Functionalized Chitosan—Carbon Dots: A Fluorescent Probe for Detecting Trace Amount of Water in Organic Solvents

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*Supporting Information

ABSTRACT: A novel nanoprobe was designed and synthesized by functionalizing chitosan—carbon dots (CDs) with a modified bipyridine-based heterocyclic molecule, 4-(pyridine-2-yl)-3H-pyrrolo[2,3-c]quinoline (PPQ), to detect trace amount of water via fluorescence methods. The functionalized CDs (PPQ-CDs) were thoroughly characterized using dynamic light scattering, UV−vis, X-ray diffraction, Fourier transform infrared, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, and NMR techniques. The modified fluorescence intensity of PPQ-CDs was found to be an excellent indicator for water in organic solvents. The PPQ-CDs showed very weak fluorescence intensity in organic solvents due to a possible photoinduced electron transfer (PET) process between PPQ pyrrole nitrogen and acceptor groups of CDs. However, sequential addition of trace amount of water led to continuous enhancement in the fluorescence intensity for the PPQ-CD nanocomposites. The mechanism was proposed to follow suppression of the PET process due to the formation of “free-ions” by the proton transfer from the CD carboxyl group to pyrrole nitrogen through water bridging. The limit of water detection was determined to be 0.023% (v/v) in DMSO.

1. INTRODUCTION

Carbon dots (CDs)1,2 have recently drawn increasing attention due to their important qualities like water solubility, tunable fluorescence, biocompatibility, chemical inertness, facile and inexpensive synthesis, and good photostability. Most importantly, their intrinsic fluorescence and nontoxicity render them as attractive substitutes to traditional quantum dots.3,4 These carbon nanoparticles are typically less than 10 nm and predominantly composed of carbon. The CDs can be synthesized by a “top-down” approach5 by breaking down larger carbon materials, which mainly includes laser ablation,6 arc discharge,7 and electrochemical oxidation,8 whereas a “bottom-up” approach8 is building CDs from smaller carbon sources, which includes microwave syntheses,9 combustion,10 or supported synthetic11 methods.

Due to the tunable optical properties of CDs, they can be used to develop a smart sensing system for biomolecules,12−15 metal ions,16−20 organic pollutants,21 and trace amount of water.22 Depending on the route of synthesis and the materials used, the amino, carboxyl, and hydroxyl groups remain on the CD surfaces in different proportions.23 They not only ensure water solubility but also provide further scopes for surface passivation and functionalization. There is a significant impact of surface functionalization on the photoluminescence properties of CDs. The functionalization on the CD surfaces can be achieved either by covalent or noncovalent interactions.24 Covalent interactions include the reaction of the functional molecule with the −COOH or −NH2 groups present on the CD surfaces. Noncovalent interactions include van der Waals force or π interactions between the CDs and molecules used in the functionalization process. Gupta et al.25 have synthesized nitrogen-doped PEGylated CDs from chitosan gels and functionalized them with dithiothreitol (DTT) for sensing Hg2+ at the picomolar level. Li et al.26 have developed a lanthanide-based hybrid on−off−on optical nanoprobe through the functionalization of CDs with ethylenediaminetetraacetic dianhydride for detecting biomarker 2,6-pyridinedicarboxylic acid (DPA), Cu(II), and biothiols. In another study, Jiang et al. have synthesized white light-emitting CDs (WCDs) using Tween 80 as the carbon source,27 as the long-chain alkyl group on the surface of the WCDs suppressed aggregation-caused quenching. Further, the surface groups of the WCDs detected lipophilic substances and applied for label-free luminescence imaging of the latent fingerprint.

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On the other hand, in synthetic chemistry, it is extremely important to exclude water from the reaction mixture. While using water-sensitive reagents in the laboratory, dehydration procedures are routinely performed beforehand to confirm that no water is present such that reproducible observations are obtained, because a trace amount of water in organic solvents can adversely affect the course of some of the most common organic reactions such as Grignard reaction, Wittig reaction, Friedel–Crafts reaction, Claisen condensation, etc. However, it is usually a difficult and tedious process for an organic chemist to ensure the anhydrous conditions at a common laboratory setup. Therefore, practical, rapid, and naked-eye detection for determining trace amount of water contaminant is highly useful on a day-to-day basis without using sophisticated analytical instruments. Recently, metal–organic framework (MOF)-based fluorescent nanoprobes were also used to detect...
trace water in organic solvents via a ratiometric method. However, the main drawbacks with MOF substrates are the complicated synthesis and possibility of leaking of the photoactive guests into the solution. Traditionally, the Karl Fischer method is used for measuring trace amount of water content in a sample, but compared to the sophisticated traditional method, fluorescence-based optical sensors have become more popular due to their selectivity, sensitivity, easy fabrication, and simple analysis of the result. However, many of the probes were used to determine the water content by quenching the original fluorescence signal. Hence, it is important to develop and study simple, less expensive, and advantageous fluorescent "turn-on" sensors for water detection.

In this report, we have prepared PEGylated CDs from chitosan gels and functionalized the CDs with a bipyridine-based heterocyclic molecule, 4-(pyridine-2-yl)-3H-pyrrol[2,3-c]quinoline (PPQ), through covalently conjugating PPQ on the CD surfaces using carbodiimide chemistry. The free CDs and the functionalized product (PPQ-CD) were characterized by dynamic light scattering (DLS), UV–vis, X-ray diffraction (XRD), Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), NMR, and fluorescence spectroscopic techniques.

The sizes of the as-prepared CDs and PPQ-CDs were measured by DLS and HRTEM techniques (Figure 1A). From DLS measurements, the particle sizes were found to be in the ranges of 2.3–5.6 nm and 2.7–7.6 nm for CDs and PPQ-CDs, respectively. However, the obtained sizes measured by DLS showed the hydrodynamic radius of the particles with maxima at 3.4 and 4.3 nm for CDs and PPQ-CDs, respectively. However, the HRTEM image of the same

Figure 2. 1H NMR spectra of (i) the PPQ molecule in deuterated DMSO and (ii) PPQ-CDs in D2O.
PPQ-CDs furnished a smaller size compared to that obtained from DLS as the particles were estimated to be in the range of 3−4.8 nm with a maximum at 3.9 nm. Further, we performed absorption studies for CDs, PPQ and PPQ-CDs individually to confirm the functionalization process (Figure 1B). The UV−vis spectrum of CDs in water showed the peaks at 264 and 330 nm, which were present due to π−π* transitions of the C−C structure. The absorption peak values were similar to the CDs already reported in the literature. PPQ in DMF also showed a main absorption peak at 340 nm. However, the absorption spectra of PPQ-CDs in water represented a combination of PPQ and CDs absorption features with an overall red shift in the spectra due to the difference in solvent polarity (Figure 1B(ii)). The surface functionalization process was further characterized by XRD technique (Figure 1C). A broad peak at 2Θ = 23° was seen for CDs (Figure 1C(i)), confirming the presence of mainly highly distorted carbon atoms. In Figure 1C(ii), several sharp peaks in the range of 2Θ = 15−30° were observed for the PPQ molecule, whereas the obtained XRD pattern in Figure 1C(iii) was also found to be commensurate with the functionalization process as both sharp peaks of the PPQ molecule were observed with a small shift in the peak values along with slight peak broadening around 2Θ = 23° from CDs. FTIR measurements were also performed for further verification of the coupling of PPQ on the CD surface (Figure 1D). The FTIR spectrum of CDs showed a strong peak at 1651 cm−1, indicating the presence of the −COOH group, whereas the broad peak around 3421 cm−1 corresponded to −OH and −NH stretching vibrations. The peaks at 2915 and 1107 cm−1 corresponded to C−H stretching and C−O bond stretching, respectively. The covalent attachment of PPQ onto the CD surface was confirmed by the shift of the carbonyl peak of carboxylic acid from 1651 to 1636 cm−1, endorsing the formation of an amide linkage. Meanwhile, during the functionalization process, the intermediate acylation step for CDs was also confirmed by the presence of the −COCl peak at 1709 cm−1.

Moreover, the observation obtained from a simple thin-layer chromatography (TLC) experiment (Figure S5) suggested that PPQ was covalently bound with the hydrophilic CDs as the retardation factor (Rf) for PPQ-CDs was found to be zero, while for free PPQ, it was 0.5 in 10% ethyl acetate/hexane solution.

2.2. 1H NMR Study. 1H NMR spectra of PPQ and PPQ-CDs are shown in Figure 2. The NMR experiment for PPQ was carried out in deuterated DMSO, but PPQ-CDs were dissolved in D2O. The peaks obtained in the range of 7−13 ppm in Figure 2(i) were due to the heteroaromatic ring protons of the PPQ molecule. On the other hand, the PPQ-CDs contained the characteristic peaks of both PPQ and CDs. The appearance of broad peaks around 6−9 ppm in Figure 2(ii) could be assigned to the heteroaromatic protons of PPQ. The sharp peaks at 1.23 and 2.67 ppm were due to the protons from CDs. Hence, this result further indicated the successful functionalization of the PPQ molecule on the CD surfaces. Additionally, the peak around 12.24 ppm that corresponds to the NH proton remained absent in PPQ-CD spectra, which further confirmed the conjugation of the PPQ molecule with CDs.

2.3. XPS Studies. X-ray photoelectron spectroscopy (XPS) is a powerful technique to probe the surface composition and was therefore chosen to probe the surface chemical composition of pure CDs and functionalized CDs (Figure 3). In XPS, it is known that the appearance of peaks around 286, 400, and 532 eV corresponds to C 1s, N 1s, and O 1s, respectively. After deconvolution, the C 1s XPS spectrum of CDs consisted of three peaks corresponding to the sp2-hybridized carbon atom C≡C/C−C at 284.7 eV, C−OH at 286.3 eV, and O−C−O− of the carboxylic group at 288.57 eV. After functionalization, new peaks were observed confirming the formation of an amide linkage between the carboxylic group of CDs and NH of the PPQ molecule. The peak of PPQ-CD at 285.34 eV confirmed the presence of C−N from the amide group, while other two peaks at 284.06 and 283.68 eV were assigned to the C−N and C−O functional groups.
285.72 eV could be assigned to C=C and C−OH, respectively. The N 1s spectrum of CDs consisted of two peaks at 399.14 and 407 eV, which could be assigned to nitrogen in the forms of N−C and N−H, respectively, but after functionalization, a single peak around 399.94 eV was observed, which probably corresponded to nitrogen in the form of C3N (aromatic nitrogen of pyrrole involved in the formation of the amide linkage). The XPS spectrum of O 1s of CDs contained three peaks at 531.7, 532.60, and 536.29 eV, which were ascribed to oxygen in the forms of C−OH, O=C−O, and H−O−H, respectively. After functionalization, a single peak at 531.70 eV was observed, representing the C−OH group only on the CD surface, indicating the disappearance of the O=C−O peak as carboxylic acid of CDs was converted to amide after PPQ functionalization (Figure 3). Apart from this, the elemental analysis data obtained from XPS for CDs and PPQ-CDs (Table S1) suggested that CDs were composed mainly of carbon, nitrogen, and oxygen, and the content of each element had increased slightly after functionalization, which perhaps confirmed successful conjugation of PPQ with CDs.

2.4. Application of PPQ-CDs in Water Detection. The as-prepared CDs showed a characteristic behavior of excitation wavelength-dependent photoluminescence intensity (Figure 4). It was seen that the emission bands were shifted bathochromically with increasing excitation wavelength, which showed the distribution of surface energy traps on the CDs. It showed an emission maximum at ~450 nm when excited at 350 nm; therefore, all further experiments were also carried out at 350 nm excitation.

After functionalization, the emission spectra of PPQ-CDs were collected in different dry organic solvents like ethanol, THF (tetrahydrofuran), DCM (dichloromethane), DMSO (dimethyl sulfoxide), DMF (dimethylformamide), toluene, and including water. As shown in Figure 5, the emission intensity of PPQ-CDs was found to be maximum in water, while in other organic solvents, the emission was evidently quenched when excited at 350 nm. The quenching of fluorescence could be due to the photoinduced electron transfer (PET) process from nitrogen of PPQ to the acceptor of the CDs. This observation prompted us to contemplate PPQ-CDs as a potential turn-on fluorescent sensor for water detection in organic solvents.

Among different solvents, DMSO was selected as it showed the minimum fluorescence intensity for PPQ-CDs (Figure 5b). If we compare the PET process in EtOH and DMSO, it is known that the rate of PET is much slower in polar protic solvent EtOH compared to the rate of PET in polar aprotic solvents. The probable reason was cited as the ordered structure of EtOH due to H-bonding. So, in our case, the minimum fluorescence intensity of PPQ-CDs was observed in DMSO, probably due to the efficient PET process in an aprotic solvent devoid of H-bonding. First, we collected the absorption spectra of PPQ-CDs in different DMSO/water mixture solutions, where water concentrations were increased successively (Figure S1). As evident from the study, there was no appreciable change in the optical density and shape of the peaks upon the stepwise addition of water, indicating only weak ground state interactions. However, with the successive increase in the water content, the fluorescence intensity of PPQ-CDs in DMSO increased continuously as shown in Figure S2 and Figure 6a. As shown in Figure 6b, the fluorescence intensity increased linearly with increasing water content (0−40%, v/v), and then the increase was quadratic in nature from 40 to 68% (v/v) water addition. We observed that the quantum yield of CDs also increased from 12% (without functionalization) to 25% (after water addition to the PPQ-CDs; Calculation S1). The calibration curve for water detection is shown below in Figure 6b, which follows the equation \( F = 7.22 \times [\text{H}_2\text{O}] + 27.68 \) \((R^2 = 0.99, [\text{H}_2\text{O}] = 0−68\%\)), where \( F \) stands for the emission intensity of PPQ-CDs in DMSO upon addition of water.
The water content in DMSO can be quantitatively detected through the known calibration equation. On the basis of the following equation, the detection limit (DL) of the sensor can be estimated as

\[ \text{detection limit (DL)} = \frac{(3.3 \sigma)}{K} \]

where \( \sigma \) is the standard deviation and \( K \) is the slope of the calibration curve. The DL of PPQ-CDs was found to be 0.023% in DMSO.

Moreover, the sensing process was instantaneous, as revealed by the time-dependent fluorescence intensity data of the sensor (Figure S11). After DMSO, water detection was also carried out with two more organic solvents, namely, ethanol and DMF (Figures S8 and S9). Similar enhancement in the emission intensity of PPQ-CDs was registered with an increase in the water content. The detection limits were found to be 0.092% (v/v) in ethanol and 0.32% (v/v) in DMF. In fact, when compared with the previous reports for water detection using CDs, the DL obtained from the current work is comparable among the peers (Table S2). Meanwhile, to confirm the substantial role of water in the enhancement process, a comparative study was also performed, where the same amount of DMF and Millipore water was successively added to PPQ-CDs, and fluorescence intensities were measured. To our satisfaction, it was found that in the case of Millipore water, the enhancement was approximately 6–7 times more (Figure S6), indicating the crucial role played by water. Suitable blank studies were also performed by functionalizing the CDs with only oxalyl chloride (Figure S3) and oxalyl chloride followed by aniline (Figure S4). In both cases, we have seen a decrease in emission intensity with stepwise addition of water. Further, a continuous decrease in emission intensity was also observed for free CDs with stepwise addition of trace amount of water (Figure S7).

2.5. Mechanism of Water Detection. Due to proton-accepting and conducting properties of water, it has been the
most widely used solvent for proton transfer studies. Water acts as a passive medium for the initial deprotonation step in the proton transport mechanism.\(^{49,50}\) The emission data showed the fluorescence enhancement of PPQ-CDs with stepwise addition of water. This enhancement could be attributed to the suppression of PET due to the formation of PPQ-functionalized CDs with stable fluorescent ionic species between the protonated nitrogen (proton acceptor/electron donor) of PPQ and the carboxyl group (proton donor/electron acceptor) on the surface of the CDs by hydrolysis. In Scheme 2, a simplified model was presented, where the PPQ-CDs were initially nonfluorescent due to the PET process between nitrogen of PPQ and the carboxyl group on the surface of the CDs by hydrolysis. In Scheme 2, a simplified model was presented, where the PPQ-CDs were initially nonfluorescent due to the PET process between nitrogen of PPQ and the carboxyl group of CDs. With the addition of water, the hydrogen-bonded complex (HBC) or water complex was formed. Further, the complete system underwent proton rearrangement and reached equilibrium with hydrogen-bonded ions (HBI). With more water, solvent-separated ions (SSI) were formed when water molecules efficiently solvated HBI, and finally SSI produced solvent-separated free ions (FI).\(^{51}\) Overall, the enhancement mechanism followed an excited-state proton-transfer process from the CD surface to PPQ through water bridging between the groups staying in close proximity.

Scheme 3 illustrates the enhancement mechanism in terms of molecular orbitals of the acceptor (CDs) and the donor (PPQ). Upon excitation of the fluorophore, an electron of the highest occupied molecular orbital (HOMO) was promoted to the lowest unoccupied molecular orbital (LUMO), which enabled the PET process from the HOMO of the donor (PPQ) to that of the fluorophore (CDs).\(^{52}\) This resulted in fluorescence quenching for the CDs, as the electron was prevented to come back to the ground state by the radiative process. However, after protonation at the quinoline nitrogen with the addition of water, the relevant HOMO of the donor (PPQ) probably became lower in energy than that of the CDs, such that it could not donate electrons anymore. Consequently, PET was no longer possible, and the fluorescence intensity was increased.

2.6. Fluorescence Lifetime Studies. Fluorescence lifetime measurement is considered as an important characterization method, where a substantial decrease in the lifetime with associated quenching will confirm the PET mechanism. Hence, we have recorded the lifetime decay patterns for the as-prepared CDs in water, PPQ-CDs in organic solvents, and PPQ-CDs in organic solvents followed by water addition. As seen from the decay patterns (Figure 7a) and the lifetime values (Table 1), the PET mechanism was evident for the
Table 1. Lifetime of Samples Calculated from Time-Resolved Fluorescence Decay Curves

| sample                        | \(\tau_1^a\) (ns) | \(\tau_2^a\) (ns) | \(\tau_3^a\) (ns) | \(\alpha_1^b\) | \(\alpha_2^b\) | \(\alpha_3^b\) | \(\chi^2\) | \(\tau_f\) (ns) |
|-------------------------------|-------------------|-------------------|-------------------|----------------|----------------|----------------|--------------|----------------|
| CD in water                   | 0.55              | 2.30              | 6.62              | 43.26          | 29.32          | 27.41          | 1.11         | 2.96           |
| PPQ-CD in DMSO                | 0.22              | 1.44              | 7.52              | 41.14          | 45.75          | 12.11          | 1.03         | 1.66           |
| PPQ-CD in ethanol             | 0.42              | 1.24              | 5.86              | 84.14          | 9.97           | 5.89           | 1.17         | 0.82           |
| PPQ-CD in DMF                 | 0.20              | 1.07              | 5.17              | 40.77          | 51.75          | 7.48           | 1.05         | 1.02           |
| PPQ-CD in DMSO with water     | 0.14              | 2.35              | 4.70              | 2.04           | 96.09          | 1.87           | 1.08         | 3.13           |
| PPQ-CD in ethanol with water  | 0.23              | 2.35              | 5.59              | 9.46           | 80.18          | 10.36          | 1.00         | 2.48           |
| PPQ-CD in DMF with water      | 0.06              | 2.01              | 3.09              | 8.78           | 75.77          | 15.45          | 1.06         | 2.00           |

*1Lifetime of the particular component. 2Contribution of each component.

functionalized CDs in organic solvents when compared to the as-prepared CDs in water. The average lifetime was calculated using the following equation:\(^{53}\)

\[
\tau_f = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i^2}
\]

where \(\tau_i\) is the lifetime of the particular component, \(a_i\) is the contribution of that particular component, and \(\tau_f\) is the average lifetime. It was observed that PPQ-CDs have a nanosecond lifetime, which makes them suitable for biological and optoelectronic applications.\(^{54}\) The multiple lifetime components implied that there were various emission species on the surface of CDs. However, it was found that the lifetimes of PPQ-CDs increased significantly with the addition of water (Figure 7b and Table 1) along with the enhancement in the fluorescence quenching was suppressed with the addition of water (Scheme 3).

2.7. Visual Detection of Water with PPQ-CDs. A visual detection protocol (Figure 8) was also established, which was made possible by taking the PPQ-CDs in DMSO in a solid matrix and thereby observing their fluorescence with the addition of water. Similar visual detection was reported recently for sensing \(\text{H}_2\text{O}_2\) in different natural water samples using functionalized vanadium oxide quantum dots.\(^{55}\) For our study, MCM-41 nanoparticles were synthesized from a known procedure\(^{56}\) and used as the solid matrix to encapsulate PPQ-CDs for the visual detection of water. First, a TLC strip was covered with the MCM-41 powder at different locations to create the test spots. Then, 10 \(\mu\)L of PPQ-CD solution in DMSO was added to each of them. For visual observation of the fluorescence, the TLC test strip was kept under 365 nm UV lamp illumination in the dark, and the photographs were taken using a camera. It was found that, with the addition of water, the blue fluorescence of the PPQ-CDs was clearly observed, and an increase in the intensity was also found to be commensurate with the concentration of water, while the spot containing only PPQ-CDs without water showed very weak fluorescence intensity (Figure 8b), indicating the efficacy of the method for the visual detection of water.

3. CONCLUSIONS

We have developed a nanosensor by functionalizing the chitosan-based CDs with a nitrogen-containing heterocyclic molecule for the rapid and sensitive detection of trace amount of water present in the organic solvents. The fluorescence intensity of the functionalized CDs was quenched in organic solvents by PET, as confirmed by the steady-state and fluorescence lifetime measurements, but, with the addition of water, the electron-donating center was blocked by protonation due to the intramolecular excited-state proton transfer process. As a result, PET became ineffective, leading to instantaneous enhancement in the fluorescence intensity. With 68% (v/v) water addition, a striking ∼40-fold enhancement in the fluorescence intensity was observed in DMSO. However, free CDs and CDs functionalized with the molecule, which was devoid of potential electron-donating centers, did not show any enhancement with the addition of water. Further, we have also shown a visual detection protocol for determining the water content in a common laboratory setup with the aid of the UV excitation chamber. The functionalized CDs may also find great potential applications as a humidity sensor in environmental monitoring systems and paper industry. Further works are underway by preparing various red-emitting CDs and possible functionalization on them.

4. MATERIALS AND METHODS

4.1. Chemicals. Chitosan and CTAB (cetyltrimethylammonium bromide) were purchased from Sigma-Aldrich, while poly(ethylene glycol) (PEG) was obtained from Sisco Research Laboratories. TEOS (tetraethyl orthosilicate) was procured from TCI Chemicals, and ammonia was purchased from SD Fine Chemicals Limited. The solvents used in the study were of analytical grade. THF was dried before use. Millipore water was used for the preparation of all the solutions.

4.2. Instruments. Dynamic light scattering (DLS) measurements were carried out on a Malvern particle size analyzer (Zetasizer nano series, Nano-ZS) at room temperature. Absorption spectra of the samples were recorded on a Shimadzu UV-3600 plus. XRD measurements were performed on a Rigaku Ultima IV X-ray Diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 1.54 \text{ Å}\)). The 2\(\Theta\) range was from 10 to 60° in a
with the addition of water, detection Limit of the sensor in DMF and ethanol, synthesis of carbon dots (CDs), time-dependent fluorescence intensity of PPQ-CDs in DMSO with the addition of elemental analyses of CD and PPQ-CDs from XPS, comparison of detection limits with different fluorescent probes for water detection, and quantum yield calculation (PDF)

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The dimethylaminophosphorus acid (DMAP) mediated coupling of ethylenediamine (EDA) to aminated carbon dots (CDs) has been reported for the first time. This approach offers a facile route to the synthesis of functionalized CDs with well-defined properties. The functionalized CDs exhibit improved photoluminescence (PL) efficiency compared to the pristine ones. The PL properties of the functionalized CDs can be tuned by adjusting the ratio of EDA to DMAP. The CDs can be used as fluorescent probes for the detection of water in various solvents, including organic solvents. The detection sensitivity and selectivity can be further improved by using a two-step detection strategy. This method shows promise for the application of CDs in the detection of water in various environmental and biological samples. The functionalized CDs have potential applications in fluorescence imaging, bioassays, and other fields where high sensitivity and selectivity are required. DOI: 10.1021/acs.chemcomm.9b07221

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