Logic Implications from Pyrene-DAMN Schiff base via Anion interaction and Solvent Tuning

Bashir Ahmed[1, 2], Purvee Bhardwaj[1] Erum Gull Naz[3], Wasseem Akbar*[2,3] & Masood Ayoub Kaloo*[2]

[1]Department of Physics, Rabindranath Tagore University, Bhojpur (M.P), India
[2]Department of Chemistry, Govt. Degree College Doda, Jammu & Kashmir (India)
[3]Department of Chemistry, Carrer Point University, Kota Rajasthan (India)

Corresponding Author: Masood Ayoub Kaloo

Abstract

A pyrene-DAMN based molecular scaffold has been explored for its ion recognition characterisitcs under various solvent conditions. In DMSO, selective, prompt and naked eyete sensing of F^- and CN^- was obaserved by modulation of its intramolecular charge transfer characterisitcs. Anion-stimulated fluorescence "turn on" behaviour was proposed to occur through photoinduced electron transfer phenomenon. The dual-ion sensing mode, solvent-tuned recognition along with its distinct reversible binding has been explored for various Boolean operations at molecular level. A number of simple and advanced logic functions in the form of YES (identity), NOT, OR, NOR, AND, NAND, INH and IMP have been achieved.

Key Words: Pyrene, Molecular Sensor, Absorption, Emission, Naked-eye, Diaminomalenonitirle, Boolean, Arithmetic, Fluoride.

1. Introduction

The exploration and development of new materials for electronic applications is currently an area of enormous interest. In this direction, exploration and development of novel organic materials for mimicking Boolean arithmetic applications is growing at a pace. Pyrene is one such type of material which has attracted much interest of researchers in recent years due to their fluorscence[1], applications in molecular self-assembly[2] and excellent photophysical properties.[3] Further, their chemical and photolytic robustness prompt one to investigate them for various utilities.[4] In this regard, exploration of various material applications and their further development garner much interest among the scientific community[5-6]. Keeping this thing in mind, we are aiming to explore the highly conjugated charge transfer materials synthesized

from Diaminomaleonitrile (DAMN). This is due to the fact that they are easy to synthesize and easy to purify and hence economically viable for exploring material applications. Besides they are highly robust nature towards light, heat and possess fast signal transduction capability due to extensive conjugation. To the best of our knowledge, no such reports exist in the literature wherein Pyrene-DAMN Schiff base type materials have been utilized for logic gate applications.

2. Materials and Methods

2.1 General Information

All the solvents and concentrated HCl were purchased from commercial sources and distilled water was obtained from the lab. For exploring of molecular interaction behavior, tetra butyl salts (TBA) of various anions were obtained from Himedia. Anions prior to the use were kept in desecrator. Absorption measurements were carried out using Shimadzu Spectrophotometer (Model no: UV-1900i, Serial no: A12535981544, Lab Solutions UV software. For absorption titration, 2.75 ml volumes of receptor in dimethyl sulphoxide (DMSO) were used in a quartz cuvette at 25 ± 5 °C. Emission studies were carried out on a Horiba Jovin Vyon Fluoro log 3-111 spectrophotometer using slit width of 5/5 nm. Absorption and emission spectral changes were measured immediately after addition of anions, acids to the receptor solution. All curves were fitted with a using Origin 8.0 (Origin Lab). Bar plotting was done in Excel. 2007.
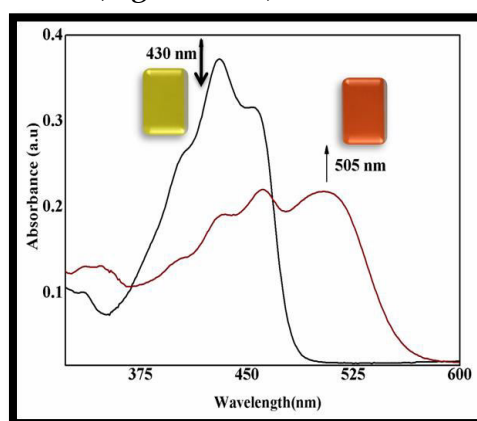
3. Results

3.1 Approach

In previous studies related to anion recognition by DAMN Schiff bases,[7] it has been realized that even minor structural alteration leads to strong and prompt modulation of photophysical properties and hence their sensitivity towards anion binding. With all these things in mind, Pyrene Schiff base architecture **1** (Figure 1) has been opted for anion recognition study under organic solvent conditions and in presence of anions with TBA as counter ion. This is further expected to strongly influence the electronic property of this Schiff-base and hence alteration of the inherent charge-transfer states. To our surprise, the receptor entity thus chosen has been found to deduce selective interaction with F^- & CN^- in presence of other anions at micro-molar level and binding events were noticed visually through naked-eyes. The reversible sensing behaviour along with solvent-tunable signal read-out performance in absorption as well as fluorescence mode has been presented with various digital functions. Here both simple as well as complex Boolean logic gates in the form of OR, NOR, AND, NAND, INH[8], IMP[9] were demonstrated.
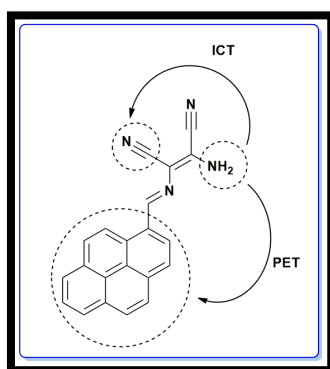
Figure1. Chemical Structure of Molecule (**1**) with ICT and PET Channels assigned.

3.2 Anion Interaction Studies through UV-Vis Spectroscopy

Molecule (**1**) is a yellow solid and soluble in most of the organic solvents. The molecular framework possesses a π-donor-acceptor[10] (π-D-A) framework favouring an intramolecular charge transfer (ICT) pathway from amine to nitrile group and photo induced electron transfer (PET) from amine nitrogen to Pyrene fluorophore (Figure 1).[11-12] Owing to the presence of polar N-H bonds in amine group, the anion-recognition behaviour of the molecule was brought into focus and to further understand the electronic properties of the system. Anion recognition[13] ability was investigated through the addition of solutions of anions[14] (F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, HSO_4^-, CH_3COO^-, $H_2PO_4^-$ and CN^-) in the form of tetrabutyl-ammonium salt (TBA) in DMSO to **1**. In DMSO, **1** (22 μM) displays an intense charge transfer absorption band at 430 nm which could be attributed to the π- $π^*$ transitions in the molecule. Addition of F^- to **1** resulted in strong red-shift of 75 nm of the intrinsic absorption towards a broad signal around at 505 nm (Figure 2). The spectral behaviour was in turn detected through naked-eyes by the appearance of an immediate colour changes of the DMSO solution of **1** from yellow to red (Fig. 2- inset).

Figure 2. Absorption titration of **1** (22×10^{-6}M) in presence of 10 equivalents of fluoride ion

Similar type of results was obtained from **1** in presence of other anions capable of some hydrogen bonding. However apart from similar sensing behaviour of F^- and CN^- with **1**, CH_3COO^- and $H_2PO_4^-$ displayed week effect (Figure 3). The above colorimetric changes

can be easily reversed by the addition of a dilute solution of protic acid like trifluoro acetic acid (TFA) to the solution of **1** in presence of these anions. The observations reveal a probable hydrogen bond-donation or deprotonation based mechanism of receptor **1** to anion. This leads to the ICT enhancement from deprotonated amine to the nitrile group across channel 1.
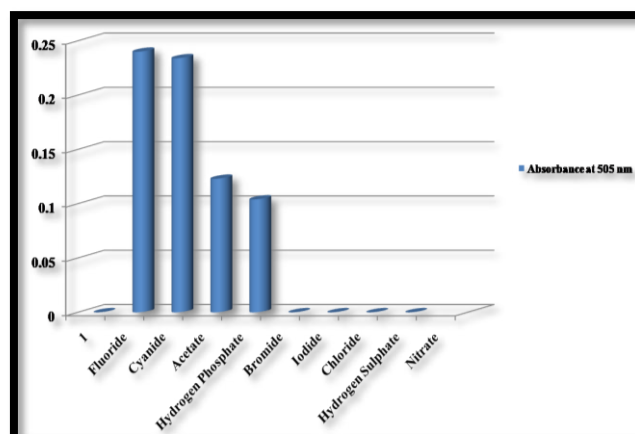
Figure 3. Interaction various anions with **1**. Observations were made with 10 equivalents of fluoride and cyanide, while others were added in 100-fold concentrations. All the experiments were carried at room temperature.

3.4 Anion Interaction Studies through Emission Spectroscopy

As pyrene is a well know fluorophore, following absorption spectral studies, we studied the anion recognition process via emission spectroscopy. It is to be noted that **1** (7 µM) is weekly fluorescent when excited at 430 nm, but upon interaction with CN^- /F^- induces an emission enhancement at 575 nm which gets intensified with further additions (Figure 5). This is called as fluorescence "turn on" behaviour. This can be attributed to the blockade of PET amine site to the pyrene in presence of anions. Other anions apart from F^-, CN^-, CH_3COO^- and $H_2PO_4^-$ produced no effect on the emission properties of the system. However, weaker basic anionic species like CH_3COO^- and $H_2PO_4^-$ resulted in a less intense emission response compared to that of F^- and CN^-.
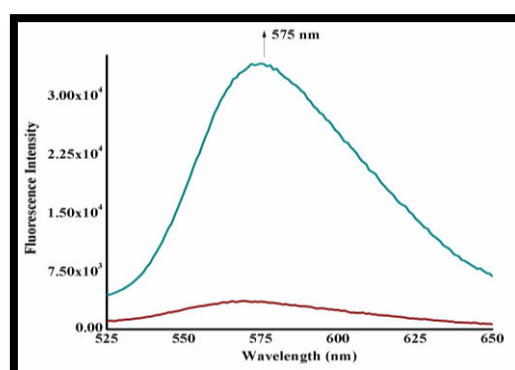

Figure 5. Emission behavior of **1** (7×10^{-6} M) in presence of **10** equivalents of fluoride ion.

3.5 Anion discrimination Studies

Since the anion sensing shown by **1** is based on hydrogen bonding between molecule and anions or maximum through the acid-base interaction, altering the hydrogen bonding capability or basicity of such anions (proton acceptors) under the circumstances can drastically affect the electronic properties or signal-read-out behaviour from the molecular solution under study. As we know, fluoride anion is known to possess strong hydration enthalpy compared to cyanide.[15] Thus in highly polar solvents like water or methanol; drastic influence can be expected on the recognition processes. As per expectations, we could achieve selective recognition of cyanide in a mixed solvent system (H_2O/DMSO: V/V (1.5 ml/8.5 ml). It was noticed that upon addition of around >1.0 percent of H_2O into the solvent, complete vanishing of the fluoride interaction happened. The observation reveals a promising potential of the given system for sensing of both cyanide and fluoride at micro molar level, further tuning of solvent system can easily be exploited for their discrimination.

3.6 Logic Arithmetic Implications

On the basis of the above observations, the receptor was explored for logical arithmetic applications under various combinations of anions/H^+ as chemical inputs and optical signals (absorption and emission) as outputs.[16-17] These inputs and outputs were coded with binary digits 'o' for 'OFF' and '1' for 'ON' (Figure 6). Here, for demonstrating the logic behaviour, upon monitoring changes in absorption spectra solely in DMSO, presence of both of CN^- and F^- demonstrates a two-input NOR function at 430 nm and an OR function at 505 nm, with optical outputs in the form of A430 and A505 respectively (Figure. 6). Similarly, another OR logic gate can be constructed in the emission mode with F575 as output.

| INPUTS		OUTPUTS		
F/CN⁻	H⁺	A430	A505	F575
0	0	1	0	0
1	1	0	1	1
0	1	0	1	1
1	0	0	1	0
Functions		NOR	OR	OR
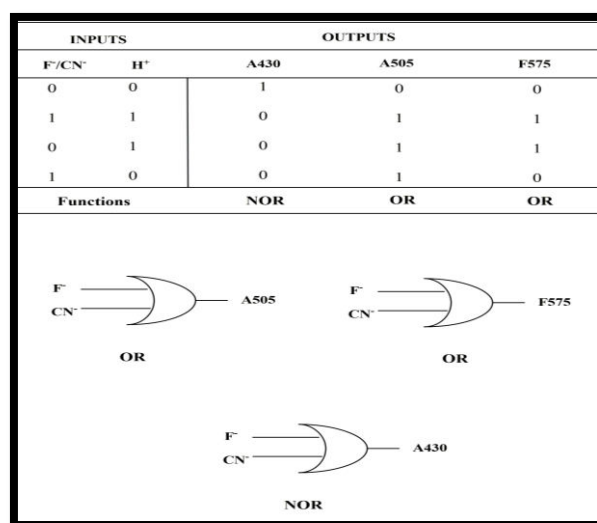
Figure 6. (Above) Truth table. (Below) presentation of various logic gates with optical signals at various wavelengths corresponding to the inputs in the form of F^- and CN^-.

However, under the mixed solvent conditions (H$_2$O/THF: V/V (1.5 ml/8.5 ml), two input molecular logic gate turn into a single input logic gate with CN$^-$ based chemical input only. Hence two YES or IDENTITY functions or buffer can be obtained at 505 nm and 575 nm in absorption and emission modes respectively. While intrinsic absorption (430 nm) of molecule presents a NOT with A430 as the output (Figure. 7).
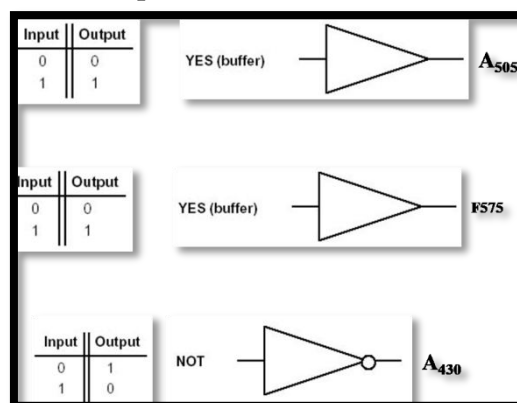
Figure 7. Truth table and presentation of single input YES ans NOT gate in presence of CN$^-$ under mixed solvent confitions.

Besides above, the reversibility induced by the protic acids by masking the effect of anions (F$^-$/CN$^-$) was also studied for exploration of logic arithmetic applications. The outputs generated by fluoride and cyanide can be fully reversed by addition of TFA. This reproducible switching behaviour of molecule reflects an inhibit (INH) logic function, employing anions (F$^-$/CN$^-$) and cation (H$^+$) as inputs to the corresponding optical output at 505 nm.[18] While setting A430 as another optical output, an implication "IMP" logic gate can be fabricated (Figure. 8). IMP exists with complementary behaviour to the INH but is supplementary with "IF THEN" situation.[19-20]
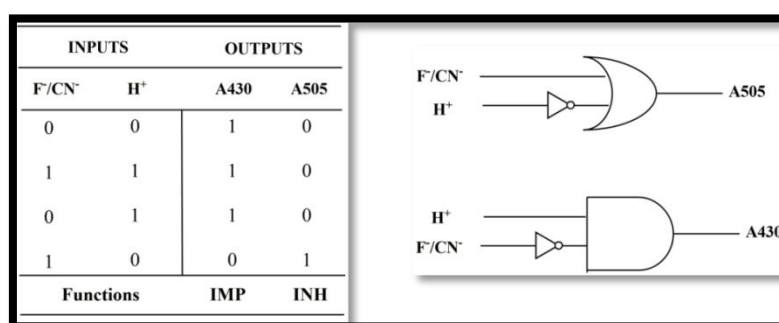
Figure 8. Presentation of two-input implication and inhibition function based logic gates (right) and corresponding truth table (left).

We further utilized the interfering other anions like acetate and phosphate for construction of complex and important logic functions from **1** in DMSO. Both the anions exhibit weak changes in the spectral properties of receptor compared to fluoride and cyanide owing to their weak basicity or hydrogen bonding capability as discussed earlier. Thus their contribution results in the production of weaker optical

signals as out puts which fall below the threshold limit (A ≥ 0.2 in figure 8 below). However, inclusion of both the anions produces an additive effect in spectral properties of **1**. The behaviour can be expressed in the form of two-input AND gate at 505 nm (Figure 9). Similarly the intrinsic absorption state at 430 nm can be articulated in the form of a two-input NAND gate with A430 as output.
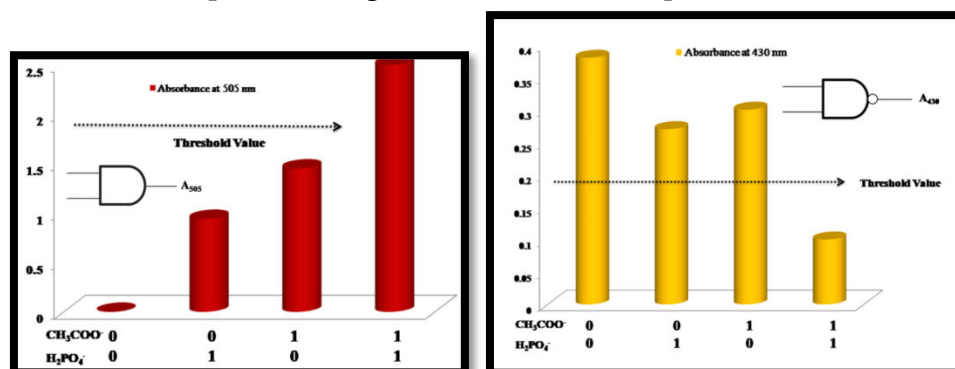
Figure 9. Presentation of two-input AND (Left) & NAND (Right) logic gate.

4. Conclusions

We have explored and developed pyrene-DAMN Schiff base as a sensitive dual-ion receptor for fluoride and cyanide under organic solvent conditions. The anion sensing attributes to the modulation of ICT by intermolecular proton transfer from polarized – NH_2 moeity to anion. Importantly, anion-driven fluorescence "turn on" phenomenon was achieved. The molecule displayed reversible switching by alternate addition of anion and protic acid. The dual-anion sensing of **1** was further discriminated by tuning of solvent under consideration. Anion recognition behaviour was also studied with Boolean logic applications. In this direction, an ample number of simple and complex logic functions in the form of YES (identity), NOT, OR, NOR, AND, NAND, INH and IMP have been obtained in absorption and emission mode.

5. Acknowledgments

6. Conflicts of Interest : Authors declare no conflicts of Interest.

7. References

1. K. Müllen, J. P. Rabe, Acc. Chem. Res.2008, 41, 511-520; b) X. Feng, W. Pisula, K. Müllen, Pure Appl. Chem. 2009, 81, 2203-2224; c) Z. Kowser, U. Rayhan, T. Akther and T. Yamato, Mater. Chem. Front., 2021, 5, 2173-2200.

2. S. Chandrasekhar, Liq. Cryst.1993, 14, 3-14; b) M. T. Allen, S. Diele, K. M. D. Harris, T. Hegmann, M. Kariuki, D. Lose, J. A. preece, C. J. Tschierske, J. Mater. Chem.2001, 11, 302-311; c) K. S. Raja, S. Ramakrishnan, V. A. Raghunathan, Chem. Mater.1997, 9, 1630-1637.

3. Y. S. Liu, P de Mayo, W. R. Ware, J. Phys. Chem.1993, 97, 5987-5994; b) R. Dabestani, I. N. Ivanov, Photochem. Photobiol.1999, 70, 10-34.

4. H. Yu, J Environ Sci Health C Environ CarcinogEcotoxicol Rev.2002, 20, 149-183; b) S. Müller, K. Müllen, Phil. Trans. R. Soc. A2007, 365, 1453-1472; c) D. Türp, T. T. T. Nguyen, M. Baumgarten, K. Müllen, New J. Chem.2012, 36, 282-298.

5. A. J. Berresheim, M. Müller, K. Müllen, Chem. Rev.1999, 99, 1747-1785; b) J. Wu, W. Pisula, K. Müllen, Chem. Rev.2007, 107, 718-747.

6. J. W. Jones, L. N. Zakharov, A. L. Rheingold, H. W. Gibson, J. Am. Chem. Soc. 2002, 124, 13378; b) F. M. Pfeffer, T. Gunnlaugsson, P. Jensen, P. E. Kruger, Org. Lett. 2005, 7, 5357; c) Y. Kim, F. P. Gabbai, J. Am. Chem. Soc. 2009, 131, 3363–3369; d) Z. Xu, X. Chen, H. N. Kim, J. Yoon, Chem. Soc. Rev. 2010, 39, 127–137; e) Z. Ekmekci, M. D. Yilmaz, E. U. Akkaya, Org. Lett. 2008, 10, 461-464.

7. M. A. Kaloo, J. Sankar, Analyst 2013, 138, 4760; b) M. A. Kaloo, J. Sankar, New J. Chem. 2014, 38, 923; c) B. Kumar, M. A. Kaloo, A. R. Sekhar, J. Sankar, Dalton Trans. 2014, 43, 16164.

8. A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, Nature 1993, 364, 42; b) A. P. de Silva, M. R. James, B. O. F. McKinney, D. A. Pears, S. M. Weir, Nat. Mater.2006, 5, 787.

9. J. M. Lehn, Supramolecular Chemistry: concepts and perspectives, Wiley-VCH, Weinheim, New York, 1995; b) M. A. Ratner, J. Jortner, Molecular Electronics, Some Directions. Blackwell's, Oxford, 1997; c) M. N. Stojanovic, T. E. Mitchell, D. Stefanovic, J. Am. Chem. Soc. 2002, 124, 3555.

10. M. J. Yuan, W. D. Zhou, X. F. Liu, Zhu, Li, M. J. B. X. D. Yin, H. Y. Zheng, Z. C. Zuo, C. B. Ouyang, H. B. Liu, Y. L. Li, D. B. Zhu, J. Org. Chem. 2008, 73, 5008; b) M. Ishida, S. J. Kim, C. Preihs, K. Ohkubo, J. M. Lim, B. S. Lee, J. S. Park, V. M. Lynch, V. V. Roznyotavsiky,T. Sharma, P. K. Panda, C. H. Lee, S. Fukuzumi, D. Kim, J. L. Sessler, Nature. Chem. 2013, 5, 115.

11. D. A. Jose, D. K. Kumar, B. Ganguly, A. Das, Org. Lett.2004, 6, 3445-3448; b) M. Sarkar, R. Yellampalli, B. Bhattacharya, R. K. Kanaparthi, A. Samanta, J. Chem. Sci.2007, 119, 91–97; c) C. B. Black, B. Andrioletti, A. C. Try, C. Ruiperez, J. L. Sessler, J. Am. Chem. Soc.1999, 121, 10438-10439;

12. M. Vazquez, Luigi Fabbrizzi, A. Taglietti, R. M. Pedrido, A. M. Gonzalez-Noya, M. R. Bermejo, Angew. Chem. Int. Ed.2004, 43, 1962 –1965; e) S. V. Bhosale, S. V. Bhosale, M. B. Kalyankar, S. J. Langford, Org. Lett.2009, 11, 5418-5421.

13. Y. Zhou, J. F. Zhang, J. Yoon, Chem. Rev.2014, 114, 5511-5571; b) E. Galibraith, T.D. James, Chem. Soc. Rev.2010, 39, 3831-3842.

14. R. M. F. Batista, S. P. G. Costa, M. M. M. Raposo, Sens. Actuat. B2014, 191, 791; b) X. Cheng, R. Tang, H. Jia, J. Feng, J. Qin, Z. Li, ACS Appl. Mater. Interfaces2012, 4, 4387; c) J. M. Linares, D. Powell, J. K. Bowman, Coord. Chem. Rev.2003, 240, 57; d) P. D. Beer, P. A. Gale, Angew .Chem. Int. Ed.2001, 40, 486.

15. Trends and Future Perspectives; Springer, Dordrecht, 2005, p. 121; c) C. R. Nicoleti, V. G. Marini, L. M. Zimmermann, V. G. Machado, J. Braz. Chem. Soc. 2012, 23, 1488.

16. J. Andreasson, U. Pischel, Chem. Soc. Rev.2010, 39, 174; b) W. Li, Y. Yang, H. Yan, Y. Liu, Nano. Lett. 2013, 13, 2980; c) S. Uchiyama, N. Kawai, A. P. de Silva, K. Iwai, J. Am. Chem. Soc.2004, 126, 3032.

17. A. P. de Silva, N. D. Mcclenaghan, Chem. Eur. J.2004, 10, 574; b) X. Zhang, S. Lee, Y. Liu, M. Lee, J. Yin, J. S. Sessler, J. Yoon, Scientific Reports2014, 4, 4593; c) A. P. de Silva, S. Uchiyama, T. P.Vance, B. Wannalerse, Coord. Chem. Rev.2007, 251, 1623; d)S. Kou, N. L. Han, D. Van Noort, K. M. K. Swamy, H. K. So, H. S. Jung, K.-M. Lee, S.-W. Nam, J. Yoon and S. Park, Angew. Chem. Int. Ed.2008, 47, 872–876.

18. M.de Sousa, M. Kluciar, S. Abad, M. A. Miranda, B. de Castro, U. Pischel, Photochem and Photobiol. Sci. 2004, 3, 639; b) T. Gunnlaugsson, D. A Mac Donail, D. Parker, Chem. Commun.2000, 93.

19. K. K. Upadhyay, A. Kumar, R. K. Mishra, T. M. Fyles, S. Upadhyay, K. Thapliyal, New J. Chem.2010, 34, 1862.