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Sensory Materials for DMNB

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Abstract

Detection of DMNB by chemo sensors has been proved difficult because of their high lying LUMO level. Recently reported 4 different types of sensory materials for detection of DMNB were discussed. The focus of this review mainly lied on the sensitivity and feasibility for field use. Different strategies and approaches from different platforms for sensing DMNB is studied.

Keywords: MMOF, Zn Complex, Amplifying Fluorescent Polymers, Organic Nanofibril Film, DMNB

1. Introduction

The importance of sensing of high explosives such as trinitrotoluene (TNT) has grown tremendously over the last two decades, because of homeland security and environmental safety[1]. Detection of nitroaromatic is not the only concern, because they often do not contain nitroaromatics. Thus explosive manufacturers are currently required all the plastic to incorporate explosives taggant such as dimethyldinitrobutane (DMNB) for the purpose of detection of explosives by canins[2]. Detection with high sensitivity towards high explosives has been studied by many researchers[3-6]. However, detection of DMNB particularly difficult because although, it has a very high vapor pressure of about 2.07×10^{-3} Torr at 25°C, it also has a difficult to match reduction potential (-1.7 V vs. SCE)[7]. Current detection methods typically involve canines[8], or sophisticated analytical instruments[9]. The present explosives screening systems such as ion mobility spectrometry (IMS), mass spectrometry (MS), and gas chromatography (GC)[10] are rather limited to use, because they are time consuming and take a large space as well as costly. This calls for a small and easy to use device that can be massively deployed where needed. Fluorescence quenching of sensory materials based on the donor-acceptor electron-transfer mechanism might be a simple and promising alternative procedure. Few of fluorescent sensory materials for DMNB detection including microporous metal–organic frameworks (MMOFs)[2,11], (salophen) Zn complex[12], organic nanofibril film[13], and amplifying fluorescent polymers (AFPs)[7] that are capable of fast and reliable sensing of DMNB do stand out among other similar sensor platforms. In this review, we will discuss the sensory materials for detection of DMNB. Although, all the sensory materials was excellently demonstrated and studied, the focus will be on the sensing of DMNB.

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2. Chemo Sensor Platforms

2.1. Microporous Metal-organic Frameworks (MMOFs)

MMOFs are a new class of zeolite-like crystalline material that is one of the very promising chemo sensing platforms being studied[11], which have shown potentials for various of other applications, such as molecular storage and separation, catalysis, and sensing. An interesting property of luminescent in the solid state[14] and porous structure make it a very effective sensing platform. Like many other chemo sensing platforms, it utilizes its' luminescence property to detect dinitrotoluene (DNT) and DMNB by quenching of luminescence. Lan et al. showed for the first time, that the luminescent microporous metal–organic framework $[Zn_2(bpdc)_2(bpee)]$ (bpdc=4,4'-biphenyldicarboxylate; bpee=1,2-bipyridylethene) can be applied for quick and

reversible sensing of DNT and DMNB with high sensitivity. In the research [Zn2(bpdc)2-(bpee)]·2DMF were grown solvothermally to yield structure shown in Fig. 1. The overall structure can be viewed as bpee ligands pillaring the undulating charge-neutral [Zn2(bpdc)2] layers, which then was coated for testing DMNB vapor sensing. Upon exposure of DMNB vapor, the luminescence quenched as well as red-shifted. The red-shift can also be observed in other analytes, indicating host-guest chemical interaction. In order to recover the luminescence after a successful sensing, it needed to be heated at 150°C for about a minute. In Fig. 2, the thin layer showed a instant quenching where the thick layer showed a gradual quenching of fluorescence of guest-free structure. The structure that occupied by guest, did not show a linear quenching behavior and the intensity stayed the same after 240 seconds. Above 80% quenching within seconds is very impressive sensitivity compare to other sensor platforms.

The author indicated that the main contribution to the high sensitivity came from the high dimensional and porous structure.

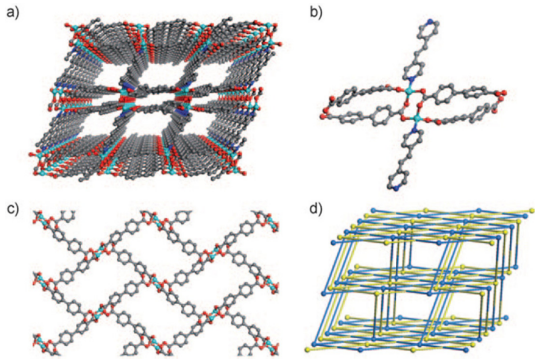


Fig. 1. Perspective view of [Zn2(bpdc)2-(bpee)]·2DMF[11].

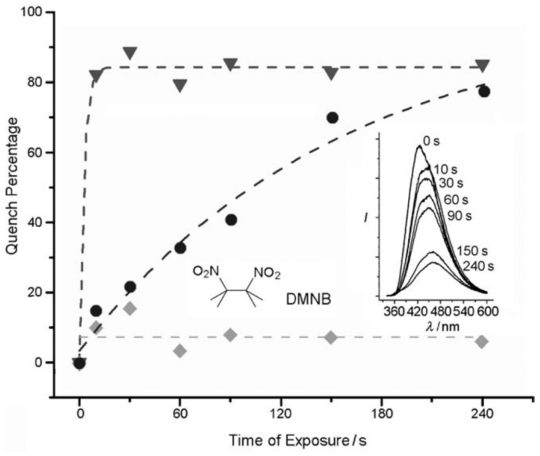


Fig. 2. Time-dependent fluorescence quenching by DMNB for thin (triangle), thick (circle) layers of guest-free structure, and thin layers (square) of guest inhabited structure. Inset: the fluorescence spectra for a thick layer of guest-free structure at the specified exposure times[11].

2.2. Zn complex: (salophen)Zn

Germain *et al.*[12] reported that (salophen)Zn also is an effective sensory material for detection of DMNB and nitroaromatics by using its luminescence property. The molecular structure of ZnL(EtOH)·EtOH is shown in Fig. 3. The solvent played an important role in fluorescence spectra and absolute photoluminescence quantum yield (PLQY). THF as a solvent showed the highest PLQY of 0.59 and PL peaks at λ_{max}=531 nm. The proposed quenching reaction was $ZnL^* + RNO_2 \rightarrow ZnL^+ + RNO_2^-$, in which the nitro compound accepts an electron from the excited state of ZnL. The author

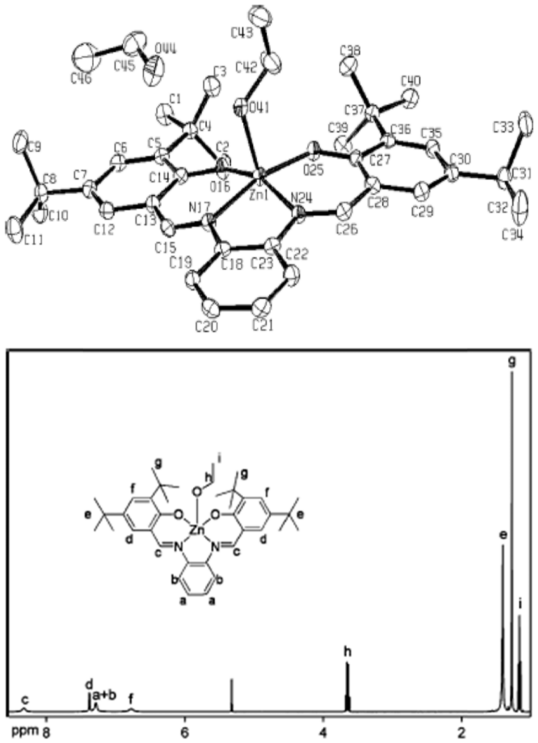


Fig. 3. ORTEP (top) and H NMR in CD_2Cl of ZnL (EtOH)·EtOH (bottom)[12].

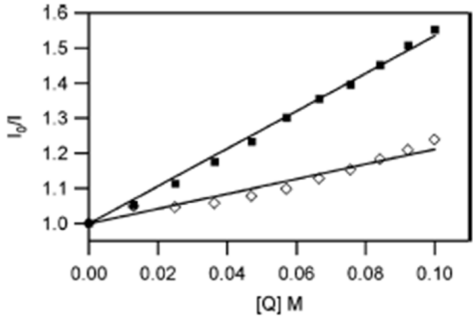


Fig. 4. Flouranscence quenching of ZnL by NT (■) and DMNB (◇)[12].

carried out test of nitro-toluene (NT) and DMNB. They both acted as quencher for ZnL in solution.

Fig. 4 shows Stern-Volmer plot, which indicates that it has higher efficiency against NT than DMNB. Because this test was carried out in solution, it can not be directly compare to the test with MMOF

2.3. Organic Nanofibril Film

Naddo *et al.*[13] reported on a fluorescence organic nanofibril film for sensing DMNB with very high efficiency. Scheme 1 shows the fabrication process by facilitating an alkoxycarbonyl-substituted carbazole-cornered conjugate tetracycle molecule (ACTC) and DMNB detection mechanism. Self-assembly characteristic of the nanofibril film makes it easy to fabricate by drop-casting a solution of ACTC a glass and solvent evaporates leaving nanofibril structures. Its fluorescence property matches well with the DMNB LUMO energy level, which makes easy for the electrons in exited state to transfer to the analyte. Fig. 5 shows huge quenching of

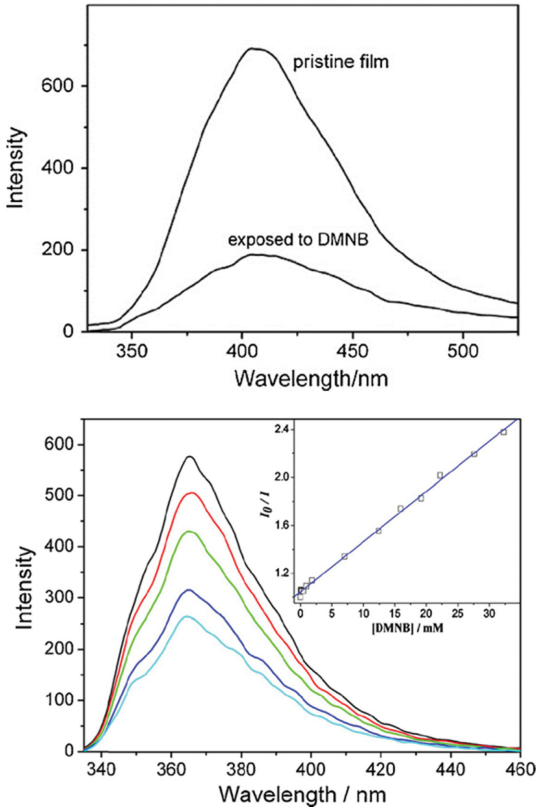
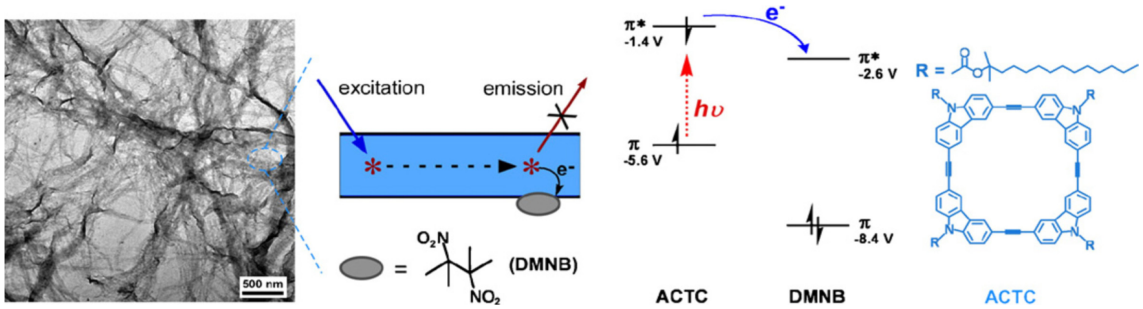


Fig. 5. Fluorescence spectra of ACTC nanofibril film before and after exposure to the DMNB vapor for 2 min (top) and ACTC in THF solution with additions of DMNB: 0.0, 1.9, 7.0, 19.0 and 28.0 mM (bottom). Stern–Volmer plot of the fluorescence quenching (inset)[13].

PL upon exposure to the DMNB vapor. The quenching test in THF solution shows linear relationship with the quencher, confirmed by Stern-Volmer plot. The repeated



Scheme 1. A TEM image (left) of the nanofibril structure and a schematic diagram showing fluorescence quenching of the nanofiber by DMNB, migration of exciton through fider; (right) energy levels of HOMO and LUMO orbitals of ACTC and DMNB showing electron transfer from the excited state of ACTC to DMNB[13].

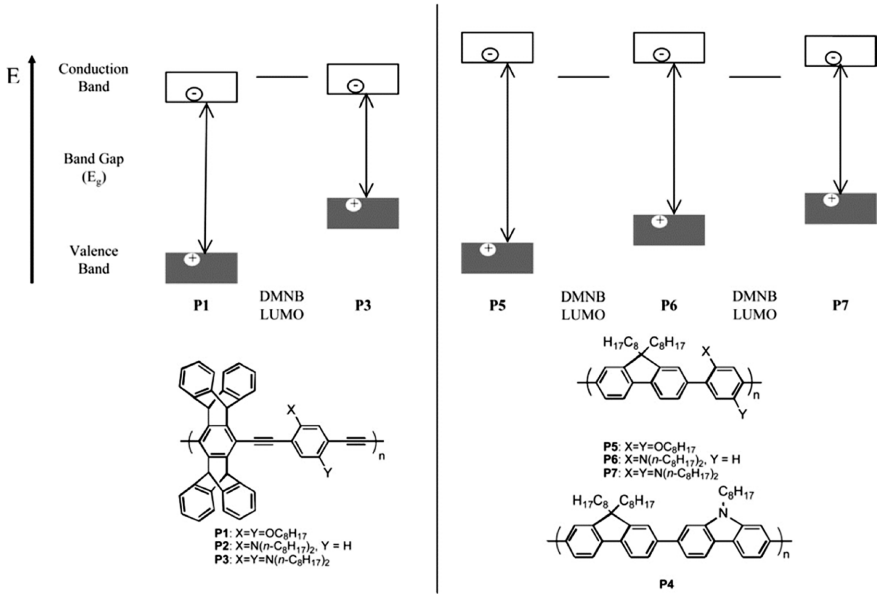


Fig. 6. In search for the best matching LUMO energy level with that of DMNB, 5 different polymer has been fabricated[7].

vapor sensing test showed that it is capable of full recovery indicating the material is very suitable for the real-life application outside the lab environment.

The author pointed out that fast response (73% of quenching in approximately 20 seconds) to the analyte was contributed by the enhanced adsorption and diffusion of DMNB.

2.4. Amplifying Fluorescent Polymers (AFPs)

Thomas III *et al*.[7] reported DMNB vapor sensory polymer, which proved difficult previously because of the high lying LUMO energy level of DMNB. Swager group has been studying detection explosives for a long period time and has set a standard for explosive trace sensors. By utilizing those already fully developed platform, demonstrated feasibility for real-life applications.

Fig. 6 depicted five different polymers with different LUMO energy levels. P5 showed the highest LUMO levels thus, picked for the DMNB vapor-sensing test.

The sensory material responded quickly to the analyte with high sensitivity. As shown in Fig. 7, the fluorescence recovered almost fully when the DMNB vapor cuts-off and again quenched when exposed to the vapor. In order to accommodate smooth electron transaction between the sensory and the anaytes, matching HOMO and LUMO energy levels between them. P5, which has the biggest energy band gap, achieved the highest quenching efficiency.

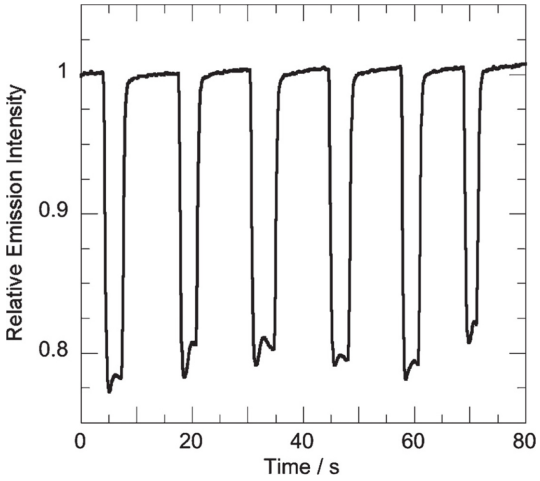


Fig. 7. On-off DMNB vapor sensing experiment, PL intensity was recorded while DMNB vapor exposure was turned on and off[7].

3. Conclusions

In this review, four different types of sensory materials for detection of DMNB were discussed. Because

of the importance of detecting DMNB concerning homeland security, many researches have been progressed. Out of many chemo sensory materials, MMOFs, (salophen) Zn complex, organic nanofibril film, and amplifying fluorescent polymers (AFPs) demonstrated the feasibilities to be real-life applications, because of their high sensitivities and fast responding time.

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