A Review on Recent Development of Fluorescent Chemosensor for Water (H_2O)

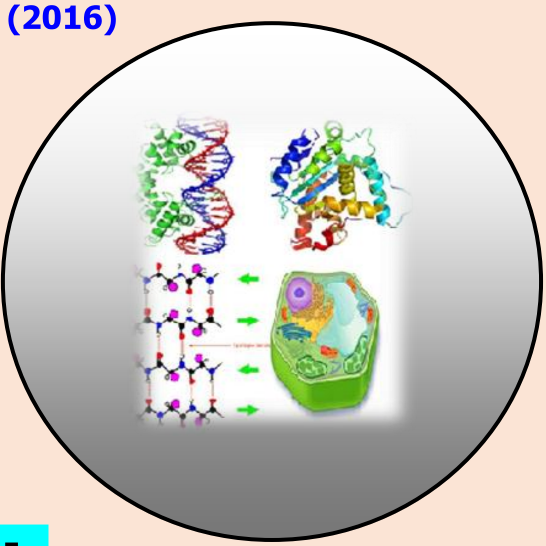
By

Krishanu Sarkar and Koushik Dhara

ISSN 2319-3077 Online/Electronic
ISSN 0970-4973 Print

UGC Approved Journal No. 62923
MCI Validated Journal
Index Copernicus International Value
IC Value of Journal 82.43 Poland, Europe (2016)
Journal Impact Factor: 4.275
Global Impact factor of Journal: 0.876
Scientific Journals Impact Factor: 3.285
InfoBase Impact Factor: 3.66

J. Biol. Chem. Research
Volume 35 (2) 2018 Pages No. 449-455



Journal of Biological and Chemical Research
An International Peer Reviewed / Referred Journal of Life Sciences and Chemistry

Indexed, Abstracted and Cited in various International and National Scientific Databases

Published by Society for Advancement of Sciences®

Journal Impact Factor: 4.275 *IC Value: 82.43 (2016)* *UGC Approval No. 62923*

J. Biol. Chem. Research. Vol. 35, No. 2: 449-455, 2018
(An International Peer Reviewed / Refereed Journal of Life Sciences and Chemistry)
Ms 35/02/6003/2018
All rights reserved
ISSN 2319-3077 (Online/Electronic)
ISSN 0970-4973 (Print)

Dr. K. Sarkar

Dr. K. Dhara

http:// www.sasjournals.com
http:// www.jbcr.co.in
jbiolchemres@gmail.com

RESEARCH PAPER

Received: 25/06/2018 **Revised: 30/06/2018** **Accepted: 01/07/2018**

A Review on Recent Development of Fluorescent Chemosensor for Water (H_2O)

Krishanu Sarkar[1],*and Koushik Dhara[2],*

[1]Department of Chemistry, Netaji Mahavidyalaya, Arambagh,Hooghly, West Bengal, India
[2]Department of Chemistry, Sambhu Nath College, Labpur, Birbhum 731303, West Bengal, India

ABSTRACT

Recently many advanced research in the field of sensing of trace amount of water in organic solvents by fluorogenic probes have made an interest area to the researchers. Fluorescence detection technique is highly attractive because of its high sensitivity and real-time approach almost in a non-destructive way. This review article covers the developments of different types of fluorogenic probes reported by different groups of scientists, their sensing mechanism, sensitivity, potential applications from 2005 to till date. Currently thisarea is in its early development stages and expected continuous improvements

Keywords: Fluorogenic Probe, Sensing and Sensitivity.

INTRODUCTION

Qualitative detection and quantitative estimation of trace amount of water mainly in various organic solvents has been a promising area for the researcher during the past few decades because water is considered as the most common impurity in organic solvents which has vital significance in chemical reactions (Wang et al., 2005),many industrial applications (Nussbaum et al., 2000), environmental monitoring etc. In organometallic chemistry, the existence of small amount of water may lead to the quenching of the reactions, lowering the selectivity of a particular compound the reaction or lowering the yields of the products and sometime causes explosions in the reaction mixture. Further in industrial process, presence of trace amount of water may lead to failure of engine and damage it. At the beginning majority of the reports for the quantitative determination of water are based on electrochemical and electrophysical sensing mechanisms (Tsamis et al., 2005) but these methods suffers a lot in lack of portability and precision. Karl Fisher method of titration (Fischer, 1935) and gas chromatography (Liang, 1990) is the most popular methods for the quantitative determination of trace amount of water in organic solvents. However this method has the disadvantage in real time sample preparations, using toxic reagents (i.e., CH_3OH, I_2 and SO_2), long experiment time and requirements of special instruments. Recently developments of fluorescence based sensors for the detection of trace amount of water in organic solvents have gained immense interest because of their simple operation, high sensitivity and high detection limit. These fluorescence based water sensors are of two types viz. 'on-off' and 'off-on' type according to their switching mode: 'on-off' (Niu et al., 2006) and 'off-on' (Ooyama et al., 2009)sensors. Between the two systems, the off-on system where fluorescence intensity increases with increasing water content in organic solvents is much more efficient system in determining water in organic solvents. Aggregation-induced emission (AIE), has become a hot research topic because of its unique optical properties and extensive applications (Hong et al., 2009). The first report of AIE-active sensor comes from Tang's group(Yu et al., 2013) and after that a large number of molecules with AIE properties have been reported by several research groups. Among these AIE active dyes, tetraphenylethene (TPE) and its derivatives have drawn much attention for their notable AIE performance, easypreparation and tunable structure modification. This review covers the recent developments to date in the fluorogenic probes for the detection of trace amount of water in organic solvents. Here, mainly the structures of the fluorogenic probe, sensing mechanism, limit of detections of the sensors are highlighted.

Fluorogenic Probes for water sensing:

The first reports in the development of fluorogenic probe for the detection of water molecule in organic solvents came from Ooyama and co-workers in 2008. They designed a new class of fluorescent probe (**1**) based on a (phenylamino) naphtha [1,2-d]oxazol-2-yl-type fluorophore (Ooyama et al., 2008) with both proton accepting and releasing sites. This is a fluorescent 'off-on' system probe and operates via photo induced electron transfer (PET) mechanism **(Fig. 1)**. In this probe, PET process operates via the electron transfer from the diethylamino group to the naphtha [1, 2-d]-oxazole fluorophore skeleton. But in presence of water, diethylamino group was protonated and consequently PET process prohibited resulting strong fluorescence emission **(Fig.2)**. It is also reported that this probe (**1**) can also function as a pH sensor as the fluorescent intensity of **1**varied with change in pH of the solution.

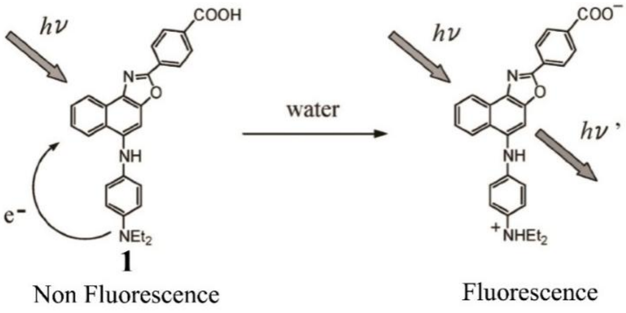


Figure 1. Proposed mechanism for the fluorogenic probe 1.

.

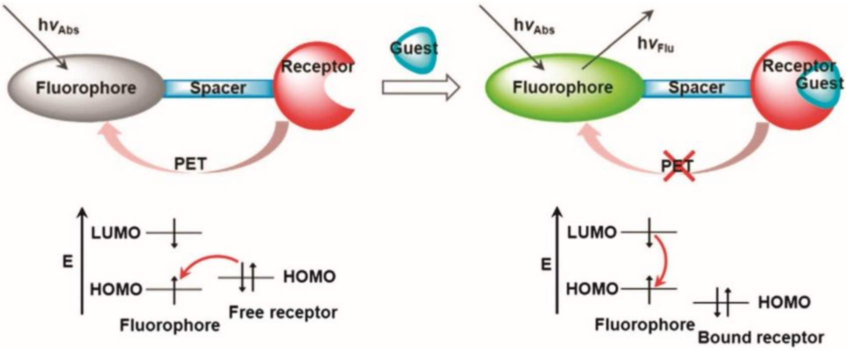
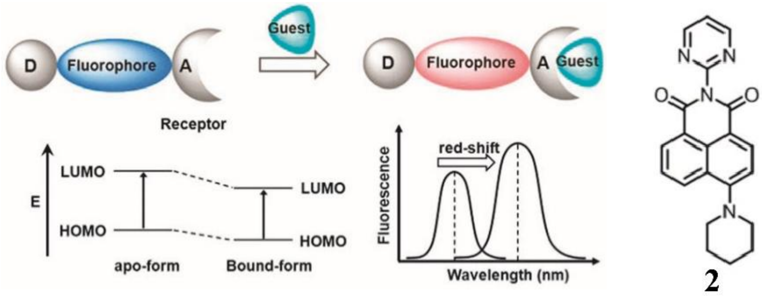


Figure 2. Schematic diagram of the PET mechanism of a fluorescence sensor.

Later Liand researchers reported a series of fluorogenic probe based on N-heteroaryl-1, 8-naphthalimides with good sensitivity to water in organic solvents. Among the series the best probe **(2),** 4-(1-piperidyl)-N-(2-pyrimidinyl)-1,8-naphthalimide (Li et al., 2011), showed very low detection limit. This N-substituted napthalimide probe operates via intramolecular charge transfer (ICT) pathway (**Fig.3**). In this probe (**2**), pyrimidine group is the electron deficient part, the electron withdrawing effect of the heteroaryl group increases the intramolecular charge transfer in the excited state of The probe, which again increases the

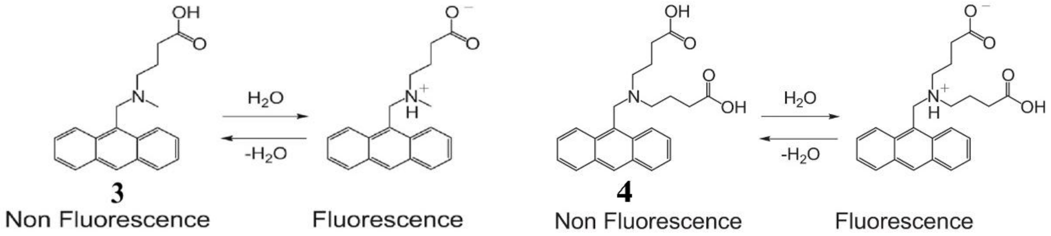


2

Figure 3. Schematic diagram of the ICT pathway (red shift) of a fluorescence sensor and the structure of the probe 2.

dipole moment of 4-(1-piperidyl) naphthalimide. The lowest detection limit of this probe in sensing water in p-dioxane, THF, acetone, and acetonitrile are 0.049, 0.020, 0.016 and 0.021%, respectively, supports **2** an efficient fluorescent water sensing probe.

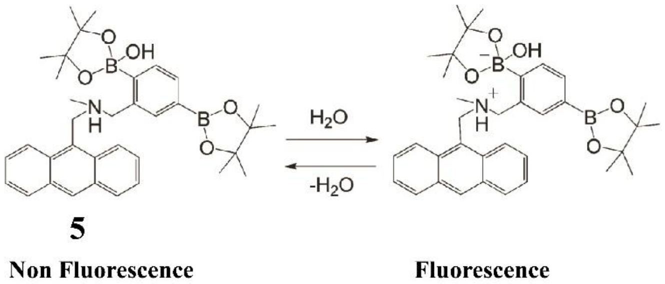
Again Ooyama and co-workers (Ooyama et al., 2011) synthesized anthracene-amino acid based fluorescent probes **(3**and**4)** which consisted of an anthracene fluorophore, a methylene spacer, and a dialkylamino part as the proton binding site.These probes showed a weak fluorescence in pure organic solvents but in presence of water fluorescence enhancement occurs due to PET inhibition (**Fig.4**).The LOD of**3** for water 0.1 wt% in THF, 1,4-dioxane,MeCNand in ethanol and the LOD of **4** for water 0.1 wt% in 1,4-dioxane, 0.4 THF, 0.1 MeCN and 0.1 wt% in EtOH.



3 **4**

Figure 4. Proposed mechanism for the fluorogenic probe 3 and 4.

Like anthracene-amino acid system, Ooyama and co-workers (Ooyama et al., 2012)reported anthracene-bisboronic ester systems (**5**) which showed better sensing efficiency to water due to rapid transformation from boronic ester to zwitterionic form consequently quenched PET phenomena (**Fig.5**). Here the limit of detection of **5** for water 0.018 wt% in 1,4-dioxane, 0.014 wt% in THF, 0.013 wt% in MeCN and 0.007 wt% in EtOH.



5

Figure 5.Proposed mechanism for the fluorogenic probe 5.

Kim and co-workers (Kim et al., 2013) reported a 4-substituted 1, 8-naphthalimide derivative (**6**) as a fluorescent probe for the determination of trace amount of water in organic solvent. In this probe napthalimide derivative act as a fluorophore, piperazinyl pentanoic acid moiety acts as the spacer-receptor part. In absence of water lone-pair of piperazine nitrogen quenched the fluorescence of the excited fluorophore due to PET process but in presence of water piperazine nitrogen gets protonated resulting PET inhibition and consequently high fluorescence generated (**Fig.6**).

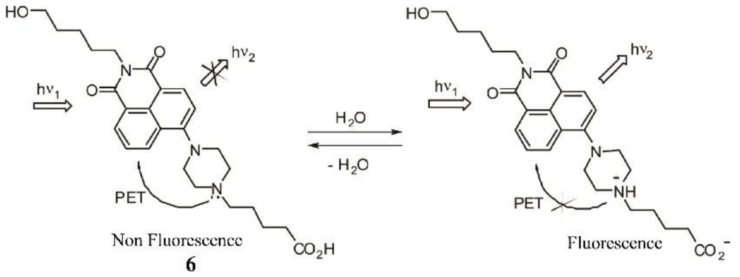


Figure 6. Proposed mechanism for the fluorogenic probe 6.

Men et al., 2013developed a novel water-triggered chemodosimeter (**7**) which is basically a Schiff base compound synthesized from condensation reaction between rhodamine ethylene diamine and 3-5-dichlorosalicylaldehyde in boiling anhydrous acetonitrile solvent (**Fig.7**). On treatment with water, this

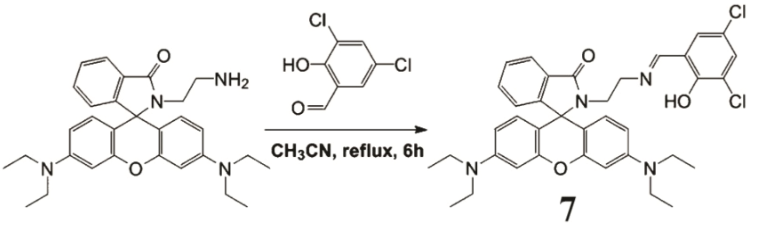


Figure 7. Synthetic route of the fluorogenic probe 7.

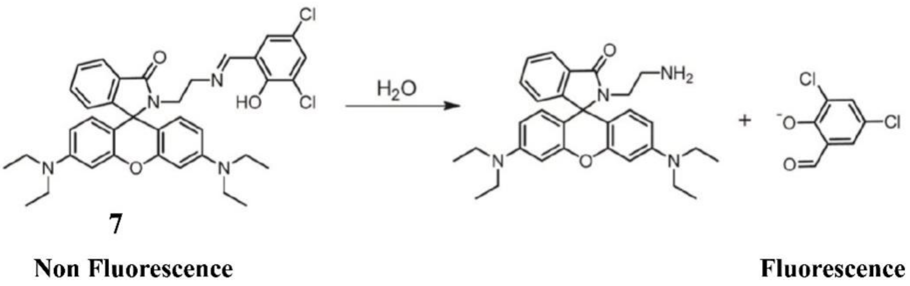


Figure 8. Proposed mechanism for the fluorogenic probe 7.

chemodosimeter cleaved into a non-fluorescent and a green fluorescent species resulting a fluorescent turn-on process **(Fig. 8)**. On the other hand, the salicylaldehyde Schiff base moiety undergoes distinct changes of UV-vis absorption band with changing the solvent polarity from apolar to polar because of the reversible enol-Keto/zwitterionic equilibrium (**Fig.9**), which is again due to the intramolecular proton transfer fromphenolic hydroxyl oxygen to imine-nitrogen (Zíolek et al., 2008, Fabian et al. 2004 and Turbeville et al. 1990).Thus this chemodosimeter probe could function as a dual channel optical detector towards water sensing. This fluorescence turn-on sensor (2.23 fold fluorescent enhancement) allowed a very low detection limit of 22 ppm (detection of water in methanol) which is advantages over other sensor in this solvent.

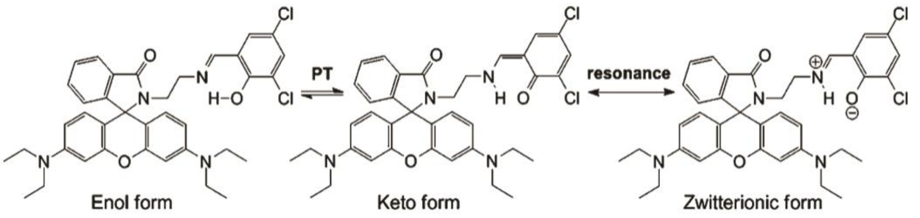


Figure 9. Enol-keto/Zwitterionic equilibrium of the probe 7.

A novel class of tetraphenylethene (TPE) derivatives TPEM (**8**) (2-((4'-(1,2,2-triphenylvinyl)biphenyl-4-yl) methylene) malononitrile) and TPEBM (**9**) (2,20-(4',4''-(1,2-diphenylethene-1,2-diyl) bis (biphenyl-4',4-diyl))bis(methan-1-yl-1-ylidene) dimalononitrile) probes were reported by Zhang et al., 2014. These sensory compounds (**8**and **9**) exhibits remarkable dual properties of solvatochromism and aggregation-induced emission (AIE) (**Fig. 10**). The presence of both electron-donating TPE moiety and the electron-accepting di-cyanovinyl moiety allowed both compounds with a remarkable solvatochromic effect and strong fluorescence emissions which changes from blue to red with change in polarity of the solvent. These fluorescent compounds could be used in both qualitative and quantitative detection of trace amount of water in organic solvents with a very low detection limit as 63 ppm and 109 ppm in THF, respectively.

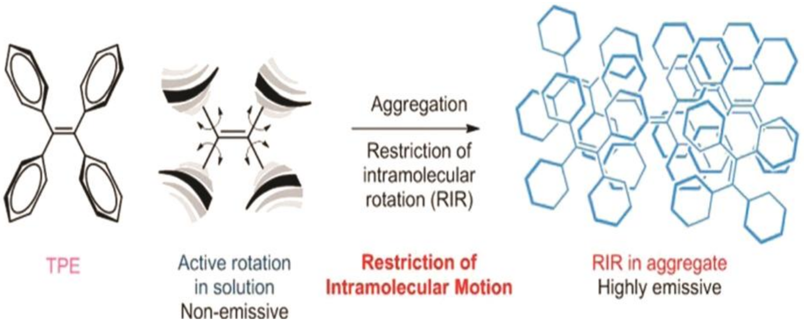


Figure 10.Schematic representation of AIE mechanism.

Within two years Men et al., 2015further reported an interesting fluorescence ratiometric hypersensitive water sensor in THF and methanol solvent. They designed a novel fluorescent zinc-salicylideneimine ensemble **(10)** as a fluorescence chemodosimeter (**Fig.11**). This fluorescent

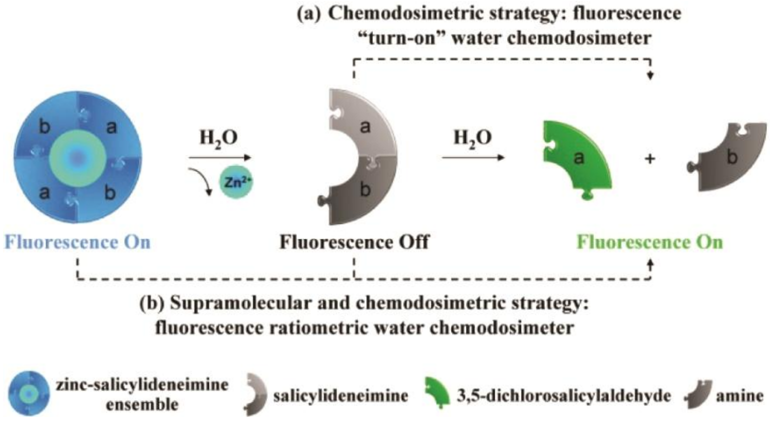


Fig. 11. Schematic representation of the water detecting mechanisms of (a) salicylideneimine and (b) zinc-salicylideneimine ensemble, respectively.

chemodosimeter in presence of water first dissociates to a non-fluorescent Schiff-base compounds from supramolecular assembly of Zn(II) and then again undergoes hydrolysis reaction and produces starting materials viz. 2-phenethylamine (PEA)and fluorescent 3, 5-dicholorosalicylaldehyde (BCSA) (**Fig.12**). Actually the blue fluorescent Zn (II) supramolecular chemodosimeter in presence of water converted to green fluorescent 3, 5-dicholorosalicylaldehyde. This novel probe showed high sensitivity towards water and could reach exceptionally low detection limits of 77 ppm in methanol solvent.

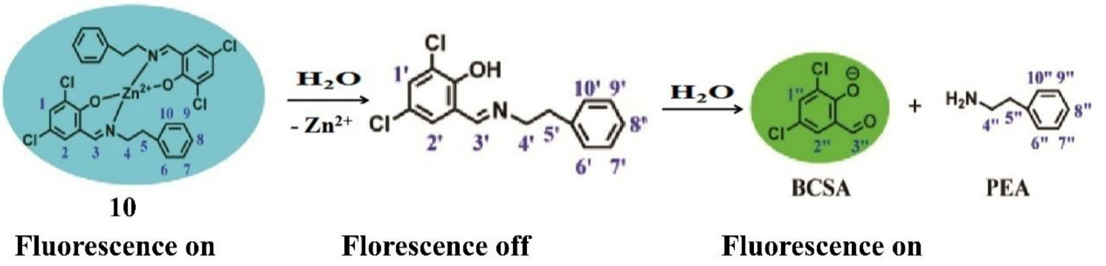
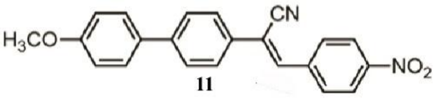


Figure 12. Schematic representation of water sensing mechanism of supramolecular andchemodosimetricprobe 10 in methanol and THF.



11

Very recently, Zhang et al. 2017developed a novel solvatochromic fluorescence sensor based on cyanostilbene derivative (**11**) having methoxy and nitro groups which act as an electron donating and electron accepting group respectively. The emission intensity of the probe (**11**) readily shows red shift with change in polarity of the solvent because of the intermolecular charge transfer (ICT) between electron donor and acceptor groups. Best sensitivity of **11** was found in detecting trace amounts of water in THF and dioxane solvent. Moreover this group developed test paper strips by loading 11into the paper in a very simple way and thus developed a simple and low cast protocol for the detection of the water content inorganic solvents. Thus this work open up a new window for developing more cyanostilbene derivatives with solvatochromism properties and find potential application in sensing.

CONCLUSION

The approaches discussed above in this review provide examples of the designing and mechanistic aspects of recently reported fluorogenic chemosensors for the detection of water molecules. Most of the systems are based on PeT, FRET, ICT, AIE etc. with various types of H_2O responsive moieties. Also probes discussed above exhibited very low detection limit (LOD) value towards water. Though, many of them still have limitations e.g. long response time and high back ground emission. Although, it is strongly desirable to develop novel fluorescent chemosensors with high sensitivity, and quick response for real-time detection of water for practical applications.

Acknowledgements

K.D. acknowledges the Department of Science and Technology (DST), Fast track research grand, New Delhi (vide project no. SB/FT/CS-142/2012) for financial support.

REFERENCES

Wang, Q. Li, X. Wang, L. Cheng, Y. and Xie, G. (2005). Effect of Water Content on the Kinetics of *p*-Xylene Liquid-Phase Catalytic Oxidation to Terephthalic Acid,Ind. Eng. Chem. Res., 44(13): 4518-4522.

Nussbaum, R. Lischke, D. Paxmann, H. and Wolf, B. (2000). Quantitative GC determination of water in small samples, Chromatographia, 51(1/2): 119-121.

Tsamis, E.D. and Avaritsiotis, J.N. (2005). Design of planar capacitive type sensor for “water content” monitoring in a production line, Sens. Actuators, A, 118(2): 202-211.

Fischer, K. (1935). Neues Verfahrenzurma ßanalytischen Bestimmung des Wassergehaltes von Flüssigkeiten und festen Körpern**,** Angew. Chem., 48(26): 394-396.

Liang, Y. Y. (1990). Automation of Karl Fischer water titration by flow injection sampling, Anal. Chem., 62(22): 2504-2506.

Niu, C.G. Guan,A.L. Zeng, G.M. Liu, Y.G. andLi, Z.W. (2006). Fluorescence water sensor based on covalent immobilization of chalcone derivative,Anal. Chim. Acta, 577(2): 264-270.

Ooyama,Y. Egawa, H. and Yoshida, K. (2009). The design of a novel fluorescent PET sensor for proton and water: A phenylaminonaphtho [1,2-*d*]oxazol-2-yl-type fluorophore containing proton donor and acceptor groups, Dyes and Pigments, 82(1): 58-64.

Hong, Y. N. Lam, J. W. Y. and Tang,B. Z. (2009). Aggregation-induced emission: phenomenon, mechanism and applications, Chem. Commun., 4332-4353.

Yu, G.C. Li, J.Y. Yu, W. Han, C.Y. Mao, Z.W. Gao, C.Y. and Huang, F.H. (2013). Carbon Nanotube/ Biocompatible Bola-Amphiphile Supramolecular Biohybrid Materials: Preparation and Their Application in Bacterial CellAgglutination, Adv. Mater., 25(44): 6373-6379.

Ooyama, Y. Egawa, H. and Yoshida, K. (2008).A New Class of Fluorescent Dye for Sensing Water in Organic Solvents by Photo-Induced Electron Transfer – A (Phenylamino) naphtha [1,2-*d*]oxazol-2-yl-Type Fluorophore with both Proton-Binding and Proton-Donating Sites, Eur. J. Org. Chem., (31): 5239-5243.

Li, Z. Yang, Q. Chang, R. Ma, G. Chen, M. Zhang, W. and Li, Z. (2011).*N*-Heteroaryl-1, 8-naphthalimide fluorescent sensor for water: Molecular design, synthesis and properties, Dyes and Pigments, 88(3): 307-314.

Ooyama, Y. Sumomogi, M. Nagano, T. Kushimoto, K. Komaguchi, K. Imae, I. and Harima, Y. (2011). Detection of water in organic solvents by photo-induced electron transfer method, Org. Biomol. Chem., 9(5): 1314-1316.

Ooyama, Y. Matsugasako, A. Nagano, T. Oka, K. Kushimoto, K. Komaguchi, K. Imae, I. and Harima, Y. (2011). Fluorescence PET (photo-induced electron transfer) sensor for water based on anthracene-amino acid, J. Photochem. Photobiol., A, 222(1): 52-55.

Ooyama, Y. Matsugasako, A. Hagiwara, Y. Ohshita, J. and Harima, Y. (2012). Highly sensitive fluorescence PET (photo-induced electron transfer) sensor for water based on anthracene–bisboronic acid ester, RSC Adv., 2(20: 7666-7668.

Kim, K.-H. Lee, W.-J. Kim, J. N. and Kim,H. J. (2013). An off-on Fluorescent Sensor for Detecting a Wide Range of Water Content in Organic Solvents, Bull. Korean Chem. Soc., 34(8): 2261-2266.

Men, G. Zhang, G. Liang, C. Liu, H. Yang, B. Pan, Y. Wang, Z. and Jiang, S. (2013).A dual channel optical detector for trace water chemodosimetry and imaging of live cells, Analyst, 138(10): 2847-2857.

Zío1ek, M. Burdzínski, G. Filipczak, K. Karolczak, J. and Maciejewski, A. (2008). Spectroscopic and photophysical studies of the hydroquinone family of photochromic Schiff basesanalyzed over a 17-orders-of-magnitude time scale, Phys. Chem. Chem. Phys., 10(9): 1304-1318.

Fabian, W.M.F. Antonov, L. Nedeltcheva, D. Kamounah, F.S. and Taylor, P.J. (2004). Tautomerism in Hydroxynaphthaldehyde Anils and Azo Analogues: a Combined Experimental and Computational Study, J. Phys. Chem. A, 108(37): 7603-7612.

Turbeville, W. and Dutta, P. K. (1990). Spectroscopic studies of the photochromic molecule N-(2-hydroxybenzylidene) aniline and its photoproduct, J. Phys.Chem., 94(10): 4060-4066.

Zhang, Y. Li, D. Li, Y. and Yu, J. (2014). Solvatochromic AIE luminogens as supersensitive water detectors in organic solvents and highly efficient cyanide chemosensors in water**,** Chem. Sci., 5(7): 2710-2716.

Men, G. Chen, C. Liang, C. Hana, W. and Jiang, S. (2015). A novel cascade strategy with supramolecular and chemodosimetric methods for designing a fluorescent ratiometric detector hypersensitive to trace water, Analyst, 140 (16): 5454-5458.

Zhang, Y. Liang, C. and Jiang, S. (2017). A solvatochromic cyanostilbene derivative as an intensity and wavelength-based fluorescent sensor for water in organic solvents, New J. Chem., 41(16): 8644-8649.

***Corresponding authors: [1]Dr. Krishanu Sarkar, Department of Chemistry, Netaji Mahavidyalaya, Arambagh,Hooghly, West Bengal, India.**

[2]Dr. Koushik Dhara, Department of Chemistry, Sambhu Nath College, Labpur, Birbhum 731303, West Bengal, India. Email: krishanu79@gmail.com; dharachem@gmail.com