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Molecular Recognition

Supramolecular Interactions at the Inorganic–Organic Interface in Hybrid Nanomaterials**

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Hybrid nanomaterials assembled from inorganic and organic materials are expanding the scope of new materials and still represent a challenge in the research field wherein new materials are synthesized for achieving specific physical properties. The properties of these hybrid materials are not only the sum of the individual contributions of both components, but are also determined by processes that occur at the interfaces between the components.[1] The resulting changes may include either totally new or improved physical and chemical properties that result in strong interaction between the organic and inorganic units.[1] These new generations of hybrid nanomaterials have attracted substantial research efforts and have been exploited for applications in various fields including optics, electronics, field emission, sensors, optoelectronics, and electromagnetics.[2,3] Generally, the hybrid systems are able to self-organize into structurally well-defined hybrid architectures with controlled properties.

The rapid development of this research area is expected to result in inorganic–organic interfaces that have remarkable molecular-recognition properties. In general, the functionalization of inorganic–organic hybrid materials with specific groups to enhance active functions can be summarized by two classes of amplification processes: 1) the enhancement of classic recognition features and 2) the amplified output signal that arises from collective phenomena between the preorganized functional units.[4] The signal expression can principally contain a contribution from the inorganic nanomaterials as well as a contribution from the organic units.[5] Many reported organic–inorganic hybrid materials are basically distinguished by improved features of classical supramolecular functions.[5,6] We have exploited organic–inorganic nanomaterials to create "molecular pockets" for chemical recognition, which is based on the molecular-recognition properties of the interface and the ability for electron transfer to occur efficiently between the organic and inorganic units. The inherent properties of the two components in the hybrid system are completely different from that of the individual inorganic and organic units.

Herein, we show that inorganic–organic hybrid nanorods (ZPDI) with molecular pockets are prepared by the assembly of ZnO nanorods (NRs) and perylene diimide derivatives (PDI) without a recognition functional group. The supramolecular interactions at the inorganic–organic interface lead to a novel principle for selective recognition of perylene molecules on a solid interface. Furthermore, the arrays of ZnO–PDI hybrid nanorods on silicon (100; ZPDIS) can separate perylene from dilute solutions with a detection limit as low as 10^{-12} M.

PDI is a conjugated molecule with unique electronic and optical properties, and is also referred an n-type organic semiconductor with a wide band gap.[7] PDI with two thiol groups and ZnO NRs with a diameter of 15 nm and length of 65 nm (Figure 2a) was prepared by reported methods (Figure 1a).[7a,8] The molecular pocket (Figure 1b) is created by a thiol–zinc bond that attaches the PDI molecule to the ZnO NRs to form the molecular pocket at the inorganic–organic interface. As the planar perylene framework of PDI (Figure 1c) favors π–π interactions between PDI and perylene, the size of the molecular pocket is suitable for intercalating the perylene molecule. In ZPDI, the emission intensities of ZnO NRs at 384 nm and PDI at 543 nm are partially reduced owing to the internal electron transfer from PDI to ZnO after photoexcitation.[5,9] After capture of the perylene molecule by ZPDI, the supramolecular interactions at the inorganic–organic interface result in almost complete quenching of the emission signals of both ZPDI and perylene. Because perylene is a good electron donor, intermolecular electron transfer occurs from perylene to PDI. The resulting extra electrons of PDI are transferred in turn to the surface of ZnO NRs. This step leads to the quenching of the ZPDI and perylene emission. Electron transfer also occurs directly between the perylene molecules and the ZnO NRs. Control experiments (see Figure S1 in the Supporting Information) confirmed that the molecular pocket was not produced between the interface of ZnO NRs and a perylene derivative without thiol groups.

The peak in the absorption spectrum of ZPDI at 354 nm (Figure 1b) is red-shifted compared to the peak of ZnO NRs at 348 nm and the absorption of PDI at 339 nm. Upon addition of perylene, the absorption of ZPDI at 354 nm shifts to 347 nm. Figure 2c shows the fluorescence spectra of a PDI solution, ZnO NRs, ZPDI, and ZPDI–perylene colloids. PDI exhibits an emission maximum at 410 nm and broad weak emission bands at 537 nm and 575 nm. The ZnO NRs show a characteristic emission at 384 nm. The emission intensities of

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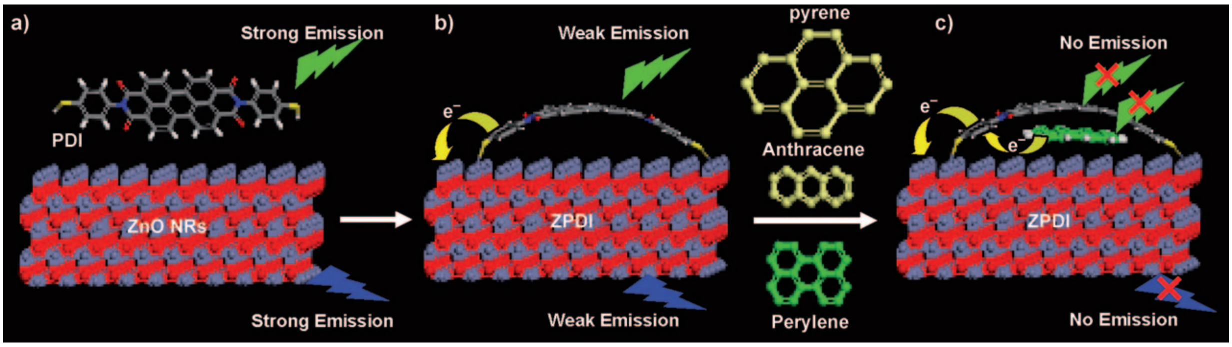

Figure 1. Illustration of the ZPDI sensor for perylene. a) model of PDI and ZnO NRs, O red, Zn gray, S yellow, N blue, H white; b) ZPDI; c) ZPDI with intercalated perylene.

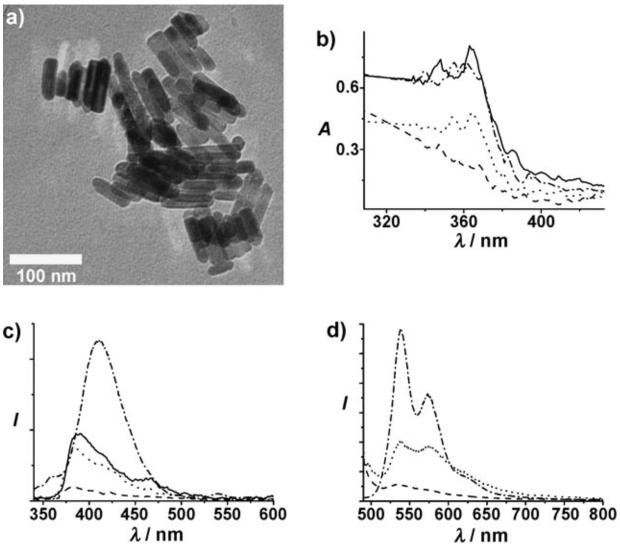

Figure 2. a) TEM image of ZnO NRs. b) The absorption spectra of PDI (–•–•), ZnO NRs (——), ZPDI (----), and ZPDI with perylene (–––) in DMF solution. The fluorescence spectra of PDI , ZnO NRs, ZPDI and ZPDI with perylene in DMF solution, c) $\lambda_{ex}=325$ nm, and d) $\lambda_{ex}=475$ nm.

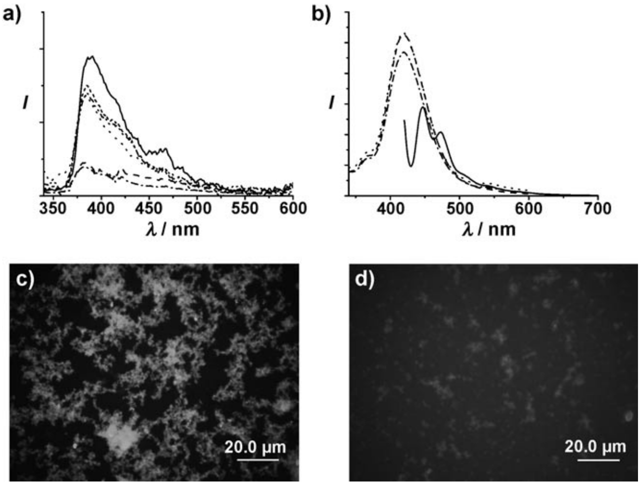

Figure 3. Emission spectra of a) ZnO NRs (——), ZPDI (•••••), and ZPDI with perylene (–•••–), anthracene (-----), pyrene (–•–•), and a PAH mixture (–––). $\lambda_{ex}=325$ nm; b) colloids of ZPDI with pyrene (–•–•, $\lambda_{ex}=325$ nm), anthracene (-----, $\lambda_{ex}=325$ nm), and PAH mixtures (–––, $\lambda_{ex}=325$ nm; ——, $\lambda_{ex}=412$ nm) in DMF solution after addition to 1 M aqueous hydrochloric acid. Confocal microscopy images of c) ZPDI and d) ZPDI with perylene (10^{-6} M; $\lambda_{ex}=470$ nm).

both the ZnO NRs and PDI are markedly reduced in the fluorescence spectra of ZPDI. When perylene was added to ZPDI, the emission signal at 384 nm was almost quenched. ZPDI therefore exhibits a selective turn-off fluorescence response to perylene molecules in solution. As shown in Figure 2d, at $\lambda_{ex}=475$ nm, PDI has a characteristic emission at 544 nm, whilst ZPDI has a weak emission at this wavelength. When perylene was added to ZPDI, the emission intensity of ZPDI at 544 nm was almost completely quenched. Results of competition experiments with ZPDI and polycyclic aromatic hydrocarbons (PAHs; perylene, pyrene, anthracene) for determination of the selectivity of ZPDI for perylene are shown in Figure 3a. The emission intensities of ZPDI are almost unchanged in the presence of pyrene or anthracene (both 10^{-4} M). However, in the presence of a PAH mixture (10^{-6} M perylene, 10^{-4} M anthracene, and 10^{-4} M pyrene), the emission intensity of ZPDI at 384 nm was reduced, thus indicating excellent selectivity for perylene over other PAHs. The ZPDI–PAHs colloid was centrifuged and added to an aqueous solution of 1 M hydrochloric acid, in order to decompose the ZnO NRs. The fluorescence spectra shown in Figure 3b display the characteristic emission of perylene and PDI; the emission signals of anthracene and pyrene are not observed, thus confirming the selectivity of ZPDI for perylene. The ability of ZPDI to monitor perylene levels in solution was demonstrated by using confocal microscopy. Nonmodified ZPDI shows green emission (Figure 3c). After intercalation of perylene, ZPDI shows a negligible fluorescence (Figure 3d). To determine the detection limit of ZPDI for perylene, titration experiments were carried out (Figure 4a). The addition of a 10^{-6} M perylene solution resulted in complete quenching of the ZPDI emission. When the perylene concentration was to 10^{-12} M, the emission of ZPDI was still clearly quenched, thus indicating that the detection limit of ZPDI for perylene is low as 10^{-12} M.

PAHs are one of the most widespread and dangerous groups of pollutants. Identification and quantification of PAHs is usually achieved by using techniques such as HPLC,

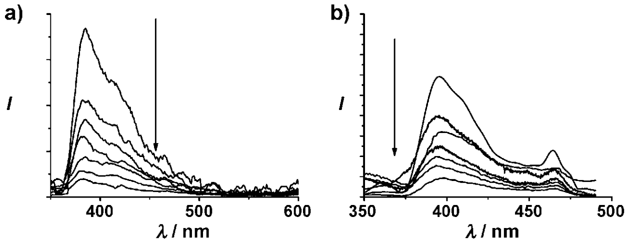

Figure 4. a) Fluorescence response of ZPDI to the addition of various concentration of perylene. b) Fluorescence response of ZPDIS after the addition of various concentrations of perylene. For (a) and (b), curves correspond to ZPDI or ZPDIS alone (highest intensity), and addition of 10^{-12}, 10^{-10}, 10^{-9}, 10^{-8}, 10^{-7}, 10^{-6}, 10^{-6} M perylene (lowest intensity), respectively. $\lambda_{ex} = 325$ nm.

amperometric detection, GC/MS, and GC/flame ionization detection (FID).[10] These methods are time-consuming and require a great deal of effort and expensive equipment. It is also possible to separate perylene from dilute solutions using ZPDI assembled on silicon substrates (ZPDIs). PDI molecules were assembled with arrays of ZnO NRs with a diameter of about 300 nm on silicon (100; Figure S2a in the Supporting Information) to form ZPDIS, which display an excellent selectivity for perylene. As shown in Figure 4b, the emission intensity of ZPDIS at 384 nm was significantly quenched when a sample of ZPDIS was immersed in solutions of perylene with various concentrations. The detection limit for perylene is also as low as 10^{-12} M. The characteristic emission signals of perylene and PDI (see Figure S2b in the Supporting Information) were observed after of ZPDIS samples mixed with 10^{-12} M perylene were decomposed with an aqueous solution of hydrochloric acid. These results suggest that ZPDIS not only detect but also separate perylene from solutions with very low concentrations. This technique is therefore be potentially useful for the study of PAH pollutants.

In conclusion, we have developed a new strategy for producing supramolecular interactions at the inorganic–organic interface of hybrid nanomaterials based on ZnO NRs and PDI. These nanomaterials contain a molecular pocket that can be used for selective detection of perylene in solutions. Detection is facilitated by the supramolecular interactions between the ZPDIs and perylene, which leads to modulation of emission signals of both the inorganic and organic components. The detection limit is as low as 10^{-12} M. Moreover, we have achieved the assembly of this molecular pocket on solid substrates for separating perylene from 10^{-12} M solution. This work demonstrates the utility of inorganic–organic hybrid nanomaterials in the detection of PAH pollutants. The same approach can be applied to other members of this family of materials in order to construct sensitive and selective sensors for other organic molecules.

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