Dendritic Fibrous Nanosilica Hybrid Materials with Near-Infrared Emission as Multifunctional Sensors for Toxic Pollutants

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Two dendritic fibrous nanosilica (DFNS)-based hybrid materials (DFNS-PDI-NR and DFNS-MDI-NR) with superior near-infrared (NIR) emission are developed. Based on the J-aggregate of neutral red (NR) modified on the surfaces of DFNS, the hybrid materials possess a narrow redshifted emission band at 866 nm compared with the monomeric NR dyes upon excitation in the visible region (575 nm). Significantly, integrating the robust support of DFNS and unique fluorescence properties of the aggregated NR dyes, DFNS-PDI-NR and DFNS-MDI-NR can serve as a novel type of multifunctional solid-state chemosensors for the detection of various toxic pollutants including transition-metal anions (Cr$_2$O$_7^{2−}$ and MnO$_4^{−}$), nitrophenols, and acetone with turn-off NIR-fluorescence signals. The quenching phenomena of DFNS-PDI-NR and DFNS-MDI-NR toward various toxic pollutants are established by nonlinear bend upward Stern–Volmer fitting. Moreover, these materials can be further used as sensitive probe materials for the determination of Cr$_2$O$_7^{2−}$ and MnO$_4^{−}$ levels in various real water samples.

1. Introduction

Detection with satisfying efficiency and accuracy toward toxic pollutants that are soluble or miscible in aqueous media has been a challenging and demanding task in modern world because of their universally serious threats to the environment and living organisms.[1] Among the analytical methodologies that are ever proposed, the technique of fluorescent sensing has been extensively investigated and attached with great significance on account of its many advantages, including high accuracy and sensitivity, adequate selectivity, easy operations, and relatively low cost.[2−12] Uniquely, near-infrared (NIR)-emissive sensors, though less frequently reported, are attracting much attention in the scope of fluorescent analysis thanks to the desirable properties of NIR light (650–900 nm) in comparison with fluorescence in the visible region, such as the slight fluorescence background, minor photodamage, and minimized light scattering.[12–15] Over the past few years, much dedication has been paid to the design and fabrication of NIR-active fluorescent sensors, yielding captivating materials including fluorescent polymers,[16] quantum/carbon dots,[17,18] and metallic nanomaterials,[19,20] while the most fundamental and economic trail to obtain NIR-emissive chemosensors still lies in the elaborate synthesis of small organic molecules that are capable of emitting NIR light upon excitation.[21] Traditional expansive organic dyes, including cyanine, perylene diimide, perylene bisimide, and boron-dipyrromethene (Bodipy)[22,23] dyes have underwent plentiful functionalization and have been used in NIR-related applications.[24−27] However, two major drawbacks have existed for long in the utilization of abovementioned NIR-emissive organic dyes for fluorescent detection: i) the sophisticated synthetic procedures of the dye molecules have hindered the versatility of NIR-active sensors; ii) the discrete dyes in solution require much effort to be separated with the soluble analytes after the sensing session. Importantly, the arranged packing of molecular motifs and the immobilization of the dye molecules on inorganic surfaces can be considered as powerful schemes to tackle these issues, respectively. J-aggregation is the slip-stacked orientation of aggregating dyes that leads to constructing coupling of the excited-state transitions dipoles. The photophysical characteristics of J-aggregation are bathochromically shifted absorption and emission spectra, narrowed absorption and emission bands, and shortened fluorescence lifetimes. The main prerequisites for dye molecules to form J-aggregates are: i) the flat elongated morphology of monomers, ii) the size of the monomers, and iii) the presence of the charged groups in the monomers.[28] Therefore, the formation of J-aggregates out
of visual-light-emitting dyes would highly promote the red-shifts of original fluorescence of the dyes, and installing dyes on rigid solid surfaces can endow enhanced stability and easy separation. In this regard, we rationally envisage that the tailored construction of organic–inorganic hybrid materials via grafting J-aggregate molecular motifs onto robust inorganic supports can afford promising solid fluorescent sensors with desired NIR emission.

As an important class of inorganic nanomaterials, nanosilica has been used as a preferable choice for the immobilization of various functional groups with tunable properties because of their high availability and facile surface functionalization. Among the reported silica materials, dendritic fibrous nanosilica (DFNS) has emerged as a unique type of analogs comprising branch-like fibrous structures on the exteriors, and has been extensively used for various applications, such as sensors, catalysis, CO₂ conversion, bioimaging, and drug delivery. Due to their unique fibrous morphology, tunable sizes, excellent physical and textural properties, large surface areas, and more significantly, high accessibility to the internal surfaces and enhanced stability, DFNS can be a prominent candidate in the hybridization with J-aggregate motifs for the construction of NIR-emissive fluorescent sensors in the solid state.

In this study, we describe the fabrication and sensing applications of two novel NIR-emissive DFNS hybrid materials based on J-aggregate, denoted as DFNS-PDI-NR and DFNS-MDI-NR. Neutral red (NR), as a commonly used fluorescent dye with planar structure and a relatively long emission wavelength (618 nm), was chosen to be modified on DFNS to afford J-aggregate via proper molecular arrangements. For the construction of the hybrid materials, DFNS was synthesized as the solid supports, and the NR-based molecular motifs (PDI-NR/MDI-NR) were installed on the DFNS surfaces via step-by-step in situ postmodification (Figure 1). Interestingly, the as-prepared DFNS-PDI-NR

![Figure 1](image-url)

*Figure 1.* (a) Schematic illustration of the synthetic procedure of DFNS. (b) Schematic illustration of the syntheses of DFNS-PDI-NR and DFNS-MDI-NR by multistep postmodification. Inset: molecular structures of the modified PDI-NR and MDI-NR. (c) i) Fluorescence spectra of neutral dye (λ<sub>ex</sub> = 530 nm, λ<sub>em</sub> = 618 nm); ii) J-aggregate emissive spectra of DFNS-PDI-NR (λ<sub>ex</sub> = 575 nm, λ<sub>em</sub> = 866 nm).
and DFNS-MDI-NR exhibit intense fluorescence emission in the NIR region at 866 nm, which is rationally attributed to the J-aggregate of NR dye in DFNS-PDI-NR and DFNS-PDI-NR materials (Figure 1). We have discovered that such NIR-emissive hybrid materials could facilitate effective detection with superior selectivity and sensitivity toward different types of toxic pollutants in aqueous media, i.e., transition-metal anions (CrO$_4^{2-}$, MnO$_4^{-}$), nitrophenols, and organic solvent (acetone) via intense fluorescence turn-off, representing the creation of a multifunctional NIR-active sensing platform. Real water samples were also tested for the validation of the sensing abilities of DFNS-PDI-NR and DFNS-PDI-NR, confirming the possibilities in real-world applications.

2. Results and Discussion


The synthetic methodology of the materials, DFNS, DFNS-PDI-NR, and DFNS-MDI-NR, has been briefly presented in Figure 1, and the detailed synthetic procedures are given in the Experimental Section. The solid support DFNS was synthesized by the conventional open-vessel heating protocol using cetyltrimethylammonium bromide (CTAB) as a structure-directing template and urea as a reducing agent.$^{[29]}$ The successful synthesis of DFNS has been validated comprehensively with various characterizations. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure 2) indicate that the DFNS possesses the morphology as monodisperse colloidal spheres in uniform diameters ranging from 240 to 420 nm, and most particle sizes are located in the range of 300–360 nm (Figure 2a–c, d–f, i). High-resolution TEM (HRTEM, Figure S2, Supporting Information) images reveal that DFNS is composed of dendritic fibrous structures that outspatial from the center of the particles. Moreover, the visual elemental mapping of DFNS (Figure 2g,h) provides the evidence that the DFNS consists of silicon and oxygen only, confirming the establishment of the silica-based material. The N$_2$ adsorption/desorption parameters including Brunauer–Emmett–Teller (BET) surface area and pore size distribution (PSD) for the DFNS are shown in Figure 2j,k, respectively, where a typical type IV isotherm can be observed for DFNS with a surface area of 603 m$^2$ g$^{-1}$ and a pore diameter of 3.95 nm (BJH desorption pore diameter). Fourier-transform infrared (FTIR) analysis has also been conducted to verify the existence of various functional groups including Si–OH, SiO$_2$–H$_2$O, and Si–O–Si in the silica sphere of DFNS (Figure 2l). The DFNS exhibits good thermal stability up to 800 °C, and a weight loss of only 76.3% was observed due to the loss of chemically adsorbed water, organic solvents, and hydroxyl groups (Figure S3, Supporting Information). The DFNS was further characterized by solid-state $^{29}$Si cross-polarization magic-angle-spinning (CP-MAS) NMR spectroscopy, where the three characteristic signals at $\delta = 90.68, 100.37$, and 110.14 ppm can be assigned to the Q2, Q3, and Q4 sites corresponding to the SiO$_2$ substructures with different condensation degrees (Figure S4, Supporting Information).$^{[34]}$

Subsequently, postmodification of DFNS was performed through four consecutive steps to yield the targeted DFNS-based NIR-emissive hybrid materials (DFNS-PDI-NR and DFNS-MDI-NR). Primary amine (–NH$_2$) groups are ideal for surface modification of silica materials due to their easy functionalization under mild conditions. Therefore, for the first step we have selected (3-aminopropyl)trimethoxysilane (3-APTES) as the linker unit, which was tethered to the DFNS surfaces via alkoxyisilane groups to yield DFNS-NH$_2$, followed by the grafting of 3,4-diaminobenzoic acid (DBA) via amide linkage to afford the diamine-functionalized intermediate product DFNS-DBA. The third and fourth steps involved the installation of isocyanate-containing linkers (1,4-phenylene diisocyanate, PDI or 4,4′-methylene diphenyl diisocyanate, MDI) and NR groups via urea linkage, giving the final NIR-emissive materials (DFNS-PDI-NR and DFNS-PDI-NR), respectively (Figure S1, Supporting Information).

The successful construction of DFNS-PDI-NR and DFNS-MDI-NR was confirmed with solid-state $^{13}$C NMR, zeta potential, UV–visible (UV–vis) spectra, and FTIR analysis via verifying the existence of each functional group in the postmodification steps. $^{13}$C solid-state NMR spectrum of DFNS-NH$_2$ shows three shielded aliphatic methylene signals (–10.24, 24, and 45 ppm), indicating the successful functionalization of 3-APTES on to the DFNS surface.$^{[35]}$ The characteristic peaks of DFNS-DBA at 90–150 ppm (aromatic carbon in the aromatic region)$^{[36]}$ and the peak at 170 ppm (black dot, amide carbonyl group)$^{[37]}$ can be ascribed to the successful attachment of DBA onto DFNS-NH$_2$. In the spectrum of DFNS-PDI, the additional peak at 155 ppm can be observed due to the carbonyl carbon of urea linkage (imidazole)$^{[38]}$ and carbon atoms of –NCO and benzene rings are overlapped with the aromatic region at 90–150 ppm. The existence of a signal at 40 ppm in DFNS-PDI-NR can be attributed to the carbon atom of dimethyl amine groups of NR (Figure 3a). Changes in the surface properties upon each step were further confirmed by zeta potential measurements. As shown in Figure 3b, the zeta potential of DFNS is $–(28.03 \pm 2.25)$ mV because of the presence of silanol groups,$^{[39]}$ while DFNS-NH$_2$ performs a positive zeta potential $+(21.9 \pm 1.70)$ mV.$^{[40]}$ DFNS-DBA shows increased positive zeta potential $+(30.6 \pm 2.49)$ mV, suggesting the presence of more amine groups after the grafting of DBA, while the zeta potential of DFNS-PDI was reduced to $–(20.3 \pm 1.75)$ mV, indicative of the capping of diamine groups of DFNS-DBA with isocyanate fragments of the PDI. After the modification of NR dyes, the afforded DFNS-PDI-NR showed a surface potential of $–(20.13 \pm 1.55)$ mV. Similarly, the calculated zeta potential of final material DFNS-MDI-NR was $–(16.76 \pm 1.62)$ mV. Thermogravimetric analysis (TGA) of both final materials showed three major weight losses between 35–220, 220–550, and 550–800 °C (Figure 3c). The first region exhibits a weight loss of 3.41% for DFNS-PDI-NR and 4.56% for DFNS-MDI-NR due to desorption of physically adsorbed water and organic solvents on the surface of materials. The weight loss of the second region is attributed to the destruction of organic contents, whereby the loss of 15.83% for DFNS-MDI-NR, compared to 10.81% for DFNS-PDI-NR, is in accordance to its higher mass of organic modification. The third region represents the dehydroxylation of surface silanol groups, which shows similar weight losses for DFNS-PDI-NR and DFNS-MDI-NR (7.13% and 6.55%) as
expected. In Figure 3d, FTIR spectra of DFNS-NH$_2$ (i), DFNS-DBA (ii), DFNS-PDI (iii), DFNS-PDI-NR (iv), DFNS-MDI (v), and DFNS-MDI-NR (vi) are given. Various C–H (–(CH$_2$)$_3$–) and N–H vibration bands can be observed in the 3150–2800 and 1650–1500 cm$^{-1}$ regions of the spectrum from (i) to (vi). The presence of amide carbonyl group in DFNS-BDA, urea carbonyl group in DFNS-PDI, and aromatic amine and C–N group in DFNS-PDI-NR are confirmed from FTIR data. The band observed at 1686 and 1515 cm$^{-1}$ for DFNS-BDA can be ascribed to the carbonyl stretching frequency of amide group.[41] The band at 1650 cm$^{-1}$ of DFNS-PDI is also due to the carbonyl stretching in the urea groups.[11] The aromatic amine and C–N groups of NR show a band at 1311 and 1219 cm$^{-1}$ in the FTIR spectra of DFNS-PDI-NR, confirming the successful synthesis of DFNS-PDI-NR.[42] Similar FTIR analysis results have also been obtained for DFNS-MDI-NR.

The morphological and surface characteristics of the final materials are investigated via SEM and N$_2$ adsorption–desorption analysis. Interestingly, the SEM images of the final materials DFNS-PDI-NR and DFNS-MDI-NR clearly demonstrate the aggregation of nanoparticles, which is in contrast to the dispersed state of DFNS before functionalization (Figure 4a,b). The BET surface areas ($S_{BET}$) of DFNS-PDI-NR and DFNS-MDI-NR are calculated to be 15 and 27 m$^2$ g$^{-1}$, respectively (Figure 4c,d), which are much lower compared to DFNS surface area (603 m$^2$ g$^{-1}$), clearly suggesting the
functionalization of the DFNS with many organic dyes. Interestingly, larger pores of DFNS-PDI-NR and DFNS-MDI-NR with diameters of ≈21 and 26 nm are found, signifying that aggregation occurred in the final materials due to the dye modification and aggregation (Figure 4e,f). The above evidences denoting the aggregation of the hybrid materials can provide useful proof for the formation of J-aggregates of NR motifs in the macroscopic aspect.

2.2. Fluorescence Properties and Pollutant Sensing of DFNS-PDI-NR and DFNS-MDI-NR

The organic–inorganic hybrid materials DFNS-PDI-NR and DFNS-MDI-NR have been fabricated in order to develop rigid solid-state fluorescent sensors. Because of the dimeric arrangement of NR in the PDI-NR/MDI-NR structures, the hybrid materials could perform different fluorescent emission comparing with the NR monomers (Figure 1b). To investigate the optical properties of the as-prepared materials, UV–vis spectra of NR and DFNS-PDI-NR/DFNS-MDI-NR have been collected in aqueous solutions. Different from the absorption pattern of pure NR dye (270 and 530 nm), both DFNS-PDI-NR and DFNS-MDI-NR show two apparently redshifted absorbance peaks as shown in Figure S5 (Supporting Information), indicating the formation of J-aggregates after the grafting of NR on the PDI/MDI groups on the robust surface of DFNS. A collection of UV–vis spectra of DFNS-NH₂, DFNS-PDI, DFNS-PDI-NR, DFNS-MDI, and DFNS-MDI-NR have also been provided in Figure S6 (Supporting Information), further demonstrating that the two redshifted characteristic peaks originate from the last modified NR groups. More importantly, the characteristic fluorescence features of the J-aggregates are validated straightforwardly by the fluorescence parameters of final materials DFNS-PDI-NR and DFNS-MDI-NR, including the strong shift of their excitation and emission peaks to longer wavelengths (λ_{ex} = 575 nm, λ_{em} = 866 nm) in comparison with the spectra of NR (λ_{ex} = 530 nm, λ_{em} = 618 nm), together with the dramatic sharpening of the emission band and shorter fluorescence lifetimes as a result of “superradiance” (as given in Figure 1c and Figure S7, Supporting Information). These spectroscopic data evidently point to the formation of J-aggregate, which is primarily based on the occurrence of an aggregation between highly polarizable groups in a head-to-tail “shifted plates” organization via π–π interactions and electrostatic interactions, inducing redshift of the absorption and emission bands. Conversely, though both originating from the π-stacked arrangement of dye molecules, H-aggregates, typical of side-by-side “sandwich” orientations with the main absorption peak blueshifted, can be excluded in this very case of NIR-emitting organic–inorganic hybrid materials.

Since the DFNS-PDI-NR and DFNS-MDI-NR can undergo protonation due to the presence of the urea –NH, the impact of pH on DFNS-PDI-NR and DFNS-MDI-NR has been tested. 

Figure 3. a) Solid-state ^13C CP-MAS NMR characterization of DFNS-NH₂, DFNS-DBA, DFNS-PDI, and DFNS-PDI-NR; b) Zeta potential analysis of the products of each step; c) TGA analysis of DFNS-PDI-NR and DFNS-MDI-NR; d) FTIR of i) DFNS-NH₂, ii) DFNS-DBA, iii) DFNS-PDI, iv) DFNS-PDI-NR, v) DFNS-MDI, and vi) DFNS-MDI-NR.
in the pH range of 2–9 in aqueous buffer media by UV–vis spectroscopy (Figure S8, Supporting Information). The materials remain stable in the pH range of 6–9 with two absorbance bands at 575 and 320 nm, whereas a new band appears at 540 nm at lower pH due to the protonation of urea groups. Therefore, neutral pH (around 7) was chosen as the preferable condition for the following sensing experiments toward various toxic pollutants (anions, nitrophenols, and acetone).

To investigate the potential of DFNS-PDI-NR and DFNS-MDI-NR for selective sensing of anions, fluorescence experiments of DFNS-PDI-NR and DFNS-MDI-NR upon addition of various potassium salts of anions (Br$^{-}$, Cl$^{-}$, Cr$_2$O$_7^{2-}$, CO$_3^{2-}$, CrO$_4^{2-}$, HCO$_3^{-}$, HPO$_4^{2-}$, F$^{-}$, I$^{-}$, MnO$_4^{-}$, NO$_2^{-}$, NO$_3^{-}$, PO$_4^{3-}$, SO$_4^{2-}$, SO$_3^{2-}$, and HSO$_3^{-}$) were carried out in aqueous buffer system at pH 7. As shown in Figures 5a and 6a, the NIR-emissive band based on J-aggregate at 866 nm of both hybrid materials quenched dramatically upon addition of Cr$_2$O$_7^{2-}$, while DFNS-PDI-NR can also perform fluorescence quenching toward MnO$_4^{-}$ among all other anions under identical circumstances at a final concentration of 80 $\times$ 10$^{-6}$ M, indicating that DFNS-PDI-NR and DFNS-MDI-NR could be potential NIR chemosensors for identifying MnO$_4^{-}$ and/or Cr$_2$O$_7^{2-}$ with superior selectivity. To further confirm our point of view, fluorescence studies involving ion interference have been performed, and the experimental results demonstrate that the existence of other anions imparts no disturbance on the quenching effect of MnO$_4^{-}$ and Cr$_2$O$_7^{2-}$ (Figures S9 and S10, Supporting Information), suggesting that the DFNS-PDI-NR and DFNS-MDI-NR can afford desirable selective detection of MnO$_4^{-}$ and Cr$_2$O$_7^{2-}$, respectively. In the case of DFNS-PDI-NR, both MnO$_4^{-}$ and Cr$_2$O$_7^{2-}$ strongly interact with $\text{–CONH–}$ groups$^{[11]}$ that are very close to each other, but these groups are far away from each other due to longer MDI linker in DFNS-MDI-NR. Therefore, Cr$_2$O$_7^{2-}$ could interact with these groups in DFNS-MDI-NR due to its bridged structure, whereas MnO$_4^{-}$ is unable to interact with these groups in DFNS-MDI-NR.
To explore the quenching mechanism, fluorescence quenching titration experiments were carried out with incremental addition of $\text{Cr}_2\text{O}_7^{2-}$ (0–80 × 10$^{-6}$ m) and/or $\text{MnO}_4^{-}$ (0–80 × 10$^{-6}$ m) to obtain the quenching parameters including Stern–Volmer (S–V) quenching constant ($K_{sv}$) and limit of detection (LOD) of the hybrid materials toward the anions. As shown in the fluorescence spectra of DFNS-PDI-NR (Figure 5b,c) and DFNS-MDI-NR (Figure 6b), the NIR emission gradually quenched with the increasing concentration of the hybrid materials toward the anions. The positive deviation of nonlinear S–V plot can be ascribed to a static fluorescence quenching or a combination of static and dynamic quenching mechanism, resulting from the simultaneous effect of self-absorption and an energy transfer process.\[11\] The nonlinear quenching S–V constants of DFNS-PDI-NR toward $\text{Cr}_2\text{O}_7^{2-}$ and $\text{MnO}_4^{-}$ and DFNS-MDI-NR toward $\text{Cr}_2\text{O}_7^{2-}$ are given in Table 1. The LOD values of DFNS-PDI-NR toward $\text{Cr}_2\text{O}_7^{2-}$ and $\text{MnO}_4^{-}$ and DFNS-MDI-NR toward $\text{Cr}_2\text{O}_7^{2-}$ were calculated to be 0.9353 × 10$^{-6}$, 0.9949 × 10$^{-6}$, and 1.8823 × 10$^{-6}$ m, respectively, by 3SD/S rule (SD = standard deviation of 5-blank reading of DFNS-PDI-NR and DFNS-MDI-NR, $S =$ slope of concentration vs intensity graph of anions, concentration range 0–25 × 10$^{-6}$ m, Figures S11–S15, Supporting Information). Moreover, the main elemental composition (Cr, Mn, Si) of DFNS-PDI-NR–Cr$_2$O$_7^{2-}$, DFNS-PDI-NR–MnO$_4^{-}$, and DFNS-MDI-NR–Cr$_2$O$_7^{2-}$ composites were analyzed by energy dispersive X-ray (EDX) elemental mapping (Figures 5d–f, g–i). The strong signal of Cr in DFNS-PDI-NR–Cr$_2$O$_7^{2-}$, Mn in DFNS-PDI-NR–MnO$_4^{-}$, and Cr in DFNS-MDI-NR–Cr$_2$O$_7^{2-}$ indicating the existence of Cr and Mn in their corresponding composites. With the low LOD values and high sensing selectivity, DFNS-PDI-NR and DFNS-MDI-NR can be potentially applied as NIR-emissive fluorescent chemosensors for $\text{Cr}_2\text{O}_7^{2-}$ and $\text{MnO}_4^{-}$ in aqueous solution.

Figure 5. a) Fluorescence spectra of DFNS-PDI-NR in the presence of potassium salts of various anions (80 × 10$^{-6}$ m); b) Fluorescence titration spectra of DFNS-PDI-NR in the presence of increasing concentrations of $\text{Cr}_2\text{O}_7^{2-}$ (0–80 × 10$^{-6}$ m), inset: S–V plot of DFNS-PDI-NR in the presence of $\text{Cr}_2\text{O}_7^{2-}$ (0–80 × 10$^{-6}$ m); c) Fluorescence titration spectra of DFNS-PDI-NR in the presence of increasing concentrations of $\text{MnO}_4^{-}$ (0–80 × 10$^{-6}$ m), inset: S–V plot of DFNS-PDI-NR in the presence of $\text{MnO}_4^{-}$ (0–80 × 10$^{-6}$ m); e,f) Visual elemental mapping of $\text{Cr}_2\text{O}_7^{2-}$ loaded DFNS-PDI-NR; g–i) Visual elemental mapping of $\text{MnO}_4^{-}$ loaded DFNS-PDI-NR.
Importantly, the effective detection and quantification of nitrophenols, a primary class of explosives and organic pollutants, have been in urgent need in recent years due to the concern of their major threats on environmental safety and human health. Herein, the fluorescence responses of DFNS-PDI-NR and DFNS-MDI-NR toward various aromatic phenolic compounds, such as phenol, phloroglucinol (ph-glu), o-nitrophenol (o-NP), m-nitrophenol (m-NP), and p-nitrophenol (p-NP), have been tested in water suspension (pH 7). It is noticed that the fluorescence emission band of both DFNS-PDI-NR and DFNS-MDI-NR at 866 nm was selectively quenched in the presence of m-NP and p-NP under the same conditions with a final concentration of 80 × 10^{-6} M. The fluorescence quenching efficiencies of DFNS-PDI-NR toward m-NP and p-NP are calculated as 100% and 87.94%, respectively (Figure 7a), whereas DFNS-MDI-NR has shown quenching efficiencies of 100% for m-NP and 65.10% for p-NP (Figure 7d). As shown in Figure 7b,c, the fluorescence of DFNS-MDI-NR steadily decreased with the incremental addition of m-NP and p-NP (0−80 × 10^{-6} M) and the detection limit of m-NP and p-NP, according to 3SD/S rule, are calculated to be 1.4895 × 10^{-6} and 1.5681 × 10^{-6} M, respectively (Figures S16 and S17, Supporting Information). Fluorescence quenching data are in good agreement with the nonlinear bent V plot (Figure 7b,c) with the nitrophenols concentration range of 0−80 × 10^{-6} M. Similarly, the detection limits of DFNS-MDI-NR toward m-NP and p-NP are calculated as 3.1490 × 10^{-6} and 2.6194 × 10^{-6} M (Figures S18 and S19, Supporting Information). The nonlinear S−V plot indicates a static or a combination of static and dynamic fluorescence quenching mechanism. Fluorescence quenching parameters including \( K_w \), correlation factor \( R^2 \), and LOD of DFNS-PDI-NR and DFNS-MDI-NR toward the nitrophenols are listed in Table 1.

Environmental concerns on volatile organic solvent molecules (VOSMs) motivated us to further investigate whether VOSMs will affect the J-aggregate-based NIR emission of the DFNS-PDI-NR and DFNS-MDI-NR in aqueous systems. Exclusively, we discovered that only acetone was able to affect the fluorescence of the hybrid materials among other types of VOSMs including methanol (MeOH), ethanol (EtOH), tetrahydrofuran (THF), acetonitrile (ACN), acetone, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Acetone is a commonly used volatile organic solvent in both laboratory and industrial manufacture, which proved to be harmful to human health and environment. As shown in Figure 8a,b, the quenching efficiencies of DFNS-PDI-NR and DFNS-MDI-NR toward other

Table 1. The detection parameters obtained from fluorescence studies of various pollutants (Cr\(_2\)O\(_7\)\(^{2-}\), MnO\(_4\)\(^{-}\), m-NP, p-NP, and acetone).

<table>
<thead>
<tr>
<th>Toxic pollutants</th>
<th>( K_w ) [m(^{-1})]</th>
<th>Limit of detection (LOD)</th>
<th>( R^2 )</th>
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<tbody>
<tr>
<td>DFNS-PDI-NR</td>
<td></td>
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<tr>
<td>MnO(_4)(^{-})</td>
<td>1.8884 × 10(^4)</td>
<td>0.9949 × 10(^{-6}) M</td>
<td>0.9966</td>
</tr>
<tr>
<td>Cr(_2)O(_7)(^{2-})</td>
<td>1.9268 × 10(^4)</td>
<td>0.9353 × 10(^{-6}) M</td>
<td>0.9987</td>
</tr>
<tr>
<td>m-NP</td>
<td>1.8533 × 10(^4)</td>
<td>1.4895 × 10(^{-6}) M</td>
<td>0.9935</td>
</tr>
<tr>
<td>p-NP</td>
<td>2.0317 × 10(^4)</td>
<td>1.5681 × 10(^{-6}) M</td>
<td>0.9965</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.9553 × 10(^3)</td>
<td>18 ppm</td>
<td>0.9970</td>
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| DFNS-MDI-NR     |                  |                  |      |
| Cr\(_2\)O\(_7\)\(^{2-}\) | 2.6619 × 10\(^4\) | 1.8823 × 10\(^{-6}\) M | 0.9920 |
| m-NP            | 0.9472 × 10\(^4\) | 3.1490 × 10\(^{-6}\) M | 0.9963 |
| p-NP            | 1.3370 × 10\(^4\) | 2.6194 × 10\(^{-6}\) M | 0.9983 |
| Acetone         | 0.7157 × 10\(^3\) | 7.89 ppm         | 0.9917 |

Figure 6. a) Fluorescence spectra of DFNS-MDI-NR in the presence of various potassium salts of anions (80 × 10^{-6} M); b) Fluorescence titration spectra of DFNS-MDI-NR in the presence of increasing concentrations of Cr\(_2\)O\(_7\)\(^{2-}\) (0−80 × 10^{-6} M), inset: S−V plot of DFNS-MDI-NR in the presence of Cr\(_2\)O\(_7\)\(^{2-}\) (0−80 × 10^{-6} M); c–e) Visual elemental mapping of Cr\(_2\)O\(_7\)\(^{2-}\) loaded DFNS-MDI-NR.
VOSMs are observed to be negligible, while acetone can cause fluorescence quenching with an efficiency of 100%, demonstrating superior selectivity of the materials in the detection of acetone. Interestingly, the color of water suspension of DFNS-PDI-NR and DFNS-MDI-NR changed from violet to deep yellow and light yellow after interaction with acetone. To examine the detection sensitivity toward acetone, DFNS-PDI-NR and DFNS-MDI-NR were dispersed in water (0.1 mL from 5 mg/4 mL stock solution to 3 mL in cuvette), and a gradual decrease of the fluorescence intensity was observed as an increasing amount of acetone (0–120 $\times 10^{-6}$ m) was added into these suspensions (Figure 8c,d). The decreasing trend of the fluorescence intensity at 866 nm for DFNS-PDI-NR and DFNS-MDI-NR versus the concentration of acetone can be well fitted with a first-order exponential decay (Figure 8c,d), signifying that fluorescence quenching of DFNS-PDI-NR and DFNS-MDI-NR by acetone is diffusion-controlled.[45] Additionally, as shown in Figure S20a,b (Supporting Information), the fluorescence quenching data were in good relationship with nonlinear S–V plot within the acetone concentration range of 0–120 $\times 10^{-6}$ m. The LOD values of DFNS-PDI-NR and DFNS-MDI-NR toward acetone were calculated to be 18 and 7.89 ppm, respectively (Figures S21 and S22, Supporting Information). The detection parameters of $\text{Cr}_2\text{O}_7^{2-}$, $\text{MnO}_4^{-}$, $p$-NP, $m$-NP, and acetone are comparable to the literature results based on other materials, and more excitingly, DFNS-PDI-NR and DFNS-MDI-NR are the new functionalized hybrid materials utilized to sensing abovementioned toxic pollutants in NIR window (Tables S1–S3, Supporting Information).

3. Application in Real Samples

To inspect the practical applications of DFNS-PDI-NR and DFNS-MDI-NR as NIR fluorescent sensors, the proposed method was applied for detection of $\text{Cr}_2\text{O}_7^{2-}$ and $\text{MnO}_4^{-}$ in real aqueous samples including tap water and pond water obtained in the university campus. The experimental results are shown in Tables 2 and 3, whereby various concentrations of anions were spiked to the tap and pond water. The spiking recoveries of $\text{Cr}_2\text{O}_7^{2-}$ anions are in the range of 93.06–109.72% and the relative standard deviations (RSD) are lower than 2.52%. Real samples spiked with $\text{MnO}_4^{-}$ have also been verified (Table 2). The recovery efficiencies also fall in the range of 97.90–109.08%, and the corresponding RSD values vary from 0.23% to 3.03%. These results strongly proposed that the DFNS-PDI-NR and DFNS-MDI-NR can serve as promising fluorescent materials in the application for the detection of $\text{Cr}_2\text{O}_7^{2-}$ and $\text{MnO}_4^{-}$ in real samples. The detailed procedures are elaborated in the Supporting Information (Figures S23–S25, Supporting Information).
4. Conclusion

In conclusion, two NR-functionalized organic–inorganic hybrid materials, i.e., DFNS-PDI-NR and DFNS-MDI-NR have been constructed, which displayed NIR fluorescence signal at 866 nm based on J-aggregate upon excitation at visible region at 575 nm with selective and sensitive sensing properties toward toxic chemicals (Cr$_2$O$_7^{2-}$, MnO$_4^{-}$, m-NP, p-NP, and acetone) and also showed attractive recognition of transition metal anions in real water samples. The colloidal spherical morphology and dendritic fibrous nature of DFNS were confirmed by SEM and TEM, and the N$_2$ adsorption–desorption analysis exposed a decrease in surface area after the multistep postmodification, which strongly specified that organic contents have been situated on the surface of DFNS,

Table 2. Analytical results of Cr$_2$O$_7^{2-}$ detection in tap water and pond water through DFNS-PDI-NR and DFNS-MDI-NR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr$_2$O$_7^{2-}$ spiked [× 10$^{-6}$ M]</th>
<th>Found [× 10$^{-6}$ M]</th>
<th>Recovery [%]</th>
<th>RSD [%], n = 2</th>
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<tr>
<td>DFNS-PDI-NR</td>
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<td>21.19</td>
<td>105.95</td>
<td>1.27</td>
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<tr>
<td>Pond water</td>
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<td>27.92</td>
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<tr>
<td>Tap water</td>
<td>30</td>
<td>54.86</td>
<td>109.72</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>50</td>
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<td></td>
<td>30</td>
<td>31.27</td>
<td>104.23</td>
<td>1.04</td>
</tr>
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<td></td>
<td>50</td>
<td>54.51</td>
<td>109.02</td>
<td>2.36</td>
</tr>
<tr>
<td>DFNS-MDI-NR</td>
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<td>21.29</td>
<td>106.45</td>
<td>1.93</td>
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<tr>
<td>Pond water</td>
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<td>32.06</td>
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<td>0.71</td>
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<tr>
<td>Tap water</td>
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<td>102.30</td>
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<td>31.46</td>
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<td>2.52</td>
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<td>50</td>
<td>54.19</td>
<td>108.38</td>
<td>0.50</td>
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Table 3. Analytical results of MnO$_4^{-}$ detection in tap water and pond water through DFNS-PDI-NR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MnO$_4^{-}$ spiked [× 10$^{-6}$ M]</th>
<th>Found [× 10$^{-6}$ M]</th>
<th>Recovery [%]</th>
<th>RSD [%], n = 2</th>
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<tbody>
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<td>DFNS-PDI-NR</td>
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<td>107.40</td>
<td>2.50</td>
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<td>103.16</td>
<td>0.23</td>
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<tr>
<td>Tap water</td>
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<td>109.08</td>
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<td>97.90</td>
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<td>53.00</td>
<td>106.00</td>
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</table>
demonstrating the successful fabrication of the hybrid materials. The afforded materials showed excellent sensing capacities toward transition metal anions (Cr$_2$O$_7^{2-}$ and MnO$_4^{-}$), nitrophenols (p-NP and m-NP), and acetone, whereby fluorescence studies on the former two analytes suggested a static or combination of static and dynamic fluorescence quenching mechanism, indicating a self-absorption or an energy-transfer process, while the decreasing trend of the fluorescence intensity of the NIR emission versus the concentration of acetone could be well fitted with a first-order exponential decay, signifying that fluorescence quenching of DFNS-PDI-NR and DFNS-MDI-NR by acetone was diffusion-controlled. These materials epitomize the first example of the J-aggregate-based NIR-emissive hybrid materials, and also the first illustration as multifunctional NIR-active sensors for the detection of various toxic pollutants in aqueous systems. We envision that such research should not only inspire the design of NIR-emissive hybrid materials via facile synthetic methods but also accelerate the development of fluorescent sensors with enhanced efficiencies and multiple functionalities.

5. Experimental Section

Materials and Instrumentation: CTAB, 3-APTES, p-xylene, 1-pentanol, DBA, PDI, MDI, NR, tetraethylthiolsilicate (TEOS), urea, potassium salts, nitrophenols, hydrochloric acid (HCl), NR dye (i.e., 3-amin-7-dimethylamino-2-methylphenazine hydrochloride, Basic Red 5), and ethanol were purchased from commercial sources and used without further purification. 23Si and 13C solid CP NMR spectra were collected on a Bruker-500 MHz NMR spectrometer. FTIR spectra were recorded on a Vertex 80 V spectrometer. UV–vis spectra and fluorescence spectra were collected on Japan Shimadzu UV-1800 and Shimadzu FR-5300PC spectrometers, respectively. SEM images were collected on a HITACHI SU8082 instrument. TEM images were collected on a Tecnai G2 S-Twin F20 instrument at an accelerating voltage of 200 kV. TGA was performed under an air atmosphere with a heating rate of 10 °C min$^{-1}$ by using a NETZSCH STA449F3 QMS403D thermogravimetric analyzer. X-ray diffraction (XRD) measurements were carried out using a PANalytical B.V. Empyrean powder diffractometer. Nitrogen-sorption analysis was performed on a Micromeritics 3Flex analyzer. The specific surface area was calculated from the adsorption branch using BET method. The gas sorption measurements were carried out in a Quantachrome Autosorb iQ2 TPX automated gas sorption system equipped with highly accurate pressure transducers and a thermostatic bath. Zeta potential was obtained on a Zetasizer Nano ZS instrument.

Synthesis of Highly Monodisperse DFNS under Refluxing Conditions: All the reactions were carried out using a 2 L four-neck round bottom (RB) flask under reflux with a water condenser. The DFNS was synthesized according to the reported process with moderate modification.[29a] In a typical synthetic procedure, CTAB (10 g, 0.027 mol) and urea (12 g, 0.2 mol) were dissolved in 600 mL of deionized water under 30 min constant stirring at 800 rpm using a magnetic stirrer at room temperature. Then a homogeneous mixture was prepared by addition of 50 mL TEOS into 250 mL of p-xylene, which was added dropwise into the above solution over 30 min under stirring condition. This reaction mixture was then further stirred for 30 min. 1-Pentanol (30 mL) was then added slowly in the above reaction mixture and stirred for another 30 min. Finally, the above reaction mixture was refluxed for 7 h under stirring at 800 rpm. After cooling, the product was collected by filtration and washed with deionized water and ethanol 4–5 times. After drying for 8 h at 70 °C, CTAB template was removed 3–4 times by solvent extraction (250 mL methanol + 5 mL HCl (1 mol)) process to obtain pure DFNS and dried under vacuum at 70 °C for 24 h.

Preparation of DFNS-NH$_2$: DFNS-NH$_2$ was synthesized according to a procedure reported in the literature.[31] An amount of 2 g of dried DFNS was dispersed in dried toluene (100 mL), and then 3-APTES (5 mL) was gradually added and the mixture was refluxed for 12 h. Finally, the solid product was filtered, washed with ethanol, and dried under vacuum at 70 °C for 24 h.

Preparation of DFNS-DABA: DFNS-NH$_2$ (2 g) and DABA (500 mg) were dispersed/dissolved in anhydrous CH$_2$Cl$_2$ (10 mL) and stirred for 30 min. The mixture was added dropwise to a solution of N, N'-dicyclohexylcarbodiimide (DCC, 150 mg, 0.726 mmol), and 4-dimethylaminopyridine (4-DMAP, 50 mg, 0.409 mmol) were dispersed/dissolved in anhydrous CH$_2$Cl$_2$ (10 mL) at 0 °C. The above mixture was stirred for another 24 h at room temperature. Finally, the product was collected by filtration and washed with CH$_2$Cl$_2$, THF, and hot water 3–4 times and dried under vacuum at 70 °C for 12 h.

Preparation of DFNS-PDI and DFNS-MDI: DFNS-PDI was synthesized by the reaction of DFNS-DABA (2 g) with PDI (1 g) in acetonitrile at room temperature. After vigorous stirring overnight, the final gray-colored solid product was filtered and washed 3–4 times with acetonitrile and THF solvent to remove the unreacted PDI and then dried under vacuum for 12 h at 70 °C. DFNS-MDI was synthesized according to the identical synthetic route.

Preparation of the Hybrid Materials DFNS-PDI-NR and DFNS-MDI-NR: NR-containing final hybrid materials DFNS-PDI-NR and DFNS-MDI-NR were synthesized by the reaction of NR dye (500 mg) with DFNS-PDI (1 g) and DFNS-MDI (1 g) in dry THF at 75 °C for 24 h under N$_2$ atmosphere. The resulting DFNS-PDI-NR and DFNS-MDI-NR materials were collected by filtration and washed several times with deionized water and ethanol to remove the unreacted NR dye and dried at 70 °C under vacuum for 24 h.

UV–Vis and Fluorescence Studies: For both UV–vis and fluorescence studies, 5 mg of DFNS-PDI-NR and DFNS-MDI-NR materials were suspended in 4 mL deionized water and shaken well on a vortex shaker for 5 min to afford a uniform suspension. These solutions were utilized as stock solution and 0.1 mL solution was used for any spectral studies. The suspension was taken in a 1 cm quartz cuvette, and before and after addition of various potassium salt of anions, various aromatic compounds, and various solvents including acetone to the suspension, the cuvette was shaken well. The process was repeated for each fluorescence reading. UV–vis spectra were recorded in the range of 200–800 nm and fluorescence spectra were recorded in the range 600–900 nm with the excitation wavelength of 575 nm.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
Keywords
dendritic fibrous nanosilica, fluorescence probes, J-aggregates, near-infrared emission, toxic pollutants

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