



Cite this: *Chem. Commun.*, 2016,
52, 2095

Received 13th November 2015,
Accepted 7th December 2015

DOI: 10.1039/c5cc09403h

www.rsc.org/chemcomm

A naphthalimide-based fluorescent sensor for halogenated solvents†

Li Dai,^{ab} Di Wu,^c Qinglong Qiao,^a Wenting Yin,^a Jun Yin^{*c} and Zhaochao Xu^{*a}

A fluorescent sensor for halogenated solvents termed AMN is reported. AMN shows strong fluorescence in most halogenated solvents ($QE > 0.1$) but weak fluorescence ($QE < 0.01$) in most non-halogenated solvents. In chlorinated solvents, the fluorescence intensity decreased with the reduction of chlorine content. On the contrary, in brominated solvents the fluorescence intensity increased with the reduction of bromine content. It is worth mentioning that AMN displayed fluorescence emission centered 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, whereas in $CHBr_3$ was centered at 441 nm with a quantum yield of 0.012. AMN was shown to have the ability to differentiate CCl_4 , $CHCl_3$, CH_2Cl_2 and $CHBr_3$ halogenated solvents.

Various organic solvents have been widely used in industrial manufacturing and scientific research. For the majority of organic reactions, the choice of organic solvents is critical and directly related to reaction efficiency. The mass use of organic solvents is causing environmental problem that is obtaining increasing attention.¹ Accordingly, detection and discrimination of different types of organic solvents remains an area of intense interest. Despite some traditional methods and technologies, such as gas chromatography, high-performance liquid chromatography, ion chromatography and mass spectrometry,^{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 detecting and discriminating organic solvents is still a challenge.

Due to its simplicity, high sensitivity and selectivity, chemosensor technology based on colour and/or fluorescence changes has become an effective tool applied for detecting molecules.^{5,6} For most of fluorescent dyes, their absorption and fluorescence emission are solvent-dependent and directly related to solvent polarity; therefore, they can be used as 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 intermolecular hydrogen bond formation.¹⁰ Li *et al.* constructed a luminescent MOF material, which can qualitatively sense various polar and non-polar VOC solvents (including single and mixed species).¹¹ The majority of solvatochromic dyes 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 colorimetric and/or fluorescent changes. A recent breakthrough was reported by Kim and co-workers on the basis of a new strategy for 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

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

^a Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
E-mail: zcxu@dicp.ac.cn

^b University of Chinese Academy of Sciences, Beijing 100039, China

^c Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China.
E-mail: yinj@mail.ccnu.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cc09403h

cause 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 are still no efficient sensors that can distinguish the halogenated solvents from halogen-free solvents. In this study, 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 a dramatic enhancement of fluorescence with a fluorescent quantum yield of 0.607.

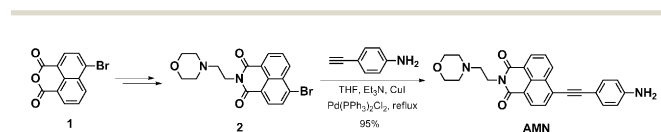
The synthetic route for fluorescent sensor **AMN** is outlined in Scheme 1. The compound **2** was prepared using commercially available 4-bromo-1,8-naphthalic anhydride **1** as the starting material according to the reported procedure.²¹ Subsequently, a Pd-catalyzed Sonogashira coupling reaction based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

Studies were first carried out to explore the UV-Vis absorption and fluorescence spectra of the **AMN** sensor (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 (Fig. S1A in ESI†) with larger molar-extinction coefficients (Table 1). The maximum absorption peaks were related to the dielectric constants of the medium and the molar extinction coefficient lay between 10 000 and 17 000 $\text{M}^{-1} \text{cm}^{-1}$. These results suggest that the system involved in an intramolecular charge transfer (ICT) from the amino

group to the naphthalimide moiety. In addition, the maximum absorption displayed a 10–24 nm red-shift in solvents with bigger dielectric constants compared to the solvents with lower dielectric constants.

Investigation of the solvent-dependent fluorescence emission displayed **AMN** fluorescence only in solvents with lower dielectric constant such as toluene with the highest fluorescent quantum yield of 0.189 upon excitation at 420 nm (Table 1 and Fig. S1B in ESI†). In comparison to the emission in toluene, **AMN** displayed very weak fluorescence in other non-halogenated organic solvents (Table 1). In these polar solvents, the emission wavelength red-shifted to around 600 nm with a large Stokes shift over 150 nm. The excited state **AMN** molecules interacted with polar solvents and changed the distribution of the electronic dipole orientation, which may adversely affect the ground state and excited states of the fluorescent molecule and reduce the energy of the excited state, causing a red shift of the emission spectra and decrease of the quantum yields. Along with increasing the solvents polarity, the quantum yields were less than 0.001 in solvents with dielectric constants over 20, as shown in Table 1. Solvents with larger polarity would significantly increase the rate of nonradiative transition of the excited state molecule, and then reduce the fluorescence quantum yield.

Subsequent studies of UV-Vis absorption and fluorescence spectra in halogenated solvents were performed under the same conditions. According to the UV-Vis absorption spectra presented in Fig. 1a, **AMN** showed a broad absorption band from 370 nm to 520 nm except for in CHBr_3 . Observation from the UV-Vis absorption spectrum suggests that **AMN** had a maximum absorption at 383 nm in CHBr_3 , whereas the maximum absorption in other halogenated solvents occurred at 420–430 nm with similar molar-extinction coefficients (Table 2). The clear blue shift of maximum absorption implies that **AMN** can serve as an



Scheme 1 The synthesis route for **AMN**.

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

Solvent	Dielectric Constant	λ_{ex} (nm)	λ_{em} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	ϕ
Toluene	2.24	422	544	14 280	0.189
Ether	4.2	429	576	13 640	0.0454
Dioxane	2.2	425	568	12 960	0.0072
EA	6.02	428	600	16 690	0.0065
THF	7.58	435	606	16 590	0.0048
EtOH	25.7	438	—	13 120	<0.001
Acetone	20.7	431	—	12 840	<0.001
CH_3CN	37.5	423	—	14 820	<0.001
DMF	36.71	446	—	15 240	<0.001
MeOH	31.2	432	—	13 610	<0.001
Ethylene glycol	38.66	440	—	12 600	<0.001
DMSO	48.9	446	—	13 700	<0.001
Water	80.10	418	—	11 240	<0.001

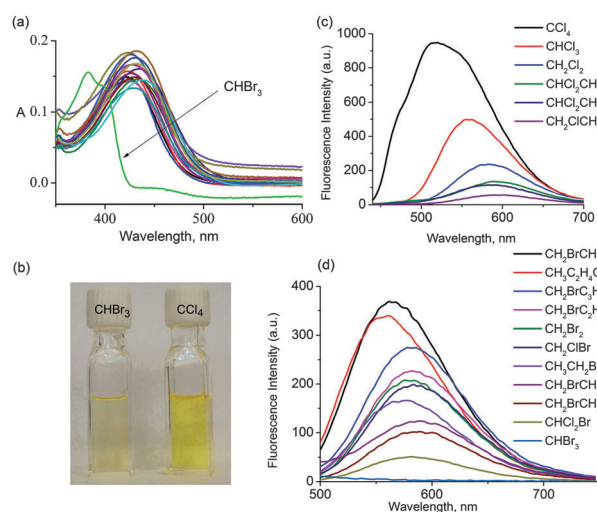


Fig. 1 The UV-Vis absorption spectra and fluorescence emission spectra of **AMN** (1×10^{-5} M) in various halogenated solvents. (a) UV-Vis absorption spectra; (b) color changes of **AMN** in CHBr_3 and other halogenated solvents (represented by CCl_4); (c) fluorescence emission spectra in chlorinated 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 ($\text{M}^{-1} \text{cm}^{-1}$)	ϕ
CCl_4	2.238	423	520	13 810	0.607
CHCl_3	4.9	422	556	14 660	0.318
CH_2Cl_2	9.1	422	584	13 470	0.128
$\text{CHCl}_2\text{CHCl}_2$	8.00	433	588	12 960	0.092
$\text{CHCl}_2\text{CH}_2\text{Cl}$	7.12	433	590	13 940	0.071
$\text{CH}_2\text{ClCH}_2\text{Cl}$	10.45	424	602	14 360	0.031
$\text{CH}_2\text{BrCH}_2\text{Br}$	4.76	432	562	13 240	0.232
$\text{C}_4\text{H}_9\text{Br}$	—	426	560	14 760	0.169
$\text{CH}_2\text{BrC}_3\text{H}_6\text{CH}_2\text{Br}$	—	432	578	14 600	0.158
$\text{CH}_2\text{BrC}_2\text{H}_4\text{CH}_2\text{Br}$	—	430	582	13 610	0.139
CH_2Br_2	7.04	431	584	13 080	0.134
CH_2ClBr	7.14	425	584	14 120	0.114
CHCl_2Br	—	427	582	15 400	0.123
$\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$	4.30	440	588	12 470	0.100
$\text{CH}_3\text{CH}_2\text{Br}$	9.39	425	574	14 120	0.087
$\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Cl}$	—	430	590	14 240	0.059
CHBr_3	4.5	383	441	13 740	0.012

indicator to distinguish CHBr_3 from other halogenated solvents even by the naked eye (Fig. 1b).

Further efforts were paid to investigate the fluorescence properties of **AMN** ($1 \times 10^{-5} \text{ M}$) in halogenated solvents. As shown in Fig. 1c and 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. It can be noted that **AMN** presented a strong fluorescence emission in CCl_4 centered at 520 nm with a highest quantum yield of 0.607. In chlorinated solvents, as shown in Fig. 1c and Table 2, the fluorescence intensity decreased and the emission wavelength red-shifted gradually with the reduction of chlorine content. For example, as solvents of similar polarity with CCl_4 , in CHCl_3 and CH_2Cl_2 solvents, **AMN** displayed emission at 556 nm with a quantum yield of 0.318 and at 584 nm with a quantum yield of 0.128, respectively. For the chlorinated ethanes, such as $\text{CH}_2\text{ClCH}_2\text{Cl}$, $\text{CHCl}_2\text{CH}_2\text{Cl}$ and $\text{CHCl}_2\text{CHCl}_2$, **AMN** showed further red-shifts in the emissions with weaker fluorescence intensity in comparison to chlorinated methanes. To the best of our knowledge, **AMN** may be the first sensor that can differentiate CCl_4 , CHCl_3 and CH_2Cl_2 .

Interestingly, in brominated solvents **AMN** displayed an opposite profile that fluorescence intensity increased with reduced bromine content (Fig. 1d and Table 2). It is worth mentioning that **AMN** displayed a typical fluorescence emission centered at 441 nm with a quantum yield of 0.012 in CHBr_3 . In other brominated solvents, **AMN** showed emission bands around 560–580 nm with similar quantum yields. Then **AMN** can also recognize CHBr_3 . The relatively weak fluorescence in brominated solvents compared to chlorinated solvents may be ascribed to the fluorescence quenching feature of the heavy atom effect from bromine. Compared with the fluorescence of **AMN** in CHBr_3 , it was found that the influence of heavy atom effects of bromine was associated with the emission behaviors. **AMN** in $\text{CH}_2\text{BrCH}_2\text{Br}$ had a stronger emission at 562 nm with a higher fluorescence quantum yield of 0.232 compared with in $\text{CH}_2\text{ClCH}_2\text{Cl}$, possibly due to the larger differences in solvents polarity.

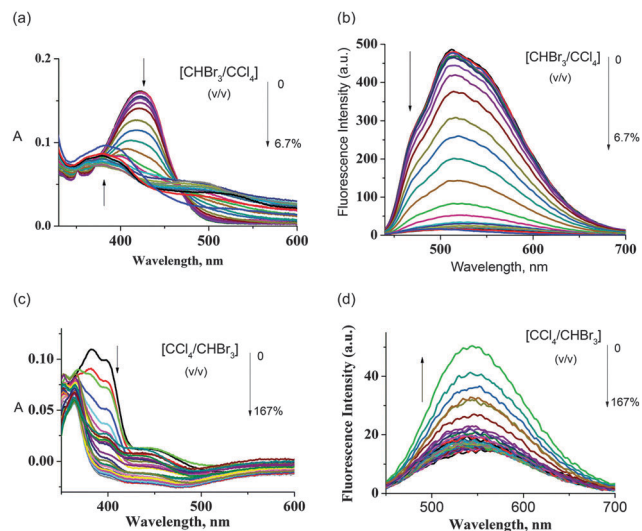


Fig. 2 (a) The UV-Vis absorption spectra and (b) fluorescence spectra of **AMN** in CCl_4 with the addition of CHBr_3 ; (c) The UV-Vis absorption spectra and (d) fluorescence spectra of **AMN** in CHBr_3 with the addition of CCl_4 .

Moreover, the fluorescence emission in solvents having two different halogen atoms, such as CH_2ClBr and CHCl_2Br , was checked. As observed in Table 2, **AMN** in CH_2ClBr exhibited almost the same fluorescence properties with that in CH_2Cl_2 and CH_2Br_2 . However, the fluorescence of **AMN** in CHCl_2Br is weaker than that in CHCl_3 . CHBr_3 and CCl_4 were selected to study the fluorescence behavior of **AMN** in their mixture solutions. In the UV-Vis absorption spectra (Fig. 2a), the maximum absorption band of **AMN** ($1 \times 10^{-5} \text{ M}$) at 423 nm decreased gradually and an increasing absorption band at 383 nm was observed upon the adding CHBr_3 . As observed in Fig. 1b, the solution colour 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 (Fig. 2b). When the excess CCl_4 was added to the solution of **AMN** in CHBr_3 , no clear changes were observed except for the decreasing absorption band at 370–420 nm (Fig. 2c). Accordingly, the fluorescence spectra of **AMN** in CHBr_3 solution exhibited a slight enhancement when excess CCl_4 was added (Fig. 2d). These studies further confirm that the heavy atom effect of bromine had a significant impact on the **AMN** emission.

To evaluate feasibility of this sensor for advanced sensing applications, a paper sensor was created for *in situ* on-site detection. A piece of filter paper was immersed in a methanol solution of **AMN** for 5 mins, and then blown dry with a stream of nitrogen. As shown in Fig. 3a, under 365 nm UV lamp irradiation, the papers emit very weak fluorescence. Upon exposure to CCl_4 and CHCl_3 solutions, 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 the **AMN** sensor can be prepared to test papers for these halogenated solvents.

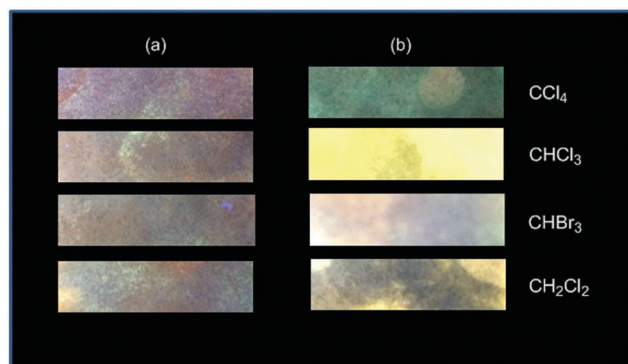


Fig. 3 Test papers with AMN (a) before and (b) after exposure to different halogenated solvents. All images were taken under a UV lamp (365 nm irradiation).

In summary, a naphthalimide-based fluorescent sensor **AMN** was developed, which displayed halogenated solvent-dependent fluorescence behavior. **AMN** can efficiently distinguish halogenated solvents from non-halogenated solvents with a turn-on fluorescence signal. In most halogenated solvents, **AMN** displayed strong fluorescence ($QE > 0.1$), whereas in most non-halogenated solvents, **AMN** showed weak fluorescence ($QE < 0.01$). In chlorinated solvents, the fluorescence intensity of **AMN** decreased with the reduction of chlorine content. On the contrary, in brominated solvents, the fluorescence intensity of **AMN** increased with the reduction of bromine content. It is worth mentioning that **AMN** displayed fluorescence emission centered 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, whereas in $CHBr_3$ was centered at 441 nm with a quantum yield of 0.012. To the best of our 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. The present sensor cannot distinguish halogenated solvent from mixtures. However, the significance of this study is to demonstrate the possibility of using a fluorescence method to identify halogenated solvents. Taking

the compound **AMN** as the starting point, the hope is that a compound with practical value will be developed in the future with the aid of an assay instrument.

We thank financial support from the National Natural Science Foundation of China (21276251, 21402191), the 100 talents program funded by Chinese Academy of Sciences, the Dalian Cultivation Fund for Distinguished Young Scholars and the National Science Fund for Excellent Young Scholars (21422606).

Notes and references

- 1 C. Jiménez-González and D. J. C. Constable, *Green Chemistry and Engineering: A Practical Design Approach*, John Wiley & Sons, Inc., 2011.
- 2 W. Buchberger and U. Huebauer, *Microchim. Acta*, 1989, **99**, 137–142.
- 3 M. I. Cervera, J. Beltran, F. J. Lopez and F. Hernandez, *Anal. Chim. Acta*, 2011, **704**, 87–97.
- 4 M. E. Miller and C. J. Cappon, *Clin. Chem.*, 1984, **30**, 781–783.
- 5 Z. Xu, J. Yoon and D. R. Spring, *Chem. Soc. Rev.*, 2010, **39**, 1996–2006.
- 6 X. Zhou, S. Lee, Z. Xu and J. Yoon, *Chem. Rev.*, 2015, **115**, 7944–8000.
- 7 V. S. Pavlovich, *ChemPhysChem*, 2012, **13**, 4081–4093.
- 8 S. Pandey, S. Baker, S. Pandey and G. Baker, *J. Fluoresc.*, 2012, **22**, 1313–1343.
- 9 Y. Marcus, *J. Phys. Org. Chem.*, 2005, **18**, 373–384.
- 10 R. F. Landis, M. Yazdani, B. Creran, X. Yu, V. Nandwana, G. Cooke and V. M. Rotello, *Chem. Commun.*, 2014, **50**, 4579–4581.
- 11 J.-H. Wang, M. Li and D. Li, *Chem. Sci.*, 2013, **4**, 1793–1801.
- 12 J. Lee, H. T. Chang, H. An, S. Ahn, J. Shim and J.-M. Kim, *Nat. Commun.*, 2013, **4**, 2461.
- 13 W. I. S. Galpothdeniya, B. P. Regmi, K. S. McCarter, S. L. de Rooy, N. Siraj and I. M. Warner, *Anal. Chem.*, 2015, **87**, 4464–4471.
- 14 C.-G. Niu, P.-Z. Qin, G.-M. Zeng, X.-Q. Gui and A.-L. Guan, *Anal. Bioanal. Chem.*, 2007, **387**, 1067–1074.
- 15 C. Niu, L. Li, P. Qin, G. Zeng and Y. Zhang, *Anal. Sci.*, 2010, **26**, 671–674.
- 16 Z. Li, Q. Yang, R. Chang, G. Ma, M. Chen and W. Zhang, *Dyes Pigm.*, 2011, **88**, 307–314.
- 17 C. Barragán-Martínez, C. A. Speck-Hernández, G. Montoya-Ortiz, R. D. Mantilla, J.-M. Anaya and A. Rojas-Villarraga, *PLoS One*, 2012, **7**, e51506.
- 18 N. Guha, D. Loomis, Y. Grosse, B. Lauby-Secretan, F. E. Ghissassi, V. Bouvard, L. Benbrahim-Tallaa, R. Baan, H. Mattock and K. Straif, *Lancet Oncol.*, 2012, **13**, 1192–1193.
- 19 A. Mujahid, H. Stathopoulos, P. A. Lieberzeit and F. L. Dickert, *Sensors*, 2010, **10**, 4887.
- 20 J.-M. Han, M. Xu, B. Wang, N. Wu, X. Yang, H. Yang, B. J. Salter and L. Zang, *J. Am. Chem. Soc.*, 2014, **136**, 5090–5096.
- 21 T. Liu, Z. Xu, D. R. Spring and J. Cui, *Org. Lett.*, 2013, **15**, 2310–2313.