RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

Fluorescent chemodosimeter based on spirobenzopyran for organophosphorus nerve agent mimics (DCP)

Shyamaprosad Goswami,* Sangita Das and Krishnendu Aich

Cite this: DOI: 10.1039/x0xx00000x

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new chromogenic as well as fluorogenic protocol based on spirobenzopyran system for the selective detection of nerve agent mimics (diethylcholorophosphate or DCP vapour) within few seconds (~30 Sec) is designed, synthesized and characterized in this paper. The nucleophilic attack from the oxygen atom of the spiro ring to the electrophilic phosphonyl group of DCP (diethylcholorophosphate), creates the opening of the spiro (SP) frame work and ultimately gives rise to the meta stable merocyanine (MC) form to give a fluorescent species which gives signal in the red region (~ 675 nm). The 'turn-on' red fluorescence and a colorimetric change from colourless to yellow was observed upon addition of DCP which evokes almost 124 and 84 folds enhancement in absorbance and emission intensity respectively, compare to the probe itself. To the best of our knowledge such type of DCP sensor based on spirobenzopyran network has not been reported to date. Moreover the detection limit of this probe was found to be in 10^{-8} M level in the solution phase. We also developed it as a portable chemosensor kit for DCP and demonstrate its practical application in real-time monitoring.

Introduction

In concern of international view point, the present increase of criminal terrorist attacks via chemical warfare (CW) agents has caused growing interest in the exposure of dangerous chemicals. Among all these CW species, nerve agents are enormously hazardous due to their extremely high poisonous effects and their simplicity of fabrication emphasizes the need to recognizing these lethal chemicals through rapid and consistent procedures.

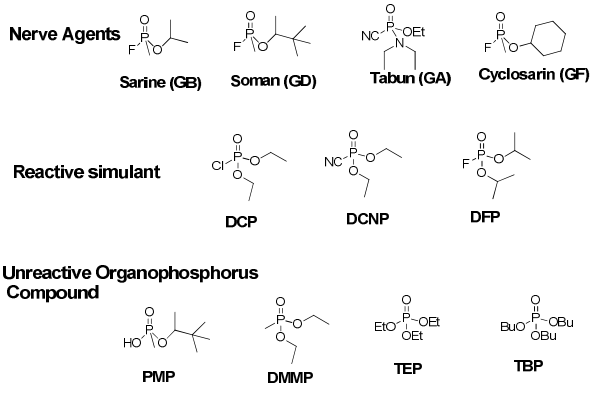


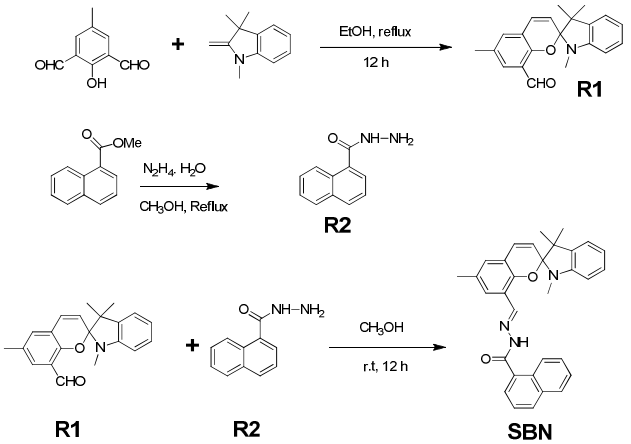
Figure 1: Structure of chemical warfare nerve agents and simulants

The high simplicity in production with dangerous poisonous effects of these organophosphorus (OP)-containing nerve agents including Sarin, Soman, Tabun and Cyclosarin are inhibitors of serine proteases, especially acetylcholinesterase underscores the need to detect these odorless and colorless chemicals. These highly toxic compounds bind with the hydroxyl groups and can inhibit acetylcholinesterase (AChE), a critical central-nervous enzyme[1–4] and making it non-functional. Many detection methods for nerve agents have been developed based on potentiometry,[5] surface acoustic wave spectroscopy,[6] gas chromatography/mass spectrometry[7] and interferometry.[8] However, these methods suffer from limitations, such as slow response, lack of specificity, limited selectivity, low sensitivity, operational complexity, non-portability, difficulties in real-time monitoring, or false positive readings.[9] Therefore, simple and efficient detection methods for nerve agents remain of high interest.[10] On the other hand spirobenzopyran moieties are widely used as molecular optical switches as well as memories.[11, 12] They have been classified as a group of photochromes, because under UV irradiation they converted into merocyanine form and revert back to its original spiro-network under day-light.[13] These spirobenzopyran rings contain a variety of advantages to be used as promising fluorescent sensor. As for examples, fast response, good quantum yield, naked eye detection etc. The main importance of such kind of platform is to avail the reversibility of

(merocyanine) MC and spiro platform, which ultimately change the color of the solution as well as turn-on the fluorescence. These technologies enabling spirobenzopyran as a photo-switchable bright fluorescent sensor and taking advantage of all the above in recent years a number of sensors have been reported but all of them are mostly based on sensing of metal ions. [14] However, despite of these elegant studies there have a significant space to improve. These spiro rings can be used as a recognizing negotiator of some toxic nerve agents giving signal at the red region and to make it successful which is still a challenging task and has in great demand. Therefore, it is necessary to develop a fluorescence probe that can be used for the detection of nerve agent mimics, preferably with 'turn on' emission locating in the red region. Herein an ICT based strategy has been implemented with a combination of spirobenzopyran and napthalene system to detect toxic chemical agent (DCP) even presence with nontoxic compounds. The sensing of organophophorous compound (OP) in spirobenzopyran moiety has not been reported to date. We envisioned here that the oxygen atom of the spiro ring could be readily used as a good nucleophile and can go a nucleophilic attack with OP nerve agents. The handle can react with electrophilic OP nerve agents within few seconds (within 30 Sec). This actually opens up the spiro frame work and giving rise to a signal at the red region (~675 nm). Furthermore, the probe exhibits noticeable color change under UV and even observable by naked eyes. Finally, it can detect both liquid and gas nerve agents (DCP) simultaneously.

Results and discussion

The synthetic route of SBN is shown in scheme 1. Compound R1 was prepared from the given literature procedure.[15] Compound R1 and R2 were treated together in dry methanol to afford the desired probe (SBN). The structure of SBN was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy (ESI, Fig. S6-S10).



Scheme 1: Synthesis of the probe (SBN)

Photo-physical studies

At first the reactivity of SBN was tested with organophosphorus compound diethyl chlorophosphate (DCP) and it respond promptly. The objective of the preparation of such kind of ICT induced benzopyran-napthalene based probe is to get a beautiful spectrum both in emission and in absorbance, which was due to the change in the photophysical properties upon interaction with DCP. This organophosphate has been widely used as simulants because they mimic almost same reactivity to that of well known nerve agents (such as Tabun, Sarin and Soman), but belonging much less toxicity. Now the chemodosimetric approach of SBN towards DCP was observed in liquid and vapour state. The charge-transfer was due to the presence of an electron donor oxygen atom which attacks the electron acceptor phosphonyl group. The opening of spiro ring changes the color of the solution from colorless to yellow, which is noticeable through naked eye. It was observed that our probe SBN exhibited high selectivity towards only DCP among other tested analytes (including ^{t}BuOOH, CH_3COCl, H_2O_2, NaOCl and some interfering metals such as Na^{+}, K^{+}, Ca^{2+}, Cr^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and nerve agent mimic like DCNP) both colorimetrically as well as fluorometrically.

UV-vis study

Now to better understand the change in absorbance, a solution of SBN (1×10^{-5} M, 25^{0}C in CH_3CN/H_2O, 1/1) and different analytes (1×10^{-4} M, 25^{0}C) were prepared in CH_3CN and added separately to the prepared solution of SBN. Only DCP was found to perturb the spectral behavior of SBN, which showed an enhancement of absorption.

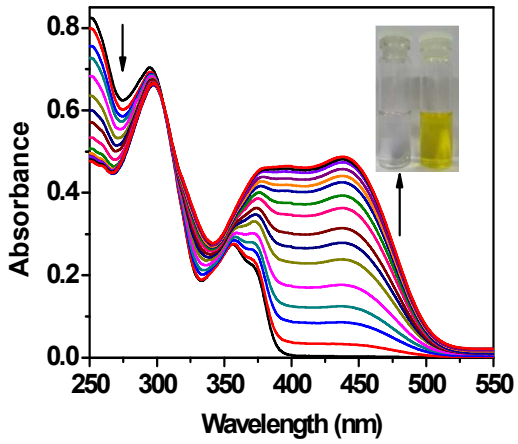
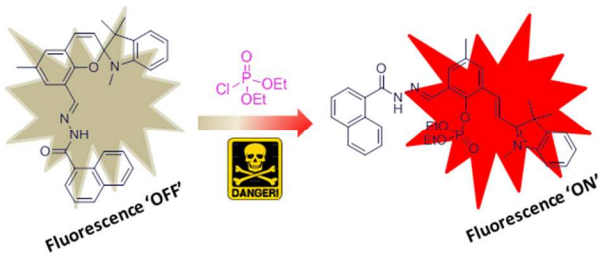


Figure 2: Change of absorption spectra of SBN (10 μM) upon gradual addition of DCP (0 to 3 equivalents). Inset: A photograph of SBN (10 μM), showing a visible color in absence and presence of 2 equivalents of DCP.

In contrast no analytes of interest did show any kind of significant effect on the absorption profile of SBN (ESI, Fig. S2). SBN, itself showed two λ_{max} at 295 nm and 355 nm and no peak at 440 nm which indicates that the probe exists

predominantly in its spiro form and it is stable in the CH_3CN-H_2O solution. Upon addition of DCP, SBN showed a huge change in its spectroscopic behavior, a new peak generated at 440 nm and it gradually increases with increasing concentration of DCP as shown in figure 2. Upon incremental addition of DCP the absorbance intensity of SBN at 440 nm increased almost 124 times, consequently the color of the solution changes from colorless to yellow. This observation indicates the opening of the spiro network and formation of merocyanine (MC) system. During the addition of DCP the absorbance intensity exhibits a linear curve of fitness relationship with DCP concentration (0 to 1.12×10^{-5} M) with a good R^2 value of 0.9964 (ESI, Fig. S4).



Scheme 2: Probable sensing scheme of SBN to DCP

To access the identity of the reaction product generated in-situ in the reaction assay, was confirmed through ^{1}H NMR titration experiment, where the free –OH gives a peak nearly at δ 13 ppm (ESI, Fig. S10-11). This observation indicates that the SBN-DCP complex may hydrolyze in assay condition to give the hydrolysis product. The formation of hydrolised product was further confirmed through HRMS, where the peak at 488.2339 strongly indicates the formation of hydrolised product (Fig. S13-14, ESI). The chemodosimetric approach was depicted in scheme 3.

Competition study

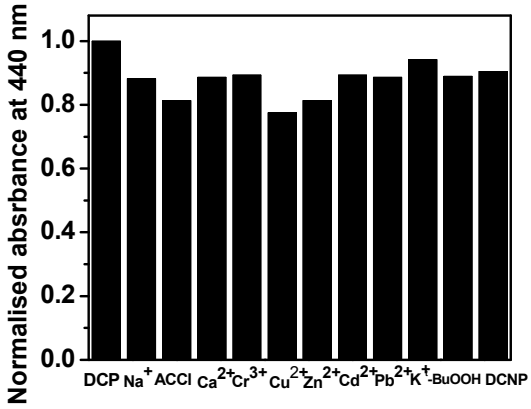


Figure 3. A comparative study of emission intensity after addition of different analytes (5 equivalents) in the solution of SBN in presence of DCP (2 equivalents)

The selectivity and the interference are the two very important parameters to evaluate the performance of a receptor. To utilize SBN (1×10^{-5} M, 25^0C in CH_3CN/H_2O, 1/1) as a selective sensor for the DCP, a competing experiment was also performed by adding DCP (2.0 equiv) in the presence of 5.0 equivalents of different analytes. The studies revealed that DCP can be detected in the presence of almost all of the interfering analytes (Fig. 3).

Emission study

A clear readout was obtained when the sensing experiment was studied by fluorescence titration experiment in acetonitrile-H_2O solution. The fluorescence spectrum of SBN in aqueous acetonitrile was recorded upon excitation at 460 nm. SBN (1×10^{-5} M, 25^0C in CH_3CN/H_2O, 1/1) itself showed a weak emission peak at 675 nm. As expected, after addition DCP (0 – 1.2×10^{-5} M) their leads an enormous change in the emission profile. A large enhancement of the emission intensity at 675 nm was noticed which is actually accompanied with the opening of the spiro network and formation of merocyanine form (Fig. 4). This observation indicates that after addition of DCP, the necleophilic attack assists from oxygen atom towards the phosphonyl group of DCP concomitantly open the spiro ring (Scheme 3). This mechanism may play behind the opening of spirobenzopyran ring of SBN to the formation of meta-stable merocyanine form, which was accompanied with the intramolecular charge transfer (ICT).

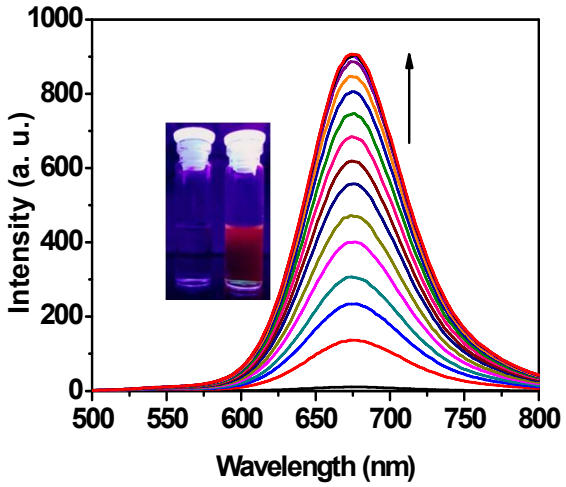
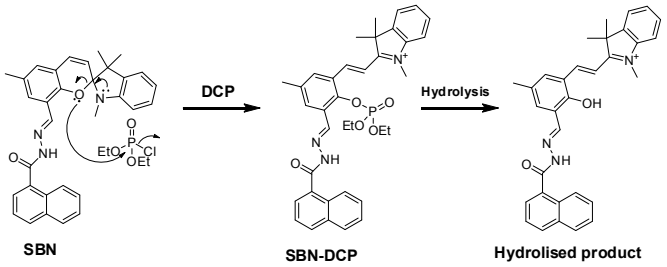


Figure 4: Change of emission spectra of SBN (10 μM) upon gradual addition of DCP .Inset: A photograph of SBN (6 μM), showing a visible color in absence and presence of 2 equivalents of DCP.

The fluorogenic response of SBN was also studied by using above mentioned guest analytes. Almost all the guest analyte are mute towards SBN. Only DCP was found to perturb the fluorescence profile remarkably. Addition of other examined analytes even in excess amount leads no significant change in the emission spectrum of the receptor. This experiment indicates this probe is exclusive detects DCP.

The detection limit of SBN for DCP was determined from the emission spectral data, using the equation DL = K × Sb_1/S, where K = 3, Sb_1 is the standard deviation of the blank solution and S is the slope of the calibration curve. [16] From the graph the

detection limit was found to be 2.1 × 10^{-8} M, indicating that SBN has a very good efficiency to detect DCP (ESI, Fig. S3). The fluorescence quantum yield of the probe was calculated. The quantum yields of SBN and hydrolyzed SBN-DCP were found to be 0.015 and 0.36 respectively, using rhodamine-B as reference (Φ = 0.66 in ethanol).



Scheme 3: Chemodosimetric approach Of SBN towards DCP

Reaction kinetics study

In case of chemodosimetric reactions, reaction kinetics study is very important factor. In this case also we have calculated the rate constant of the reaction. The fluorescence spectra of SBN after addition of 2 equivalents of DCP was recorded, which is depicted below. It was observed that after 30 seconds the increment was almost reached to its highest peak. Though the total experiment was recorded up to 2 minutes, but the intensity (675 nm) vs time plot shows a platue at almost 30 sec. It indicated that SBN is a promising receptor for DCP, which not only detects it but also response towards it very promptly.

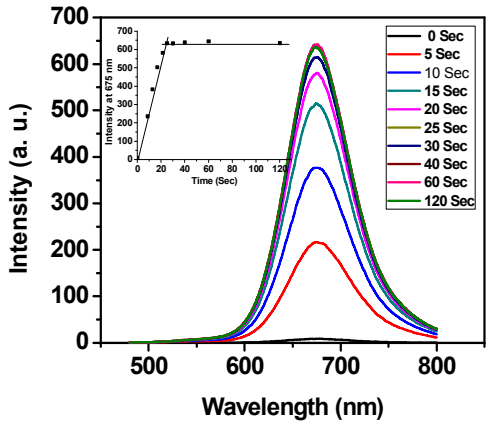


Figure 5: Change of emission spectra of SBN (10 μM) after addition of DCP (2 equivalents) with time interval.

The pseudo first order rate constant was calculated from the changes of emission curve of SBN (10 μM) at different time interval by addition of DCP (20 μM). From the time vs. emission plot (ESI, Fig. S1) at fixed wavelength 675 nm by using first order rate equation we get the rate constant = k = slope×2.303 = 0.55×10^{-2} Sec^{-1}.

pH studies

In order to investigate the sensitivity of the probe towards change in pH, pH titration experiment is extremely important. It has been observed that acid–base titration experiment with the probe does not undergo any significant fluorescence enhancement within the pH range from 6–14, now this experiment suggests that the sensor predominantly exists in the spirobenzopyran form in this pH range. In strong acidic conditions (pH < 4) the probe exhibits different nature; with decreasing pH protonation causes the opening of the spiro form and conversion merocyanine form which can be observed via naked eye as well as strong red fluorescence was observed. Now from the above experiment it can be concluded that SBN can be employed for the detection of DCP in near-neutral pH range (pH = 7.2).

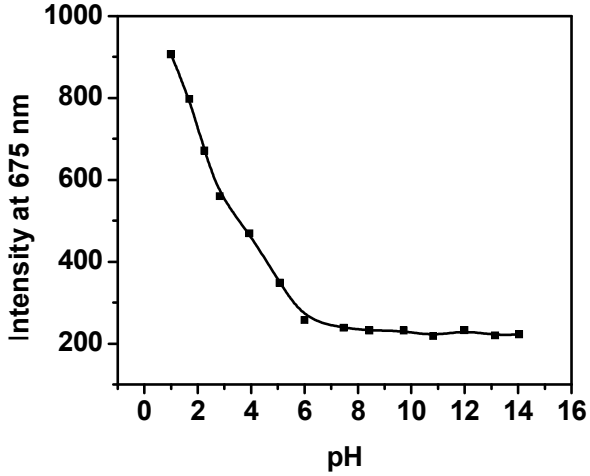


Figure 6: Fluorescence response of SBN at 675 nm (10μM, λex = 460 nm) as a function of pH in CH_3CN/ H_2O (1: 1, *v/v*), pH is adjusted by using aqueous solutions of 1 M HCl or 1 M NaOH.

Test kit

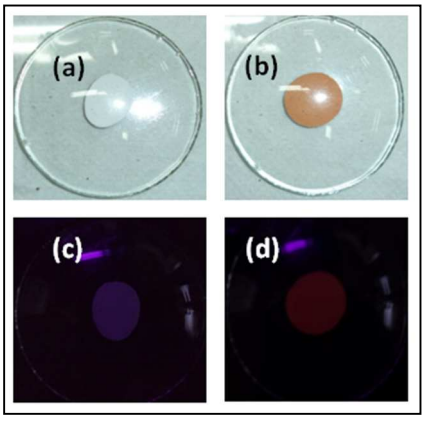


Figure 7: Photographs of TLC plates after immersion in a SBN-acetonitrile solution (a & c) and after exposed to DCP vapour for 2 minutes (b & d) taken in ambient light (left) and under hand-held UV light (right).

Motivated by the favourable in situ and rapid sensing response of SBN towards DCP, we took a step forward towards the potential application by using it as a portable kit for sensing DCP. In order to perform this application in an innovative purpose, it is preferential to detect the toxic DCP in the gas phase. It is a very simple but very important experiment because it gives instant qualitative information without resorting to the instrumental analysis. In order to perform this experiment, we prepared TLC plates which were immersed into the solution of SBN (50 μM) in acetonitrile, and then evaporated the solvent to dryness. Here the probe SBN exhibits a visible as well as fluorometric color change in presence of DCP in its gaseous form, it can be achieved by bubbling a larger volume of contaminated air into the dried TLC plate. This color change was depicted in the following Fig. 7. From this experiment it can be concluded that the probe offers a good nerve agent assay kit.

Conclusions

In summery we have reported the first fluorescence sensing of DCP (nerve agent mimic) based on spirobenzopyran-napyhalene system. The probe is highly selective, rapid and sensitive chemodosimeter for DCP. It can detect DCP within 30 seconds. In our approach, we take advantage of the nucleophilic attack from the oxygen atom to the electrophilic phosphonyl group that leads to open the spiro benzopyran ring thereby displays yellow color. Other guest anlytes such as metal catoins, peroxides etc. do not interfere in the DCP detection. The detection limit was found to be 10^{-8} M level, which indicates our probe SBN is a highly efficient sensor of DCP in acetonitrile. To demonstrate the possibility of its practical applications, dip-stick method was developed, which can detect DCP in a closed vessel in its gaseous phase.

Experimental

General

Unless otherwise mentioned, materials were obtained from commercial suppliers and were used without further purification. Thin layer chromatography (TLC) was carried out using Merck 60 F_{254} plates with a thickness of 0.25 mm. Melting points were determined on a hot-plate melting point apparatus in an open mouth capillary and are uncorrected. ^{1}H and ^{13}C NMR spectra of SBN were recorded on JEOL 400 MHz and 125 MHz instruments respectively. For NMR spectra, $CDCl_3$ was used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H and ^{1}H–C coupling constants in Hz. Fluorescence spectra were recorded on a Perkin Elmer LS 55 spectrophotometer and UV-vis titration experiments were performed on a JASCO V-630 spectrophotometer.

General method of UV-vis and fluorescence titration

UV-vis method

For UV-vis titration we used the solution of the host in the order of 1×10^{-5} M. The solution was prepared in CH_3CN/H_2O (1/1, v/v). The solution of the guest analytes in the order of 1×10^{-4} M were prepared in acetonitrile. Now different concentrations of host and increasing concentration of analytes were prepared separately. Now the spectra of these solutions were recorded by means of UV-vis method.

Fluorescence method

Now for the fluorescence titration the solution of the receptor was prepared (1×10^{-5} M) in CH_3CN/H_2O (1/1, v/v). The solutions of the guest analytes in the order of 1×10^{-4} M, were prepared in CH_3CN. Here also various concentrations of guest and increasing concentration of host were prepared and the spectra were recorded by means of fluorescence method.

Synthesis of the probe (SBN):

A mixture of R1 (0.5 g, 1.56 mmol) and R2 (0.45 g, 1.57 mmol) were dissolved in 20 ml of dry ethanol. The resulting solution was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure to get the crude product which was purified through silica gel (100-200, mesh size) column chromatography using 10 - 15% ethyl acetate in petroleum ether as eluent. The final product (SBN) was obtained as off-white solid. The solid obtained was dissolved in minimum volume of dichloromethane solution and re-precipitated using pentane. Filtered the precipitate and dried under vacuum, which afford a better purified white colored compound (yield = 62%).

M_p = 276^{0}C- 278^{0}C

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (s, 3H), 1.24 (s, 3H), 2.26 (s, 3H), 2.68 (s, 3H), 5.66 (d, *J* = 8 Hz, 1H), 6.34 (d, *J* = 8 Hz, 1H), 6.67 (t, *J* = 6 Hz, 1H), 6.80 (d, *J* = 8 Hz, 1H), 6.93 (t, *J* = 8 Hz, 2H), 7.01 (t, *J* = 8 Hz, 1H), 7.40 (t, *J* = 6 Hz, 1H), 7.48 (m, 2H), 7.62 (d, *J* = 8 Hz, 1H), 7.83 (m, 3H), 8.08 (s, 1H), 8.31 (t, *J* = 8 Hz, 1H), 9.25 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 20.4, 20.6, 26.2, 28.9, 52.0, 104.9, 106.7, 118.9, 119.1, 119.2, 121.7, 124.6, 125.7, 126.6, 127.2, 127.4, 127.6, 128.3, 129.4, 129.8, 130.0, 130.6, 131.3, 132.2, 133.8, 136.8, 142.5, 148.1, 151.2, 165.5.

HRMS (ESI, positive): calcd. for $C_{32}H_{29}N_3O_2Na$ $[M+Na]^+$ (m/z): 510.2157; found: 510.1941.

Acknowledgements

Authors thank CSIR and DST, Govt. of India for financial supports. S. D. and K. A. acknowledge CSIR for providing them fellowship.

Notes and references

[a] Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, India.

E-mail: spgoswamical@yahoo.com

† Electronic Supplementary Information (ESI) available: [NMR, HRMS of the probe and reaction product]. See DOI: 10.1039/b000000x/

1 I. Willner, V. Pavlov and Y. Xiao, *Nano Lett*., 2005, **5**, 649.
2 R. H. de Jong, *Anesth. Analg*., 2003, **96**, 819.
3 F. R. Sidell and J. Borak, *Ann. Emerg. Med*., 1992, **21**, 865.

4 S. Royo, R. Martinez-Manez, F. Sancenon, A. M. Costero, M. Parra and S. Gil, *Chem. Commun*., 2007, 4839.
5 T.J. Novak, L.W. Daasch, J. Epstein, *Anal. Chem*., 1979, **51,** 1271.
6 M.S. Niewenhuizen, J.L.N. Hartevel, *Sensor Actuat. B,* 1997, **40**, 167.
7 W.E. Steiner, S.J. Klopsch, W.A. English, B.H. Clowers, H.H. Hill, *Anal. Chem*., 2005, **77**, 4792.
8 H. Sohn, S. Letant, M.J. Sailor, W.C. Trogler, *J. Am. Chem. Soc*., 2000, **122**, 5399.
9 (a) B. Gehauf, J. Epstein, G.B. Wilson, B. Witten, S. Sass, V.E. Bauer, W.H.C. Rueggeberg, *Anal. Chem*., 1957, **29**, 278; (b) S.-W. Zhang, T.M. Swager, *J. Am. Chem. Soc*., 2003, **125**, 3420; (c) K.J. Wallace, R.I. Fagbemi, F.J. Folmer-Andersen, J. Morey, V.M. Lynth, E.V. Anslyn, *Chem. Commun*., 2006, 3886; (d) T.J. Dale, J. Rebek Jr., *J. Am. Chem. Soc,*. 2006, **128**, 4500.
10 (a) W. Xuan, Y. Cao, J. Zhou and W. Wang, ***Che**m. Commun.***,** 2013, **49**, 10474; (b)Y. J. Jang, O. Tsay, D. P. Murale, J. A. Jeong, A. Segev and D. G. Churchill ***C**hem. Commun.***,** 2014, **50**, 7531; (c) D. R. Goud, A. K. Purohit, V. Tak, D. K. Dubey, P. Kumar and D. Pardasani, *Chem. Commun*.**,** 2014, **50**, 12363; (d) A. B.-Bon, A. M. Costero, S. Gil, F. Sancenón, R. M.-Máñez, *Chem. Commun*.**,** 2014, **50**, 13289; (e) A. B.-Bon, A. M. Costero, S. Gil, R. M.-Máñez, F. Sancenón, *Org. Biomol. Chem*.**,** 2014, **12**, 8745; (f) S. E. Sayed, L. Pascual, A. Agostini, R. M.-Máñez, F. Sancenón, A. M. Costero, M. Parra and S. Gil, *ChemistryOpen,* 2014, **3**, 142; (g) V. Kumar and E. V. Anslyn, *J. Am. Chem. Soc*., 2013, **135**, 6338; (h) K. Kim, O. G. Tsay, D. A. Atwood and D. G. Churchill, *Chem. Rev*., 2011, **111**, 5345.
11 (a) R. Klajn, *Chem. Soc. Rev*.**,** 2014, **43**, 148; (b) V. I. Minkin, *Chem. Rev.*, 2004, **104**, 2751.
12 (a) Z.-Q. Guo, W.-Q. Chen and X.-M. Duan, *Org. Lett*., 2010, **12**, 2202; (b) N. Shao, J. Y. Jin, H. Wang, Y. Zhang, R. H. Yang and W. H. Chan, *Anal. Chem.,* 2008, **80**, 3466; (c) T. Sakata, D. K. Jackson, S. Mao and G. Marriott, *J. Org. Chem.,* 2008, **73**, 227; (d) J.-F. Zhu, Han. Yuan, W.-H. Chan and A. W. M. Lee, *Org. Biomol. Chem*., 2010, **8**, 3957; (e) J.-F. Zhu, W.-H. Chan, A. W. M. Lee, *Tetrahedron Lett*., 2012, **53**, 2001; (f) N. Shao, J. Y Jin, S. M. Cheung, R. H. Yang, W. H. Chan, T. Mo, *Angew. Chem., Int. Ed*., 2006, **45**, 4944; (g) G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev*., 2000, **100**, 1741; (h) V. I. Minkin, *Chem. Rev*., 2004, **104**, 2751; (i) F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev*., 2005, **34**, 327.
13 (a) T. Sakata, D. K. Jackson, S. Mao, G. Marriott, *J. Org. Chem*., 2008, **73**, 227; (b) Z. Tian, W. Wu, W. Wan, A. D. Q. Li, *J. Am. Chem. Soc*. 2009, **131**, 4245; (c) N. Shao, H. Jin, J. Wang, J. Zeng, R. H. Yang, W. H. Chan, *J. Am. Chem. Soc*. 2010, **132**, 725; (d) N. Shao, H. Wang, X. Gao, R. H. Yang, W. H. Chan, *Anal. Chem.,* 2010, **82**, 4628.
14 (a) N. Shao, J. Y. Jin, H. Wang, Y. Zhang, R. H. Yang, W. H. Chan, *Anal. Chem*., 2008, **80**, 3466; (b) J.-F. Zhu, H. Yuan, W.-H. Chan, A. W. M. Lee, *Org. Biomol. Chem*., 2010, **8**, 3957; (c) M. Tanaka, T. Ikeda, Q. Xu, H. Ando, Y. Shibutani, M. Nakamura, H. Sakamoto, S. Yajima, K. Kimura, *J. Org. Chem*., 2002, **67**, 2223; (d) H. Sakamoto, H. Takagaki, M. Nakamura, K. Kimura, *Anal. Chem*., 2005, **77**, 1999.
15 (a) J.-F. Zhu, W.-H. Chan, A. W. M. Lee, *Tetrahedron Lett*. 2012, **53**, 2001; (b) S. Goswami, K. Aich, S. Das, A. K. Das, D. Sarkar, S. Panja, T. K. Mondal and S. K. Mukhopadhyay, *Chem. Commun*., **2013**, *49*, 10793.
16 S. Goswami, S. Das, K. Aich, D. Sarkar, T. K. Mondal, C. K. Quah and H.-K. Fun, *Dalton Trans*., **2013**, *42*, 15113.

