RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

COMMUNICATION

N-alkyl derivative of 1,9-pyrazoloanthrone as a sensor for picric acid†

Karothu Durga Prasad and Tayur N. Guru Row*

Cite this: DOI: 10.1039/x0xx00000x Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The *N*-alkyl derivative of 1,9-pyrazoloanthrone has been synthesized, characterized and evaluated as a potent sensor for picric acid.

The detection of explosive chemicals immensely attracted the attention pertaining to defence, environmental and humanitarian implications.[1] The utilization of nitro compounds and nitro aromatics as explosive materials in both military and civilian applications makes them more vulnerable to offensive acts. Nitro aromatics such as picric acid (PA) and trinitro toluene (TNT) are extremely used in the production of landmines.[2] This creates a colossal threat to the civilian population as these explosives were inflexible to remove and demining. By using sophisticated analytical techniques such as IR, Raman spectrometry and X-ray, these explosive chemicals can be detected[3], however cost and portability of such equipment serve as major draw backs, even though these methods are regarded as highly efficient.

Fluorescence detection on chemical sensing of fluorescent materials provides a suitable and cost effective alternate for the detection of explosive materials due to their high responsiveness, simplicity, short response times and the capability to detect fluorescence in both solid and solution phases.[4] In recent years, several materials like oligomeric, polymeric, calix[4]arenes and nano based materials are used for detecting various explosives,[5] in which the change in fluorescence response in presence of nitro aromatics is the key feature towards the detection. However, the detection of explosives presents a challenge owing to some obstacles such as sensitivity, stability, toxicity and biodegradability of these materials.

Iptycene-based poly phenylene ethynylenes (PPE), [6a] anthracene based polymers [6b] polyphenylenebutadiynylenes, [6c] polyacetylenes,[6d] polymetaloles,[6e] silica-supported metalloporphyrins,[6f] pyrene-copolyimides,[6g] poly(2-methoxy-(2'-ethylhexloxy)-p-phenylene-vinylene (MEH-PPV),[6h] metal-organic frame works (MOFs)[6i] and dendrimers[7] are some of the widely studied examples for the detection of nitro aromatics. Except a few, many of these materials are comparatively expensive to prepare in large scale and involve heavy synthetic efforts.[8] Small molecule based fluorescent sensors for the detection of explosives have also been investigated but to a less extent.[9] Small molecules provide some advantages over the other materials in terms of preparation, well established structural features and cost-effectiveness. Small molecules like pyrene derivatives and anthracene derivatives have been investigated for the detection of nitro aromatics by fluorescence quenching.[10] Kumar *et al.*[11] reported benzocoronene and phenylene-based molecules for the selective detection of picric acid at very low concentrations. To the best of our knowledge electron rich anthrapyrazolones, having a wide variety of both physical and biological properties,[12] have not yet been explored as potential sensors for the detection of electron deficient nitro aromatics like picric acid. Herein we report on the properties of *N*-alkylated anthrapyrazolone as fluorescent sensor for the detection of picric acid and other nitro aromatics.

Condensation of 1-chloroanthraquinone with hydrazine gives 1,9-pyrazoloanthrone.[13] *N*-alkylation of 1,9-pyrazoloanthrone gives 2-hexyldibenzo[cd,g]indazol-6(2H)-one (here after abbreviated as **1**).[14] Compound **1** shown in **Fig. 1** has been purified by column chromatography and characterized by NMR, HR-MS and single crystal X-ray diffraction studies (See ESI†). Needle shaped yellow color crystals of compound **1** were obtained from a mixture of EtOAc/hexane (2:8 v/v) by slow evaporation at ambient temperature. The compound **1** crystallizes in a monoclinic space group $P2_1/n$, Z=4 (**Fig. 2a).** The packing is dominated by the presence of C-H•••O hydrogen bonding with further stability is imparted by π•••π stacking at a distance of 3.5Å (**Fig. 2b**).

---

*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India. E-mail: ssctng@sscu.iisc.ernet.in; Fax: +91 80 23601310; Tel: +91 80 22932796

†Electronic supplementary information (ESI) available: Full experimental procedures; ^{1}H and ^{13}C NMR spectra of compound; Fluoroscence life time measurements and additional data. CCDC deposit number: 1005085. For ESI and crystallographic data in CIF or other electronic format see

RSC Advances Accepted Manuscript

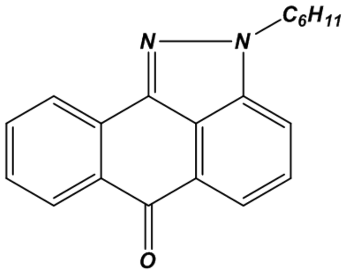


Fig. 1 Chemical structure of compound **1**

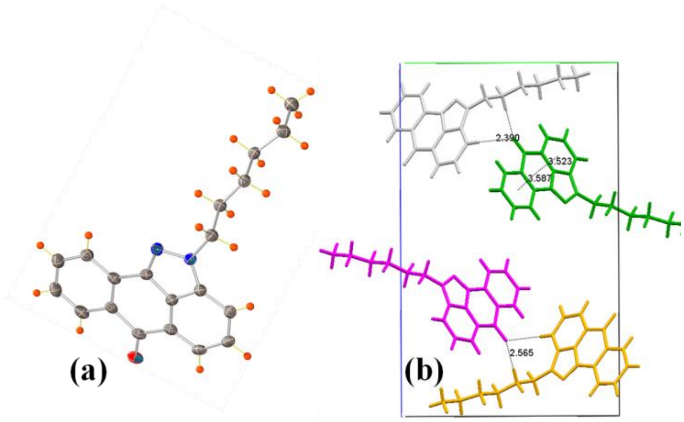


Fig. 2 (a) ORTEP diagram of compound **1** with displacement ellipsoids shown at 50% probability. **(b)** Packing diagram of compound **1** along *a*-axis.

The UV absorbance spectra of compound **1** in CH_2Cl_2 displayed distinct absorption bands with absorption maxima (λ_{max}) at 275, 302 and 425 nm respectively. Absorption and emission spectrum of compound **1** in different solvents has been explored (ESI†) to assist in establishing the nature of these bands. The longer wavelength band at 425 nm represents an intra-molecular charge transfer (ICT) band with the other high energy bands correspond to structural bands (**Fig. 3a**). Emission spectra exhibited strong band with emission maxima centred at (λ_{max}) 465 nm upon excitation at 420 nm (**Fig. 3b**). Insets of **Fig. 3b** shows blue colour fluorescence, observed for the compound **1** in CH_2Cl_2 solution while irradiating with a UV lamp (λ_{ex} =365 nm).

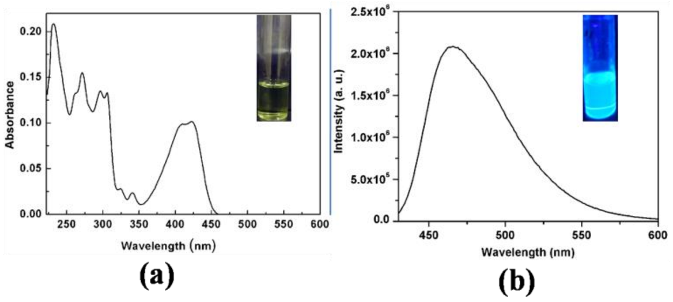


Fig. 3(a) Absorption spectra **(b)** emission spectra of compound **1** in CH_2Cl_2.

Unlike in absorption spectra, fluorescence spectra of compound **1** in different solvents exhibit a remarkable red shift. For instance, emission at 440 nm in toluene and 510 nm in methanol were observed **(Fig. 4)**. This is due to the intramolecular charge transfer originating from nitrogen lone pair to the keto group in the molecule at excited state. The full width at half maxima increases with increase in the polarity of the solvent which also proves intramolecular charge transfer. Interestingly, this observation is in contrast to the observation in most of Donor-Acceptor (D-A) systems. This may be attributed to the suppression of non radiative decay owing to the rigid nature of compound **1**. These vivid photo physical properties of compound **1** urged us to explore its sensor studies towards electron deficient nitro aromatics.

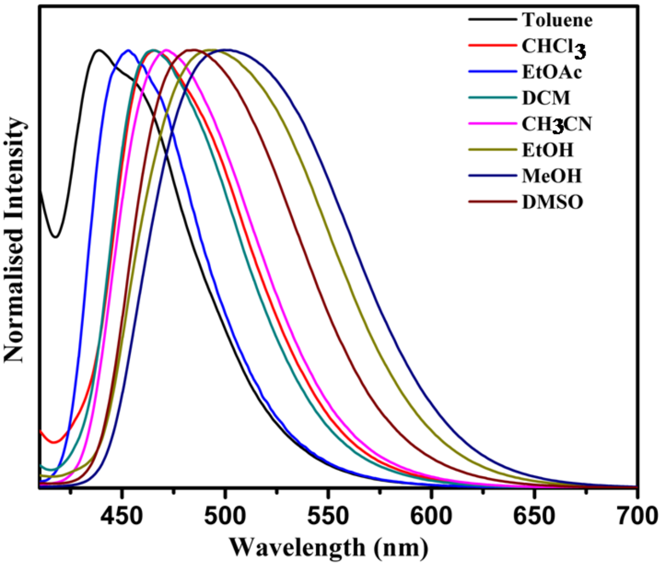


Fig. 4 Fluorescence spectrum of compound **1** in different solvents.

Titration experiments have been carried out by using several analytes in CH_2Cl_2 for the fluorescence response to evaluate the specific sensing capability of compound **1** and the results are shown in **Fig. 5**. The fluorescence quenching experiment has been performed by addition of 300μL (1×10^{-3} M; 150 equiv) of different nitro aromatics (2,4,6-trinitrophenol, 2,4-dinitrophenol, 1,4-dinitrobenzene, m-dinitrobenzene, 1,4-benzoquinone, o-nitrophenol, benzoic acid, p-nitrophenol and o-dinitrobenzene) taken in CH_2Cl_2 to 3mL of 1×10^{-5} M solution of compound **1** also taken in CH_2Cl_2. **Fig 5a** exclusively brings out the specific fluorescence quenching ability of compound **1** towards picric acid alone in comparison with other nitro aromatics. The most common analytes, 2,4-dinitrophenol, o-dinitrobenzene and o-nitrophenol displayed minimal effect on fluorescence quenching at higher concentrations **(Fig. 5b)**.

RSC Advances Accepted Manuscript

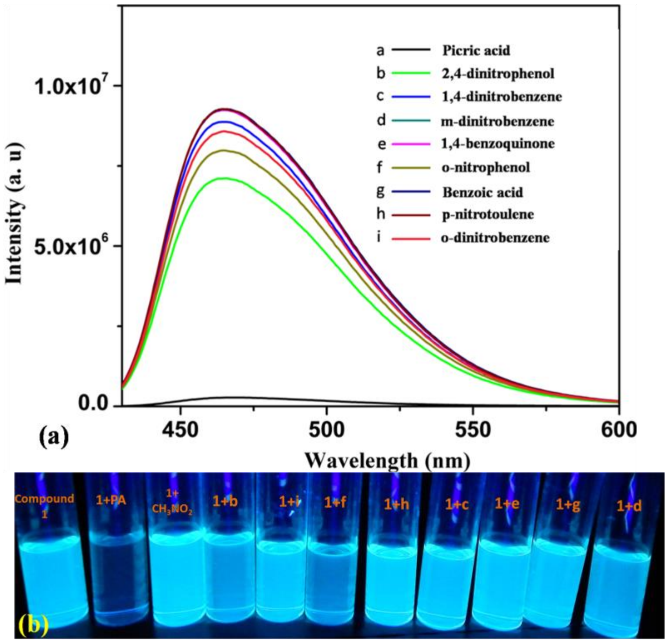


Fig. 5(a) Fluorescence spectra of compound **1** upon addition of different analytes in CH_2Cl_2. **(b)** Visual colour change of compound **1** with different nitro aromatics under UV light (λ_{ex} = 365 nm).

The fluorescence titration for compound **1** has been investigated by fluorescence quenching with the addition of picric acid (PA). The titration experiment revealed that the fluorescence emission intensity of compound **1** gradually decreases upon addition of increasing amounts of PA **(Fig. 6).** The appearance of faded blue color upon addition of PA to bright yellow color compound **1** solution indicates the formation of (**1-PA**) complex (inset in **Fig. 6**). The quenching efficiency of sensor compound **1** is found to be superior towards PA (96%) compared to other nitro aromatics (ESI†). Further, the detection limits for compound **1** (towards picric acid) was measured from the fluorescence quenching titration experiment and it is found to be 1 ppm (ESI†).

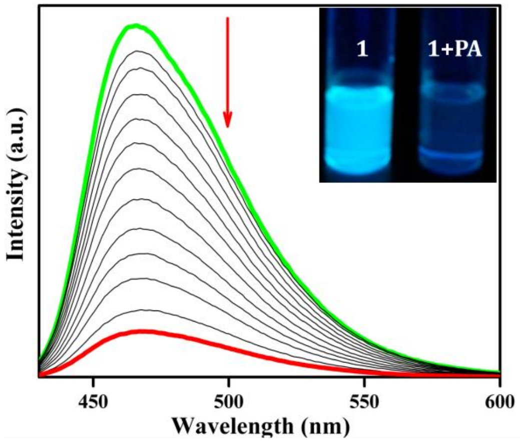


Fig. 6 Changes in the emission spectra of compound **1** in different concentrations of PA in dichloromethane. Inset: a photograph taken under UV light (365 nm), showing the fluorescence quenching upon addition of PA to compound **1**.

The selective fluorescence quenching of compound **1** upon addition of PA was further corroborated by using Stern – Volmer constant $K_{SV}=2.5\times10^7$ M^{-1} (**Fig. 7**, also ESI†). The excess addition of PA to the compound **1** displayed no change in absorption band at 425 nm. Further, ^{1}H NMR spectra (See ESI†) are invariant before and after the addition of picric acid to the sensor. In contrast, the fluorescence lifetime (See ESI†) value (2 ns) of the sensor decreased upon picric acid addition (fluorescence life time of **1-PA** is 5.8 ps) indicating the dynamic nature of quenching and a plausible excimer formation through protonation of nitrogen centre by picric acid. Thus, based on absorption, ^{1}H NMR and lifetime studies, we postulate an excited state charge transfer complex formation between sensor and picric acid resulting in dynamic quenching of fluorescence.

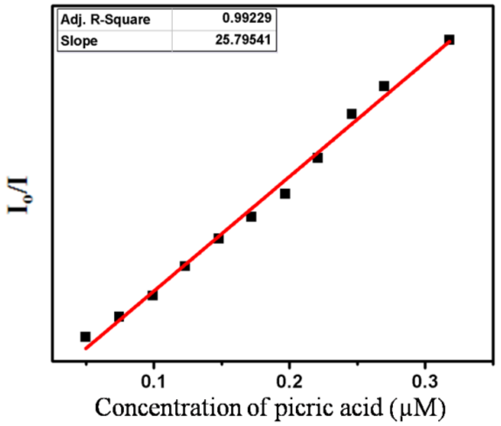
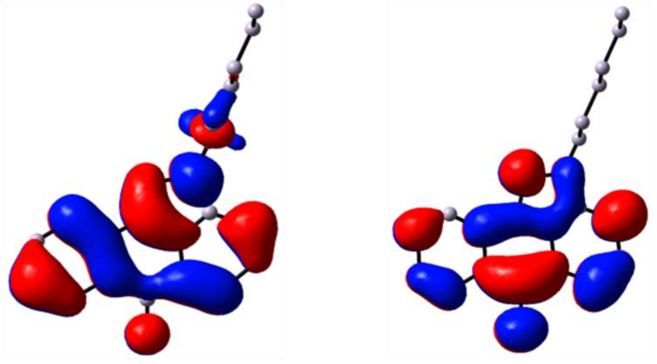


Fig. 7 Stern−Volmer plot for sensor compound **1** with PA.

To obtain deeper insights into the electronic structure of molecule, we performed density functional theory calculations using Gaussian 09 software, B3LYP hybrid functional with 6-31G (d) basis set. Frontier molecular orbital diagrams reveal that highest occupied molecular orbital (HOMO) resides on pyrazoloanthrone with small contribution from alkyl chain (**Fig. 8**). Lowest unoccupied molecular orbital (LUMO) is delocalised over entire 1,9-pyrazoloanthrone moiety.



HOMO (-6.07 eV) **LUMO (-2.56 eV)**

Fig. 8 Shapes of the considered HOMO and LUMO orbitals and their relative energy levels explored by B3LYP method with 6-31G (d) basis set.

These frontier molecular orbitals are clearly disclosed that there was strong delocalisation of lone pair of electrons on nitrogen centres. As a result, protonation of nitrogen centre upon addition of picric acid to the molecule stops the intramolecular charge transfer from nitrogen (donor) to the π-system, which

RSC Advances Accepted Manuscript

leads to the quenching of fluorescence. TD-DFT calculations were carried out to correlate the absorption and emission processes. The calculated absorption and emission values are in good agreement with the experimental values (Table 1).

Table 1 TD-DFT absorption wavelengths for compound **1** at TD-BMK/6-31G*/PCM//BMK/6-31G*/PCM level of theory.

Excited State	E/eV	E/nm	f	f
1	3.15	392	0.1461	HOMO ->LUMO (95%)
3	3.93	315	0.0186	HOMO-3 ->LUMO (94%)
4	4.26	290	0.1036	HOMO-4 ->LUMO (93%)
5	4.29	288	0.0645	HOMO-5 ->LUMO (95%)
1	3.15	392	0.1461	HOMO ->LUMO (95%)

We analysed the compound **1** coated TLC plate for the detection of picric acid (Fig. 9).

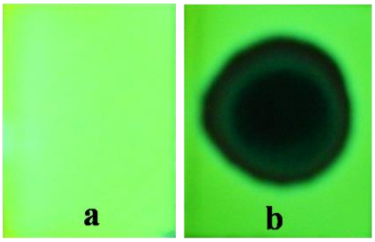


Fig. 9 Photographs of the fluorescence quenching of compound **1** coated on TLC plate for the visual detection of picric acid (PA) at different concentrations under a 365 nm UV light. (a) Pure compound **1** and (b) 10^{-5} M of PA.

Conclusions

Sensor property of *N*-alkylated 1,9-pyrazoloanthrone was studied on electron deficient nitro aromatic systems. The compound showed specific sensor activity towards picric acid and the experimental results were correlated by DFT calculations.

Authors thank the Indian Institute of Science for infrastructure facilities and financial support. KDP acknowledge fellowships from CSIR (Council of Scientific Industrial Research). TNG thanks DST for a J C Bose fellowship. We would also like to thank Dr. S. Cherukuvada for useful discussions.

Notes and references

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

1 Y. Salinas, R. Martinez-Manez, M. D. Marcos, F. Sancenon, A. M. Castero, M. Parra and S. Gil, *Chem. Soc. Rev.* 2012, **41**, 1261–1296.

2. Containing the threat from illegal bombings: an integrated national strategy for marking, tagging, rendering inert, and licensing explosives and their precursors, National Academy Press, Washington DC, 1998.

3. http://www.smithsdetection.com/mmtd.php, last accessed:

4. S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee, S. K. Ghosh, *Angew. Chem. Int. Ed*. 2013, **52**, 2881–2885.

5. S. W. Thomas III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339–1386; b) Y. Wang, A. La, Y. Ding, Y. X. Liu and Y. Lei, *Adv. Funct. Mater.*, 2012, **22**, 3547–3555; c) T. Naddo, Y. K. Che, W. Zhang, K. Balakrishnan, X. M. Yang, M. Yen, J. C. Zhao, J. S. Moore and L. Zang, *J. Am. Chem. Soc.*, 2007, **129**, 6978–6979; d) T. L. Andrew and T. M. Swager, *J. Am. Chem. Soc.*, 2007, **129**, 7254–7255; e) D. D. Li, J. Z. Liu, R. T. K. Kwok, Z. Q. Liang, B. Z. Tang and J. H. Yu, *Chem. Commun.*, 212, **48**, 7167–7169; f) G. G. Shan, H. B. Li, H. Z. Sun, D. X. Zhu, H. T. Cao and Z. M. Su, *J. Mater. Chem. C*, 2013, **1**, 1440–1449; g) S. J. Toal and W. C. Trogler, *J. Mater. Chem.*, 2006, **16**, 2871–2883; h) Y. Tao, G. T. Li and H. S. Zhu, *J. Mater. Chem.*, 2006, **16**, 4521–4528; i) Y. H. Lee, H. Liu, J. Y. Lee, S. H. Kim, S. K. Kim, J. L. Sessler, Y. Kim and J. S. Kim, *Chem. Eur. J.*, 2010, **16**, 5895–5901.

6. (a) D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537–2574. (b) B. Gole, S. Shanmugaraju, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 10046–10048; (c) D. Zhao and T. M. Swager, *Macromolecules*, 2005, **38**, 9377–9384; (d) Y. Liu, R. C. Mills, J. M. Boncella and K. S. Schanze, *Langmuir*, 2001, **17**, 7452–7455; (e) H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, *J. Am. Chem. Soc.*, 2003, **125**, 3821–3830; (f) S. Tao, G. Li and H. Zhu, *J. Mater. Chem*, 2006, **16**, 4521–4528; (g) S. Burattini, H. M. Colquhoun, B. W. Greenland, W. Hayes and M. Wade, *Macromol. Rapid Commun.*, 2009, **30**, 459–463; (h) F. Chu, L. Ye, J. Yang and J. Wang, *Opt. Commun.*, 2012, **285**, 1171–1174 (i) B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 12137–12139.

7. G. Tang, S. S. Y. Chen, P. E. Shaw, K. Hegedus, X. Wang, P. L. Burn and P. Meredith, *Polym. Chem.*, 2011, **2**, 2360–2368; b) D. A. Olley, E. J. Wren, G. Vamvounis, M. J. Fernee, X. Wang, P. L. Burn, P. Meredith and P. E. Shaw, *Chem. Mater.*, 2011, **23**, 789–794.

8. J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 5321–5322; b) J. S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864–11873; c) C. J. Cumming, C. Aker, M. Fisher, M. Fox, M. J. laGrone, D. Reust, M. G. Rockley, T. M. Swager, E. Towers and V. Williams, *IEEE T. Geosci. Remote*, 2001, **39**, 1119–1128.

9. (a) M.S. Meaney and V.L. McGuffin, *Anal. Bioanal. Chem.*, 2008, **391** 2557–2576. (b) M.E. Germain and M.J. Knapp *Chem. Soc. Rev.*, 2009, **38**, 2543–2555.

10. (a) K.-S. Focsaneanu and J. C. Scaiano, *Photochem. Photobiol. Sci.*, 2005, **4,** 817–821.(b) S. Shanmugaraju, S. A. Joshi and P. S. Mukherjee, *J. Mater. Chem.*, 2011, **21**, 9130–9138.

11. (a) V. Vij, V. Bhalla and M. Kumar, *ACS Appl. Mater. Interfaces*, 2013, **5,** 5373−5380; (b) S. Pramanik, V. Bhalla, and M. Kumar, *Analytica Chimica Acta*, 2013, **793**, 99–106; (c) V. Bhalla, H. Arora, H. Singh and M. Kumar, *Dalton Trans.*, 2013, **42**, 969–974.

12. (a) B. L. Bennett, D. T. Sasaki, B. W. Murray, E. O'Leary, S. T. Sakata, W. Xu, J. C. Leisten, A. Motiwala, S. Pierce, Y. Satoh, S. S. Bhagwat, A. M. Manning, and D. W. Anderson, *Proc. Natl. Acad. Sci. USA* 2001, **98**, 13681–13686; (b) K. D. Prasad, N. Venkataramaiah and T. N. Guru Row, *Cryst. Growth Des.*, 2014, **14**,

RSC Advances Accepted Manuscript

2118–2122; (c) K. D. Prasad, J. Trinath, A. Biswas, S. Kanagaraj, B. N. Kithiganahalli and T. N. Guru Row, *Org. Biomol. Chem.*, 2014, **12**, 4656–466.

13. (a) H. D. H. Showalter, J. L. Johnson, J. M. Hoftiezer, W. R. Turner, L. M. Werbel, W. R. Leopold, J. L. Shillis, R. C. Jackson, E. F. Elslager, *J. Med. Chem.*, 1987, **30**, 121–131; (b) W. Bradley, K. W. Geddes, *J. Chem. Soc.* 1952, 1630–1635; (c) M. Kim and D. F. Wiemer, *Tetrahedron Lett.*, 2004, **45**, 4977–4980.
14. Y. -P. Pang, A. Vummenthala, J. G. Park, S. -H. Wang, Z. Dong, A. M. Bode and Y. Y. Cho, *US Pat.* 2011/0269810 A1, 2011.

RSC Advances Accepted Manuscript