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A Naphthalimide-based fluorescent sensor for halogenated solvents

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We reported a fluorescent sensor for halogenated solvents termed AMN. AMN shows strong fluorescence in most halogenated solvents (QE > 0.1) but weak (QE < 0.01) in most non-halogenated solvents. In chlorinated solvents, fluorescence intensity decreased with the reduction of chlorine contents. On the contrary in brominated solvents, fluorescence intensity increased with the reduction of bromine contents. It is worth mentioning that AMN displayed fluorescnece emission certered at 520 nm in CCl_4 with a quantum yield of 0.607, at 556 nm in $CHCl_3$ with a quantum yield of 0.318, at 584 nm in CH_2Cl_2 with a quantum yield of 0.128, while in $CHBr_3$ certered at 441 nm with a quantum yield of 0.012. Then AMN has the ability to differentiate CCl_4, $CHCl_3$, CH_2Cl_2 and $CHBr_3$ from halogenated solvents.

Various organic solvents have been widely used in industrial manufacturing and scientific researches. For the majority of organic reactions, the choosing of organic solvents is critical and directly related to reaction efficiency. As a result of mass use of organic solvents, the causing environmental problem is obtaining an increasing attention.[1] Accordingly, detection and discrimination of different types of organic solvents remain an area of intense interest. Despite some traditional methods and technologies, such as gas chromatographic, high-performance liquid chromatography, ion chromatography and mass spectrometry *etc.*,[2-4] have been used to determine organic solvents, these methods usually suffer from the disadvantages of expensive apparatuses, time-consuming and complicated pretreatment. Moreover, the greatest challenge derives from the selectivity and specificity owing to the similar molecular structures of many organic solvents. Therefore, developing an efficient approach suitable for the detection and discrimination of organic solvents is still challenging.

Owing to its simplicity, high sensitivity and selectivity, chemosensor technology based on colour and/or fluorescence changes has become an effective tool to be applied in the detection of molecules.[5, 6] For most of fluorescent dyes, their absorption and fluorescence emission are solvent-dependent and directly related to the polarity of solvents, so they can be used as the solvatochromic materials.[7-9] Accordingly, there have been considerable efforts to develop fluorescent or colorimetric sensors for organic solvents[10-13] and water content.[14-16] Recently, Rotello and co-workers developed a triazine-based fluorescent dye, which could selectively detect hydrogen-bond donating solvents due to the formation of intermolecular hydrogen bonds.[10] Li *et al* constructed a luminescent MOF material which can qualitatively sense various polar and nonpolar VOC solvents (including single and mixed species).[11] For the majority of solvatochromic dyes, they inevitably display broad overlaps in their absorption and emission bands in different solvents. Therefore, it is extremely difficult to differentiate solvents of similar polarity by means of colormetric and/or fluorescent changes. A recent breakthrough was reported by Kim and co-workers on the basis of a new strategy of solvatochromic materials destruction or disruption by a specific solvent.[12] Their sensor can differentiate chloroform and dichloromethane colorimetrically. Recently, a bromothymol blue fluorescent dye reported by Warner and co-workers revealed a capability of discriminating MeOH and BuOH.[13]

The halogenated solvents are volatile organic chemicals consisting of a hydrocarbon chain or one hydrocarbon substituted with one or more chlorine or bromine atoms. Most of these chemicals are used as degreasers and solvents in various products such as paints. These halogenated solvents can be released into the air from contaminated waste water, from facilities that produce or use them, or from hazardous waste sites. It is necessary to separate solvent wastes into halogenated and non-halogenated waste because it costs more to dispose of halogenated materials and because halogenated wastes are sometimes incompatible with other wastes. Inhalation or ingestion of halogenated solvents can cause

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cardiac dysrhythmias, central nervous system depression and unconsciousness, and renal and hepatic injury.[17] Halogenated solvents are also human carcinogens.[18] Experimental animals exposed chronically to halogenated solvents developed tumors of the liver, lung, and kidney.

In view of the hazards of halogenated solvents, some promising chemosensors have been reported.[12, 19, 20] Unfortunately, there is still no efficient sensors that can distinguish the halogenated solvents from halogen-free solvents. In this work, we report a naphthalimide-based fluorescent sensor containing an alkynyl aniline moiety. This sensor can successfully discriminate the halogenated solvents with enhanced fluorescence emission from non-halogenated solvents with quenched fluorescence emission. It was worth mentioning that carbon tetrachloride could promote the dramatical enhancement of fluorescence with a fluorescent quantum yield of 0.607.

The synthetic route of fluorescent sensor **AMN** was outlined in Scheme 1. The compound **2** was prepared using commercially available 4-bromo-1,8-naphthalic anhydride **1** as the starting material according to the reported procedure.[21] Subsequently, a Pd-catalyzed Sonogashira coupling reaction based on 4-ethynylaniline and intermediate **2** was employed to prepare the targeting molecule **AMN** in 92% yield, which was well-characteriazed by NMR and elemental analysis.
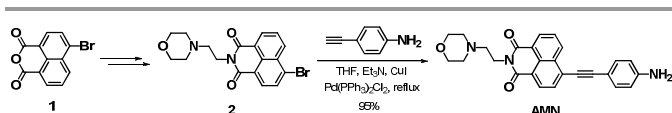
Scheme 1 The Synthesis Route of **AMN**.

Studies were first carried out to explore the UV-Vis absorption and fluorescence spectra of sensor **AMN** (1×10^{-5} M) in different non-halogenated organic solvents. Analysis of UV-Vis absorption spectra showed that **AMN** had a broad absorption band from 360 nm to 530 nm (Figure S1A in Supporting Information) with larger molar-extinction coefficients (Table 1). And the maximum absorption peaks were related to the dielectric constants of the medium and the molar extinction coefficient lay between 10000 and 17000 $M^{-1}cm^{-1}$. These results suggested that the system involved in an intramolecular charge transfer (ICT) from the amino group to the naphthalimide moiety. Additionally, the maximum absorption displayed red-shift of 10-24 nm in solvents with bigger dielectric constants in comparison to the solvents with lower dielectric constants.

Investigation on the solvent-dependent fluorescence emission displayed that **AMN** fluoresced only in solvents with lower dielectric constant such as toluene with the highest fluorescent quantum yield of 0.189 upon the excitation of 420 nm (Table 1 and Figure S1B in Supporting Information). In comparison to the emission in toluene, **AMN** displayed very weak fluorescence in other non-halogenated organic solvents (Table 1). And in these polar solvents, emission wavelength red-shifted to around 600 nm with a large stokes shift over 150 nm. The **AMN** molecules in excited state interacted with polar solvents and changes the distribution of electronic dipole

Table 1. Photophysical properties of **AMN** in various non-halogenated solvents.

Solvent	Dielectric Constant	λ_{ex} (nm)	λ_{em} (nm)	ε ($M^{-1}cm^{-1}$)	Φ
Toluene	2.24	422	544	14280	0.189
Ether	4.2	429	576	13640	0.0454
Dioxane	2.2	425	568	12960	0.0072
EA	6.02	428	600	16690	0.0065
THF	7.58	435	606	16590	0.0048
EtOH	25.7	438	/	13120	< 0.001
Acetone	20.7	431	/	12840	< 0.001
CH₃CN	37.5	423	/	14820	< 0.001
DMF	36.71	446	/	15240	< 0.001
MeOH	31.2	432	/	13610	< 0.001
Ethylene glycol	38.66	440	/	12600	< 0.001
DMSO	48.9	446	/	13700	< 0.001
Water	80.10	418	/	11240	< 0.001

orientation, which might adversely affect the ground state and excited states of the fluorescent molecule and reduce the energy of the excited state, causing the red shift of emission spectra and decrease of the quantum yields. Along with the increasing of solvents polarity, the quantum yields were less than 0.001 in solvents with dielectric constants over 20 as shown in Table 1. This should ascribe to that solvents with larger polarity would significantly increase the rate of nonradiative transition of the excited state molecule, and then reduce the fluorescent quantum yield.

Subsequent studies on UV-Vis absorption and fluorescence spectra in halogenated solvents were performed under the same conditions. According to the UV-Vis absorption spectra presented in Figure 1a, **AMN** showed a broad absorption band from 370 nm to 520 nm except for in CHBr₃. Observation from the UV-Vis absorption suggested that **AMN** had a maximum absorption at 383 nm in CHBr₃ while the maximum absorption in other halogenated solvents occurred at 420-430 nm with similar molar-extinction coefficients (Table 2). The obvious blue shift of maximum absorption implied that **AMN** can serve as an indicator to distinguish CHBr₃ from other halogenated solvents even by naked eyes (Figure 1b).

Further efforts were paid to investigate the fluorescence properties of **AMN** (1×10^{-5} M) in halogenated solvents. As shown in Figure 1c-d and Table 2, **AMN** was fluorescent in most halogenated solvents with quantum yields over 0.1. This means that **AMN** can sense halogenated solvents from non-halogenated solvents with a turn-on fluorescence. Notably, **AMN** presented a strong fluorescence emission in CCl₄ centered at 520 nm with a highest quantum yield of 0.607. And in chlorinated solvents as shown in Figure 1c and Table 2, fluorescence intensity decreased and emission wavelength red-shifted gradually with the reduction of chlorine contents. For example, as solvents of similar polarity with CCl₄, in CHCl₃ and CH₂Cl₂ solvents, **AMN** displayed emission at 556 nm with a quantum yield of 0.318 and at 584 nm with a quantum yield of
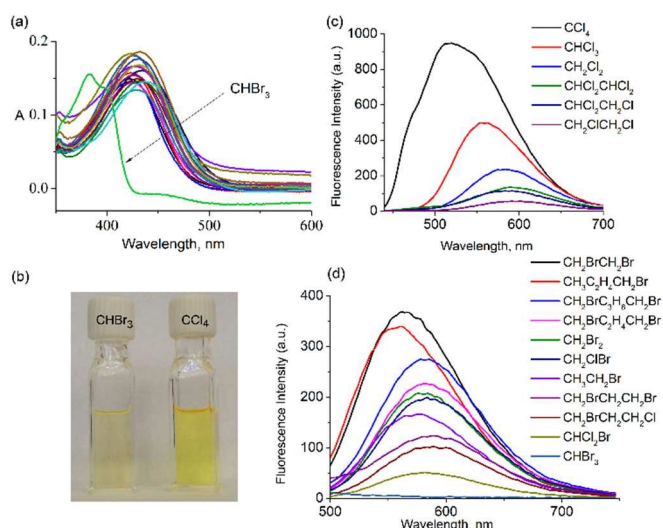
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Fig. 1 The UV-Vis absorption spectra and Fluorescence emission spectra of **AMN** (1×10^{-5} M) in various halogenated solvents. (a) UV-Vis absorption spectra; (b) Color changes of **AMN** in CHBr$_3$ and other halogenated solvents (represented by CCl$_4$); (c) Fluorescence emission spectra in chlorinated solvents (excited at 420 nm); (d) Fluorescence emission spectra in brominated solvents (excited at 420 nm; for CHBr$_3$ at 380 nm).

Table 2. Photophysical properties of **AMN** in various halogenated solvents.

Solvent	Dielectric Constant	λ_{ex} (nm)	λ_{em} (nm)	ε (M^{-1}cm^{-1})	Φ
CCl$_4$	2.238	423	520	13810	0.607
CHCl$_3$	4.9	422	556	14660	0.318
CH$_2$Cl$_2$	9.1	422	584	13470	0.128
CHCl$_2$CHCl$_2$	8.00	433	588	12960	0.092
CHCl$_2$CH$_2$Cl	7.12	433	590	13940	0.071
CH$_2$ClCH$_2$Cl	10.45	424	602	14360	0.031
CH$_2$BrCH$_2$Br	4.76	432	562	13240	0.232
C$_4$H$_9$Br	/	426	560	14760	0.169
CH$_2$BrC$_3$H$_6$CH$_2$Br	/	432	578	14600	0.158
CH$_2$BrC$_2$H$_4$CH$_2$Br	/	430	582	13610	0.139
CH$_2$Br$_2$	7.04	431	584	13080	0.134
CH$_2$ClBr	7.14	425	584	14120	0.114
CHCl$_2$Br	/	427	582	15400	0.123
CH$_2$BrCH$_2$CH$_2$Br	4.30	440	588	12470	0.100
CH$_3$CH$_2$Br	9.39	425	574	14120	0.0
CH$_2$BrCH$_2$CH$_2$Cl	/	430	590	14240	0.059
CHBr$_3$	4.5	383	441	13740	0.012

0.128, respectively. For the chlorinated ethanes such as CH$_2$ClCH$_2$Cl, CHCl$_2$CH$_2$Cl and CHCl$_2$CHCl$_2$, **AMN** showed further red-shifts in emissions and weaker fluorescence intensity in comparison to chlorinated methanes. To our best knowledge, **AMN** may be the first sensor than can differentiate CCl$_4$, CHCl$_3$ and CH$_2$Cl$_2$.

Interestingly, in brominated solvents **AMN** displayed an opposite profile that fluorescence intensity increased with the reduction of bromine contents (Figure 1d and Table 2). It is worth mentioning that **AMN** displayed a typical fluorescnece emission certered at 441 nm with a quantum yield of 0.012 in CHBr$_3$. In other brominated solvents, **AMN** showed the emission bands around 560-580 nm with similar quantum yields. Then **AMN** can also recognize CHBr$_3$. The relative weak fluorescence in brominated solvents compared to in chlorinated solvents may be ascribed to the fluorescence quenching feature of heavy atom effects from bromine. Compared with the fluorescence of **AMN** in CHBr$_3$, we found that the influence of heavy atom effects of bromine was associated with the emission behaviors. **AMN** in CH$_2$BrCH$_2$Br had a stronger emission at 562 nm with a higher fluorescence quantum yield of 0.232 compared with in CH$_2$ClCH$_2$Cl, possibly due to the larger differences of solvents polarity.

Meanwhile, we checked the fluorescence emission in solvents having two different halogen atoms such as CH$_2$ClBr and CHCl$_2$Br. As seen in Table 2, **AMN** in CH$_2$ClBr exhibited almost same fluorescence properties with that in CH$_2$Cl$_2$ and CH$_2$Br$_2$. However, the fluorescence of **AMN** in CHCl$_2$Br is weaker than that in CHCl$_3$. To investigate further properties of **AMN**, CHBr$_3$ and CCl$_4$ were selected to study the fluorescence behavior of **AMN** in their mixture solution. In the UV-Vis absorption spectra (Figure 2a), the maximum absorption band of **AMN** (1×10^{-5} M) at 423 nm decreased gradually and an increasing absorption band at 383 nm was observed upon the

addition of CHBr$_3$. As observed in Figure 1b, the solution color of **AMN** in CHBr$_3$ and CCl$_4$ was found to be light yellow and bright yellow, respectively. As a result of the influence from CHBr$_3$, the strong fluorescence of **AMN** at 520 nm in CCl$_4$ decreased quickly along with the addition of CHBr$_3$ (Figure 2b). When the excess CCl$_4$ was added to the solution of **AMN** in CHBr$_3$, no obvious changes were observed except for the decreasing absorption band at 370 - 420 nm (Figure 2c). Accordingly, the fluorescence spectra of **AMN** in CHBr$_3$ solution exhibited a slight enhancement when excess CCl$_4$ was added (Figure 2d). These studies further confirmed that the heavy atom effects of bromine had a significant impact on the emission of **AMN**.
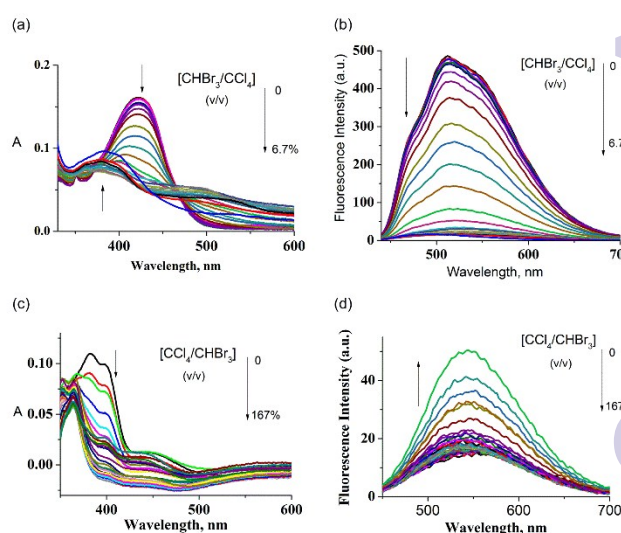

Fig. 2 (a) The UV-Vis absorption spectra and (b) fluorescence spectra of **AMN** in CCl$_4$ with the addition of CHBr$_3$; (c) The UV-Vis absorption spectra and (d) fluorescence spectra of **AMN** in CHBr$_3$ with the addition of CCl$_4$.

To evaluate feasibility of this sensor for advanced sensing applications, we created a paper sensor for in situ on-site detection. A piece of filter paper was immerged in the methanol solution of **AMN** for 5 mins, and then blown dry with a stream of nitrogen. As shown in Fig 3a, under the irradiation (365 nm) of a UV lamp, papers emit very weak fluorescence. Upon exposure to CCl_4 and $CHCl_3$ solution, a strong green and yellow fluorescence on the paper were observed, respectively (Fig 3b). The stimulation of CH_2Cl_2 made the paper show a relative weak yellow fluorescence. As expected, upon exposure to $CHBr_3$ solution, the test paper showed a very weak fluorescence. These results indicate that our sensor AMN can be prepared to test papers for these halogenated solvents.
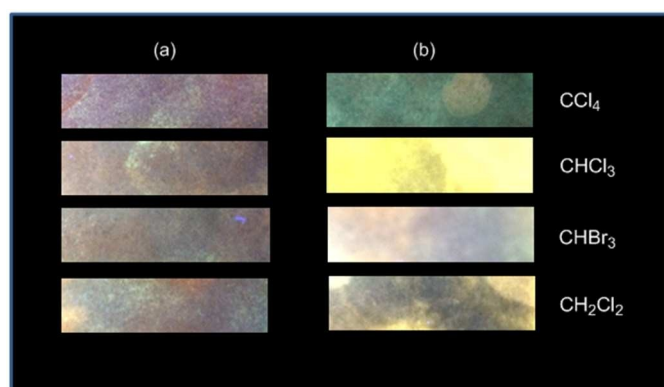

Fig. 3 Test papers with AMN (a) before and (b) after exposure to different halogenated solvent detection. All images were taken under a UV lamp (365-nm irradiation).

In summary, we have developed a naphthalimide-based fluorescent sensor **AMN**, which displayed halogenated solvent-dependent fluorescence behaviors. **AMN** can efficiently distinguish halogenated solvents from non-halogenated solvents with a turn-on fluorescence signal. In most halogenated solvents, **AMN** displayed strong fluorescence (QE > 0.1); while in most non-halogenated solvents, **AMN** showed weak fluorescence (QE < 0.01). In chlorinated solvents, fluorescence intensity of **AMN** decreased with the reduction of chlorine contents. On the contrary in brominated solvents, fluorescence intensity of **AMN** increased with the reduction of bromine contents. It is worth mentioning that **AMN** displayed fluorescnece emission certered at 520 nm in CCl_4 with a quantum yield of 0.607, at 556 nm in $CHCl_3$ with a quantum yield of 0.318, at 584 nm in CH_2Cl_2 with a quantum yield of 0.128, while in $CHBr_3$ certered at 441 nm with a quantum yield of 0.012. To our best knowledge, **AMN** may be the first sensor to have the ability to differentiate CCl_4, $CHCl_3$, CH_2Cl_2 and $CHBr_3$ from halogenated solvents. It's required to point out that the present sensor cannot distinguish halogenated solvent from mixtures. But the significance of this work is to demonstrate the possibility of using fluorescence method to identify halogenated solvents. Taking the compound AMN as the starting point, we hope that a compound with practical value will be developed in the future with the aid of an assay instrument.

Notes and references

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