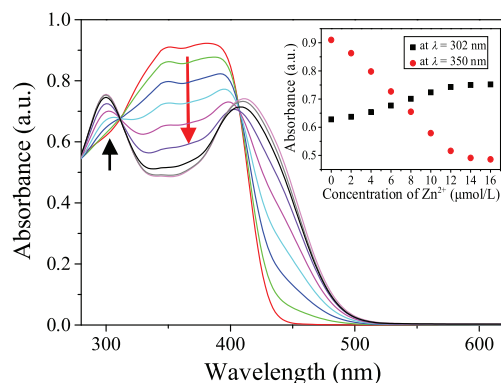


Fig. 2. UV-vis spectra of ligand **L1** (18 μ mol/L) upon the addition of a solution of $Zn(NTf_2)_2$ (per 2 μ mol/L) up to 16 μ mol/L in CH_3CN .

relations between the absorbance at both bands and the concentration of Zn^{2+} added revealed that the formation of the zinc complex was quantitative and the complex exhibited 2:3 stoichiometry. The presence of sharp isosbestic points at $\lambda = 311$ nm and $\lambda = 407$ nm indicated that only two species coexist in the equilibrium. This result demonstrated that the M_2L_3 cage compound was the only one complexation specie and the association constant of the complexation specie is relatively high.

Slow diffusion of ethyl ether into CH_3CN solution of Zn-L1 and any other efforts only provided microcrystals. Therefore, high quality X-ray diffraction data suitable for structure determination analysis were unsuccessful. Instead, to gain insight into the three-dimensional structure of Zn-L1, an MM2 energy-minimized model was prepared starting from the all- Δ diastereomer (Fig. 3). In the optimized structures, two Zn atoms constructed the vertices and each of them was wrapped around by three ligands in a same chiral configuration ($\Delta\Delta$), resulting in an overall triple-stranded *P* helicate. Circular dichroism (CD) measurements of Zn-L1 in CH_3CN solution showed no effective Cotton effect suggested a racemic mixture containing both enantiomeric cages were formed during the assembly process (Fig. S11 in Supporting information). As expected, the V-shaped carbazole ligands **L1** were twisted in a 'S'-type conformation and coupled two Zn atoms with a distance about 15.2 Å, resulting the desired Zn-L1 cage architecture with a hollow cavity. And such aromatic rich ligands equipped unique confined environment may allow guest molecules with suitable sizes to ingress and egress through π - π stacking interactions.

Importantly, the obtained cage Zn-L1 was luminescent active and showed an intense emission at $\lambda_{em} = 608$ nm, which provides a possibility to make a further research into its potential application as a luminescent detector of nitroaromatics. As shown in Fig. 4a, when adding 3.0 equiv. of PA into the CH_3CN solution of Zn-L1 (10.0 μ mol/L), the emission intensity was dramatically reduced

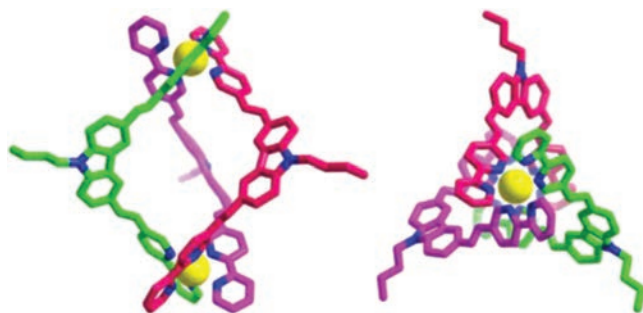


Fig. 3. The representations of MM2 energy-minimized model of Zn-L1 in different directions. Hydrogen atoms and are omitted for clarity. Color code: C = green, purple, and red; N = blue; Zn = yellow.

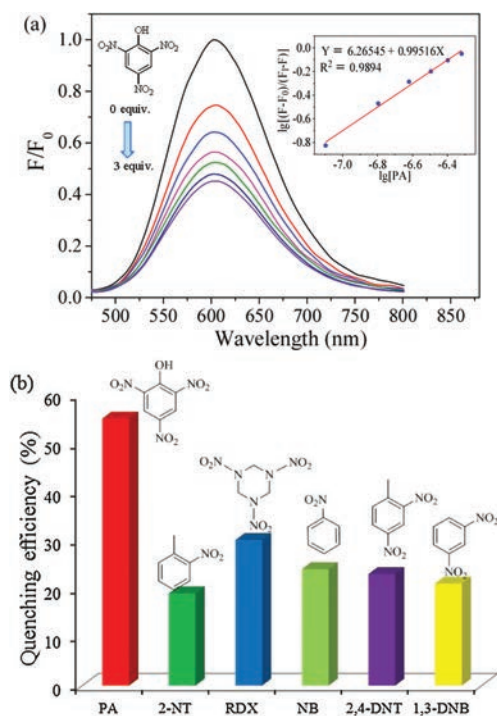


Fig. 4. (a) Family of luminescence spectra of Zn-L1 upon the addition of PA. Inset: Hill-plot titration curve showing 1:1 host-guest behavior; (b) The quenching efficiencies of different nitroaromatic compounds.

around 55%. Hill-plot titration curve suggested a 1:1 host-guest behavior with an association constant calculated as 1.84×10^6 L/mol (Fig. 4a, inset). On the contrary, other common nitroaromatic compounds such as 2-nitrotoluene (2-NT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), nitrobenzene (NB), 2,4-dinitrotoluene (DNT), 1,3-dinitrobenzene (DNB), only showed quenching efficiency of the intensity declined about 25%, yet PA exhibited nearly 2 times higher quenching efficiency than all others (Fig. 4b and Fig. S12 in Supporting information). These results clearly demonstrated the selectivity to PA towards other nitroaromatics. This phenomenon can be explained by the more electron-deficient nature of PA relative to other nitroaromatics, leading to a stronger electron transfer and ultimately more efficient quenching [29,30]. The photo-induced electron transfer (PET) process is the essential reason for the decrease of the fluorescence intensity. The formation of the host-guest molecule between PA and cages facilitated the energy transfer from the electron-rich donor of these cages to the electron-deficient nitro-aromatics and thereby the enhanced emission quenching than other explosives.

Furthermore, isothermal titration microcalorimetry (ITC) experiment was performed to ensure the quantitative accuracy of the titration data and provided insight into the thermodynamics for host-guest complexation [31]. As showed in Fig. 5, upon the addition of PA (10.0 mmol/L) to a CH₃CN solution of Zn-L1 (1.0 mmol/L), the typical titration curve indicated that the host-guest complexation species generated with the molar ratio 1:1, matching well with the fluorescent titration results and giving additional proof that the recognition occurred within the cavities of Zn-L1. The calculated ΔH and $T\Delta S$ values were about -39.29 and -11.74 kJ/mol, respectively, which suggested that the complexation species was enthalpically driven.

In addition, upon the addition of PA (3.0 equiv.) to the solution of Zn-L1 in CH₃CN, ESI mass spectrum of the mixture displayed a new intense peak at m/z 703.56, which was assigned to the inclusion $[\text{PA} \subset \text{Zn-L1}]^{3+}$ by the comparison of the peak with the simulation result obtained on the basis of natural isotopic

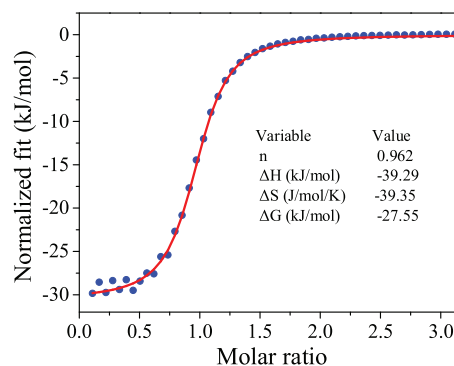


Fig. 5. ITC experiment of Zn-L1 (1.0 mmol/L) in CH₃CN upon the addition of PA (10.0 mmol/L).

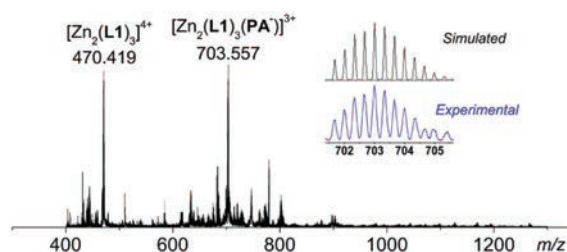


Fig. 6. ESI mass spectrum of Zn-L1 in CH₃CN upon addition of 3.0 equiv. of PA, the inset shows the simulated and experimental isotopic patterns at m/z 703.553.

abundances (Fig. 6). The formation of a host-guest complex between the π -electron-rich cavity and electron-poor nitroaromatic (PA) was possibly crucial for the selective detection. As expect, when the free ligand L1 was used as the luminescent detectors under the same condition, as shown in Fig. S13 in Supporting information, the addition of PA exhibited only negligible effects on the fluorescence intensity of cage. Thus, the selectivity and sensitivity were reasonably attributed to the encapsulation of the PA within the cavity of the cage Zn-L1. Based on the simulated structure of the cage, it was reasonable for the formation of host-guest species between the aromatic rich carbazole-based ligand and electron-deficient PA molecule near the windows of the cage with strong π - π stacking interactions.

In summary, we reported here the synthesis and characterization of a luminescent metal-organic cage Zn-L1 via the coordination self-assembly approach based on carbazole ligands with a V-shaped conformation. The cavity of cage Zn-L1 which equipped aromatic rich ligands showed the encapsulation ability to one picric acid molecule, and showed the highest emission quenching efficiency towards picric acid than other nitroaromatic explosives. Thus, the present results demonstrated that the formation of the host-guest species by using a luminescent metal-organic architecture host sensor can be viewed as a suitable class of compounds for further development of efficient sensors for explosives constituents by enhancing the binding interaction between them.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccl.2019.04.059>.

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