

## Supramolecular Assemblies

# An Elaborate Supramolecular Assembly for a Smart Nanodevice for Ratiometric Molecular Recognition and Logic Gates

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**Abstract:** Ingenious approaches to supramolecular assembly for fabricating smart nanodevices is one of the more significant topics in nanomaterials research. Herein, by using surface quaternized cationic carbon dots (CDots) as the assembly and fluorescence platform, anionic sulfonatocalix[4]arene with modifiable lower and upper rims as a connector, as well as in situ coordination of Tb<sup>3+</sup> ions, we propose an

equilibrium characteristics of the supramolecular interaction can eventually endow this nanodevice with functions of fluorescent ratiometric molecular recognition and as a nanologic gate with two output channels.

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### Introduction

Supramolecular assembly has aroused increasing interest in surface modifications and functionalization of nanoplatforms for fabricating various nanodevices with well-controlled structure and multiple functions.<sup>[1]</sup> Yang and co-workers reported a carboxylatopillar[5]arene-modified Au nanoparticle (NP)based nanodevice prepared by supramolecular assembly for sensing the herbicide paraquat.<sup>[2]</sup> A similar strategy has also been explored for other nanomaterials including polymer dots, magnetic/silver/silica NPs, quantum dots, graphene, etc.<sup>[3]</sup> In these architectures, macrocycles are particularly striking as supramolecular building units and examples include calixarenes, cyclodextrins, cucurbiturils, and pillararenes, which can serve as responders, modulators, or even building blocks.<sup>[1c,4]</sup> In particular, calix[4]arenes have emerged as molecular scaffolds for building appropriate binding cores owing to their wide range of topological features. Notably, the ingenious design of supramolecular assembly processes towards smart nanodevices with enhanced functions remains challenging.

Carbon dots (CDots) have attracted considerable attention because of their superior properties including tunable fluorescence, excellent water solubility, low toxicity, etc. Diverse surface groups can be readily introduced onto CDots through various synthesis methodologies. This is controlled by the synthetic conditions and choice of precursors, which include primary amines, carboxylic acids, hydroxyls, etc.<sup>[5]</sup> Tremendous efforts have been devoted to modifying CDots to achieve different applications,<sup>[6]</sup> including using different linking strategies such as covalent bonding,<sup>[7]</sup> coordination,<sup>[8]</sup> and  $\pi$ – $\pi$  interactions.<sup>[9]</sup> However, the available methods often suffer from inefficient reaction yields and complicated purification processes.<sup>[10]</sup> Supramolecular assembly strategies likely serve as substitutes for conventional covalent modifications and simplify the fabrication of multifunctional CDots need to be further studied.

Here, we propose an elaborate supramolecular assembly strategy for the facile fabrication of a CDot-based smart nanodevice for fluorescent ratiometric molecular recognition and use as a logic gate (Scheme 1). This strategy employs surface quaternized cationic CDots as the assembly and fluorescence platform, which allows tedious syntheses and substrate modifications to be avoided. The CDots can also provide quaternary ammonium to precisely immobilize functional units through supramolecular interactions with excellent luminescent properties.

The anionic sulfonatocalix[4]arene (**SC4A**) as an important macrocyclic receptor displays strong binding ability and high selectivity toward various analytes.<sup>[11]</sup> It was chosen as the supramolecular functional block because it not only serves as the supramolecular connector on the surface of the CDots, but also generates an outer functional layer through coordination of the hydroxyl groups with metal cations. Owing to the strong driving forces for the inclusion of quaternary ammonium groups in the cavity, as well as the electrostatic interactions with the sulfonate groups, bifunctional **SC4A** can be precisely assembled on the surface of the quaternized CDots. In addition, luminescent Tb<sup>3+</sup> ions, with tunable fluorescence signals towards the analytes in the exchangeable coordination sphere, can be incorporated in this architecture by coordination with

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Scheme 1. Schematic illustration of the supramolecular assembly of CDots@SC4A-Tb<sup>3+</sup> nanodevice and the ratiometric sensing mechanism for  $H_2PO_4^-$  detection.

the hydroxyl groups on **SC4A**, which also serves as a sensitizer for the coordinated  $Tb^{3+}$  ions.

This system takes advantage of the unique spectroscopic characteristics of the Tb<sup>3+</sup> ions, including long fluorescence lifetimes, large Stokes shifts, and sharp line-like emission bands arising from partially forbidden f–f transitions.<sup>[12]</sup> Meanwhile, the CDots can be employed as the fluorescence interior reference to improve detection accuracy and sensitivity. This can also be used to fabricate a logic gate. Based on this elaborate supramolecular assembly, the nanodevice can be used as a fluorescent ratiometric probe for phosphates. Also, it provides an opportunity to be employed as a nano-logic gate with two output channels.

#### **Results and Discussion**

The rationally designed nanodevice was constructed with consecutive supramolecular loading of **SC4A** and coordinative incorporation of Tb<sup>3+</sup> ions on the quaternized CDots (Scheme 1). First, the quaternized CDots were synthesized by carbonization of the salt precursor containing betaine hydrochloride and tris(hydroxymethyl)aminomethane (Tris). The carbonization was conducted at a moderate temperature (250 °C) to obtain CDots with exposed ammonium units (Scheme S2 in the Supporting Information).<sup>[13]</sup> The as-prepared CDots exhibited blue fluorescence and were highly soluble in water and polar organic solvents. They were used as building blocks for the functionalization by controlled assembly with **SC4A** through the multiple binding ability between the quaternary ammonium moieties and hydrophobic cavity of **SC4A**.<sup>[14]</sup>

The chemical structure of the CDots has been investigated by different methods, such as transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). These method indicate the successfully preparation of surface quaternized CDots (see the Supporting Information). The highest emission wavelength was 440 nm when the CDots were excited at 350 nm. Figure S4 (in the Supporting Information) shows the yellow aqueous solution of the CDots emitting strong blue fluorescence under the 365 nm lamp. Once the CDots are further functionalized to enable use in practical sensing applications, they must remain stable toward ambient environments. To investigate the stability, the fluorescence intensity of the CDots with interferences in solution was measured. Remarkably, no significant change in the signal was observed in the presence of various metal cations or anions (Figure S5 in the Supporting Information).

The formation of CDots@SC4A was easily achieved by mixing the surface guaternized CDots with SC4A at room temperature and stirring the resulting solution for 12 h. Unbound SC4A was then removed by using dialysis bags for 72 h. The resulting adduct, CDots@SC4A, was further functionalized by coordination of the hydroxyl groups of the immobilized SC4A with  $Tb^{3+}$  to form a SC4A- $Tb^{3+}$  complex on the surface of the nanomatrix. The excitation energy is transferred from the excited triplet state level ( $T_1$ ) of the ligand **SC4A** to Tb<sup>3+</sup>, sensitizing the emission of Tb<sup>3+</sup>.<sup>[15]</sup> The successful assembly of SC4A on the surface of CDots was investigated by transmission electron microscopy (TEM), zeta potential measurements, X-ray photoelectron spectroscopy (XPS), and Fourier transform infra-red (FTIR) spectra. From a typical TEM image of CDots@SC4A (Figure 1 a), we see that the CDots@SC4A were well dispersed with an average size of 5 nm. The assembly of SC4A on the surface of CDots was confirmed by a change in zeta potential from + 11.5 mV (bare CDots) to - 15.1 mV (after interaction with SC4A). It is well known that SC4A is negatively charged because of its four sulfonic groups.<sup>[14a]</sup> The final negative value of the zeta potential indicates that the surface of the CDots has



**Figure 1.** a) TEM images and b) HR-TEM images of CDots@**SC4A**. c) XPS spectrum scan of CDots@**SC4A** (light line) and CDots (dark line). d) Emission spectra upon titration of Tb<sup>3+</sup> into CDots@**SC4A** solution in 10 mm HEPES buffer pH 7.4, ranging from 0 to 90  $\mu$ m Tb<sup>3+</sup>,  $\lambda_{ex}$ =275 nm.

been successfully functionalized with **SC4A** based on supramolecular interactions (Figure S7 in the Supporting Information).

The XPS spectra were recorded to explore the chemical composition and chemical bonds of CDots@SC4A. As shown in Figure 1 c, the CDots@SC4A show four peaks at 283.6, 400.1, 530.6, and 167.0 eV in the XPS spectrum. These are attributed to C1s, N1s, O1s, and S2p, respectively. The high-resolution XPS spectra of C1s, N1s, O1s (Figure S3 in the Supporting Information) further confirmed that the CDots@SC4A nanohybrid has hydroxyl, carbonyl, carboxylic, and amine groups. The appearance of new peaks at 167.0 eV (S2p) and 231.2 eV (S2s) in the XPS spectrum (Figure 1 c) is assigned to the sulfonic group of SC4A and confirms the successful surface modification of the CDots by SC4A. The high-resolution XPS S2p spectrum can be devolved into two sets of components with binding energies of 168.0, 167.9 eV and 166.2, 165.7 eV. These peaks correspond to oxidized forms of sulfur (Figure S8 in the Supporting Information). According to the spectra, the 168.0 and 167.9 eV are  $SO_3^-$  states and the 166.2 and 165.7 eV are attributed to the partial presence of sulfur in oxidized forms. The lower binding energy can be explained by electron transfers from the CDots, in particular from the surface positively charged amine groups to sulfonic groups.<sup>[16]</sup> FTIR spectra (Figure S9 in the Supporting Information) were further used to identify the surface modification process of the CDots@SC4A nanohybrid. The CDots exhibited absorption peaks for N–H (3391 cm<sup>-1</sup>), C= H (2929 cm<sup>-1</sup>), and C–O (1449 and 1056 cm<sup>-1</sup>). These peaks are also found in the spectra of CDots@**SC4A** and illustrate that the CDots serve as the matrix without undergoing structural change during the formation of the CDots@**SC4A** nanohybrid.<sup>[17]</sup> Strong absorbance peaks for SO<sub>3</sub><sup>-</sup> are observed in both **SC4A** and CDots@**SC4A** at 1189 and 1049 cm<sup>-1</sup>. This indicates the attachment of **SC4A** to the CDots. In addition, the peak at 1639 cm<sup>-1</sup> in the **SC4A** spectrum is slightly shifted to 1649 cm<sup>-1</sup> in the CDots@**SC4A** spectrum. This represents the characteristic absorption of a phenyl unit<sup>[18]</sup> and confirms that **SC4A** is successfully assembled on the CDots through supramolecular interactions to form the CDots@**SC4A** nanohybrid.

After introducing Tb<sup>3+</sup> ions to generate an ionic outer layer and obtain the nanoprobe CDots@**SC4A**-Tb<sup>3+</sup>, the outer layer interaction between **SC4A** and Tb<sup>3+</sup> in aqueous solution was verified with fluorescence, UV/Vis spectra, and XPS measurements. When different concentrations of Tb<sup>3+</sup> ions were introduced into CDots@**SC4A** aqueous system, the emission intensities of the Tb<sup>3+</sup> ions were enhanced as a result of efficient energy transfer from the **SC4A** ligands to the Tb<sup>3+</sup> ions (Figure 1d). The observed spectrum patterns correspond to the <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>6</sub> (494 nm), <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> (545 nm), <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>4</sub> (587 nm), and <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>3</sub> (625 nm) transitions. These are particular to the Tb<sup>3+</sup> -centered luminescence, sensitized by the **SC4A** ligand by the antenna effect.<sup>[15a,b,19]</sup> The enhancement of the fluorescence in-



tensity should be attributed to the coordination of  $Tb^{3+}$  with the phenolic hydroxyl group of **SC4A** and the formation of the CDots@**SC4A**-Tb<sup>3+</sup> nanohybrid. Similarly, the blue–green fluorescence may be attributed to the synergistic effect of the surface **SC4A**-Tb<sup>3+</sup> complex and CDots core.

To rule out the possibility of nonspecific binding between the CDots and  $Tb^{3+}$ , a control experiment was performed in which the CDots were mixed with  $Tb^{3+}$  in HEPES buffer. No significant signal change was observed in the control experiment (Figure S11 in the Supporting Information). The chemical composition was also characterized by XPS spectra to verify the formation of CDots@**SC4A**-Tb<sup>3+</sup>. A weak peak at 150.9 eV could be assigned to Tb4d (Figure 2a). This confirms the suc-



**Figure 2.** a) High-resolution Tb 4d XPS spectrum. b) UV/Vis absorption spectral responses of CDots@**SC4A** in aqueous solution upon the addition of 0– $25 \ \mu M \ Tb^{3+}$  (inset: enlarged area).

cessful coordination of Tb<sup>3+</sup> with **SC4A** on the surface of the CDots. The high-resolution XPS spectrum of Tb3d also shows two peaks corresponding to  $3d_{5/2}$  (1240.1 eV) and  $3d_{3/2}$  (1275.9 eV) of Tb<sup>3+</sup> (Figure S10 in the Supporting Information).<sup>[20]</sup> Evidence for the formation of CDots@**SC4A**-Tb<sup>3+</sup> is also seen in the UV/Vis absorption spectra. Upon addition of Tb<sup>3+</sup>, the UV/Vis absorption spectrum of the CDots@**SC4A** solution blueshifts and is slightly enhanced (Figure 2 b). This illustrates that the Tb<sup>3+</sup> ions bind to the surface of the CDots@**SC4A** through a coordinative interaction.

Phosphates play pivotal roles in a variety of fundamental physiological processes such as genetic storage and regulation, energy metabolism, signal processing, DNA replication and transcription, etc.<sup>[21]</sup> Developing selective and cost-effective phosphate recognition probes that work under physiological conditions is important for phosphate-related biomedical diagnosis and environmental remediation.<sup>[22]</sup> In bio-systems (pH 7.4),  $H_2PO_4^{-}$  and  $HPO_4^{2-}$  commonly coexisted and are at a dynamic equilibrium state. Thus, we chose H<sub>2</sub>PO<sub>4</sub><sup>-</sup> as an example to illustrate the detecting ability of our nanoprobe. Figure 3 a shows that the green fluorescence of  $Tb^{3+}$  is quenched in the presence of  $H_2PO_4^{-}$ , but the blue fluorescence of the CDots ( $\lambda_{em} = 440 \text{ nm}$ ) remains constant. The other anions  $(AcO^{-}, \ BF_{4}^{-}, \ PF_{6}^{-}, \ Br^{-}, \ C_{2}O_{4}^{\ 2-}, \ CF_{3}SO_{3}^{-}, \ CIO_{4}^{-}, \ CO_{3}^{\ 2-}, \ F^{-},$ HCO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, 25  $\mu$ M) tested in this system do not exert significant guenching effects on the fluorescence intensity of the nanoprobe (Figure 3b, dark-colored bars).

Interference experiments were also carried out by comparing the fluorescence ratios of the nanoprobe solution in the presence of these anions (Figure 3b, light-colored bars). The apparent decrease in the emission intensity of the probe solution upon addition of the  $H_2PO_4^-$  was not affected by the coexistence of other anions. Moreover, the presence of common cations like Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Ag<sup>+</sup>, and Cd<sup>2+</sup> did not create interference for the detection of  $H_2PO_4^-$ ; only Cu<sup>2+</sup> showed minor quenching (Figure S12 in the Supporting Information).

The fluorescence sensing experiments demonstrated that the nanoprobe is highly selective for H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. This can be explained by stronger interactions between  $H_2PO_4^{-}$  and  $Tb^{3+}$ versus the interactions between the phenolic hydroxyl groups in SC4A with  $Tb^{3+}$ .<sup>[15c,22a]</sup> To prove the different interaction strengths, we calculated the association constants between  $H_2PO_4^{-}$  and  $Tb^{3+}$  as well as the  $Tb^{3+}$  and CDots@SC4A. The association constant between  $H_2PO_4^-$  and  $Tb^{3+}$  was estimated to be  $7.85 \times 10^5 \,\mathrm{M}^{-1}$  from the linear regression using a Stern-Volmer plot (Figure S15 in the Supporting Information). The association constant ( $K_s$ ) between the CDots@SC4A and Tb<sup>3+</sup> can be found by titrating Tb<sup>3+</sup> into the CDots@SC4A solution (Figure S16 in the Supporting Information). This  $K_s$  value was estimated to be  $3.9218 \times 10^4 \,\text{m}^{-1}$ , which is far smaller than the  $K_s$  value for  $H_2PO_4^{-}$  and  $Tb^{3+}$ . Therefore, the observation of fluorescence quenching at 545 or 490 nm of the CDots@SC4A- $Tb^{3+}$  may be due to the substitution of SC4A by  $H_2PO_4^{-}$ anions. Phosphates have no antennae effect on the Tb<sup>3+</sup>-centered emission. Similarly, the other anions have much poorer bonding ability with Tb<sup>3+</sup> than SC4A, and thus they cannot replace the **SC4A** on the CDots@**SC4A**-Tb<sup>3+</sup>.

The ratiometric sensing behavior of the CDots@**SC4A**-Tb<sup>3+</sup> toward phosphates was further investigated in HEPES buffer (10 mm, pH 7.4). Upon addition of  $H_2PO_4^-$ , there is a gradual decrease in the fluorescence intensity at 490 and 545 nm (Figure 3 c, Figure S9 in the Supporting Information). The highest fluorescence intensity ratios are at 490/545 nm and 440 nm ( $I_{490}/I_{440}$  and  $I_{545}/I_{440}$ ). Figure 3 d plots the  $I_{545}/I_{440}$  signal as a function of  $H_2PO_4^-$  concentration. The ratio of  $I_{545}/I_{440}$  gradually de-



**Figure 3.** a) Fluorescence intensity ratio of the CDots@**SC4A**-Tb<sup>3+</sup> to H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and other relevant species. b) Effect of different anions (1: CDots@**SC4A**-Tb<sup>3+</sup>, 2: AcO<sup>-</sup>, 3: Br<sup>-</sup>, 4: C<sub>2</sub>O<sub>4</sub><sup>-2-</sup>, 5: CF<sub>3</sub>SO<sub>3</sub><sup>--</sup>, 6: Cl<sup>-</sup>, 7: ClO<sub>4</sub><sup>--</sup>, 8: CO<sub>3</sub><sup>2-</sup>, 9: F<sup>-</sup>, 10: HCO<sub>3</sub><sup>--</sup>, 11: HSO<sub>4</sub><sup>--</sup>, 12: l<sup>-</sup>, 13: NO<sub>3</sub><sup>--</sup>, 14: SCN<sup>-</sup>, 15: SO<sub>4</sub><sup>2-</sup>) on the fluorescence properties of CDots@**SC4A**-Tb<sup>3+</sup>. The dark-colored bars represent the addition of anions (25  $\mu$ M) to the solution of CDots@**SC4A**-Tb<sup>3+</sup> (pH 7.4). The light-colored bars represent the subsequent addition of 25  $\mu$ M H<sub>2</sub>PO<sub>4</sub><sup>--</sup> to the solution. c) Fluorescence spectra of CDots@**SC4A**-Tb<sup>3+</sup> in HEPES (10 mM, pH 7.4) obtained upon titration with H<sub>2</sub>PO<sub>4</sub><sup>--</sup> from 0 to 25  $\mu$ M, under excitation at 275 nm. d) The plot of *I*<sub>545</sub>/*I*<sub>440</sub> as a function of H<sub>2</sub>PO<sub>4</sub><sup>--</sup> concentration obtained with CDots@**SC4A**-Tb<sup>3+</sup> (pH 7.4).

creased with increasing H<sub>2</sub>PO<sub>4</sub><sup>-</sup> concentration and reached a plateau when the concentration of  $H_2PO_4^-$  was higher than 20 µм. There is good linearity between 50-350 nм with a correlation coefficient of 0.997 (Figure 3 d, inset). The detection limit was 33.86 nm based on a signal-to-noise ratio of  $3.^{\scriptscriptstyle [23]}$  This is better than or comparable to those obtained with other fluorescent probes for  $H_2PO_4^{-}$ . Other phosphates such as  $PO_4^{3-}$ ,  $\mathrm{HPO_4^{\ 2-}},$  and PPi are also able to quench the fluorescence of the CDots@SC4A-Tb<sup>3+</sup> effectively. The different guenching ability towards the common phosphates are shown in the Supporting Information (Figure S14, Table S1). In addition, the reversibility and reusability of this nanodevice were evaluated by repeated complex/stripping cycles by adding Tb<sup>3+</sup>/H<sub>2</sub>PO<sub>4</sub><sup>-</sup>; the fluorescence spectrum was recorded after each step. The results demonstrate that the procedure can be repeated at least five times (Figure S17 in the Supporting Information).

Formation of logic gates using changes in optical responses is important because they can be used to solve complex problems on the molecular level.<sup>[24]</sup> The CDots@**SC4A**-Tb<sup>3+</sup> nanodevice can be used as a fluorescence logic gate by using CDots@**SC4A**, Tb<sup>3+</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> as the chemical inputs. As shown in Figure 4a, the fluorescent change can be described and manipulated as a logic gate by a threshold of CDots@**S**-**C4A**, Tb<sup>3+</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. The absence and presence of these ions were defined as the 0 and 1 states, respectively. The eight possible input combinations are shown in the truth table in Figure 4b. This system can form two different patterns of logic gate at the two different wavelengths. The fluorescence channel at 440 nm in the absence and presence of CDots@**SC4A** can be represented by a "YES" logic gate (Figure 4). Only the presence of CDots@**SC4A** can implement the change in fluo-



**Figure 4.** a) Schematic illustration of the fabrication procedures for the novel nano-logic gate based on the CDots@**SC4A**-Tb<sup>3+</sup> assay. b) Fluorescence response of CDots@**SC4A** at 440 nm and 545 nm in the absence and presence of Tb<sup>3+</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and truth table for the logic gate.



rescence at 440 nm. This provides an output signal of 1. The channel at 490/545 nm is composed of two INHIBIT gates. In the absence of both  $Tb^{3+}$  and  $H_2PO_4^-$  (100), the CDots@**SC4A** has no significant emission at 490 or 545 nm (considered as output signal "1"). However, upon addition of  $Tb^{3+}$  (input signal 110), a new emission at 490 or 545 nm emerges, owing to the antenna effect of **SC4A** on the CDots surface due to  $Tb^{3+}$ . When the hybrid is treated with  $H_2PO_4^-$  (input signal 101), no fluorescence change is seen at 545 nm. This results in a fluorescence signal pattern of 0.

However, in the presence of CDots@**SC4A**, Tb<sup>3+</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (input signal 111), the quenching effect of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> results in an emission decrease at 490 or 545 nm. Thus, the fluorescence signal pattern at 490/545 nm in the presence of CDots@**SC4A**, Tb<sup>3+</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (111) is 0. Therefore, only the input combinations (110) led to an output of 1, or the on state; all other input combinations correspond to an output of 0, or the off state. With two different channels of fluorescence signals, this logic gate system using CDots@**SC4A**-Tb<sup>3+</sup> was constructed and successfully used at the molecular level. The logic system presented here demonstrated two different logic modes within the same system by monitoring two different wavelength channels. Such a multifunctional logic gate device is easy in design and convenient to operate.

### Conclusion

We have described an elaborate supramolecular assembly strategy to fabricate a CDot-based nanodevice for ratiometric molecular recognition and use as a nano-logic gate. By taking advantage of the dynamic equilibrium characteristics of supramolecular interactions, the ingeniously designed nanodevice can be endowed with enhanced functions. The in-depth investigations of the devised architecture indicate that it can be successfully applied for selective and sensitive phosphate detection as well as a nanoscale logic gate. This strategy provides a convenient methodology to fabricate nanodevices with controllable properties by supramolecular assembly. This can be potentially applied in wide-ranging applications such as bioprobes, nanoreactors, and medical diagnostics.

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**Keywords:** carbon dots · nanodevices · nano-logic gate · ratiometric molecular recognition · supramolecular assembly

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