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Fluorescent and colorimetric sensors for detection of humidity or water content

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Abstract

In this tutorial review, we describe the current state of the art in water sensors and provide an overview into the major advances made in this field post 2000. The field is currently still in its early development stages and subject to continuous improvements, and the current work provides a structured approach describing the different sensing mechanisms and potential future applications associated which each of these. With these developments and their potential implications for the diverse scientific fields requiring tight control over the water content, we strongly believe the discipline is potentially at the threshold of translation into more widespread application and we hope the current review might allow for an expedited process thereof.

Key learning points

1. The general concept and importance of detecting water in chemical reactions and industrial processes.
2. What are the design strategies for optical water responsive probes?
3. The diversity of water sensing mechanisms such as photo-induced electron transfer, intramolecular charge transfer, proton transfer, water-induced decomplexation of dyes, water-induced interpolymer π-stacking aggregation, solvatochromism, etc.

4. The diversity of water sensing systems such as association based probes, reaction based probes and probes based on physical interactions.
5. Perspectives and potential future directions for the design of optical water sensors.

1. Introduction

The detection and quantitation of water, being the most common impurity in organic solvents is of crucial importance in chemical reactions and industrial applications alike.[1] For example, in chemistry, particularly in organometallic chemistry, the presence of water will lead to the quenching of the reactive organometallic compounds, inhibiting the reaction or lowering the yields, and furthermore due to the high reactivity of the aforementioned organometallic reagents, the presence of water can under some circumstances lead to catastrophic failures, such as fires and explosions. An example of an industrial process where the presence of water plays a crucial yet detrimental role, is petroleum based fuels. The presence of water will cause a drop in an engine's performance, but more importantly, when the temperature is low enough, emulsification and phase separation may occur, causing clogged fuel ducts, leading to engine damage and failure.

Classic and currently industry-wide methods for the determination of water content are based on electrochemical and electrophysical sensing mechanisms,[2] the scopes of which fall outside the current review. The wide applications of these methods are due their robustness and ease of calibration and use. However their limitations include a lack of portability and precision and, due to the electronic systems at the core of the method, are liable to electromagnetic radiation. In the laboratory scale the most broadly used technique is the Karl-Fisher titration.[3] This method, originally developed in the 1930's is based on the simultaneous reaction of iodine and water (eqn (2)) with a premade alkyl sulphite reagent (eqn (1)). The consumption of a known amount of iodine, detected by either a volumetric (for relatively high amounts of water, >0.1%) or a colorimetric approach (most suitable for low amounts of water, <0.1%), can thus be correlated to the amount of water introduced to the system. The virtually universal detection range of the method (0.001–100% H_2O) and the relatively straightforward applicability provides a rational to the method's popularity. A major disadvantage however is the inability of real-time monitoring of the water content, as this method require *ex situ* analysis, as outlined above.

$$\mathrm{ROH} + \mathrm{SO_2} + \mathrm{B} \longrightarrow \mathrm{(BH)SO_3R} \qquad (1)$$

$$\mathrm{(BH)SO_3R} + \mathrm{I_2} + \mathrm{H_2O} + 2\,\mathrm{B} \longrightarrow 2\,\mathrm{[BH]I} + \mathrm{[BH]SO_4R} \qquad (2)$$

(ROH: alcohol, usually methanol or ethanol and B: base, frequently imidazole or pyridine)

In order to overcome the limitations of the two most popular methods described above, recent research has focussed on developing highly sensitive methods for the *in situ* analysis of water content in organic solvents. The progress reported in this tutorial review focusses on fluorescent and colorimetric molecular sensors, as the sensitivity and detection limits of these methods as well as their straightforward application are ideally suited for this purpose. When comparing the sensitivity of colorimetric and fluorescent sensors, generally speaking fluorescence allows for greater sensitivity and is thus associated with lower detection limits. The reason for this observation is that whilst the absorbance is a relative method, the absorbance being the logarithm of the ratio of the intensities of light emitted by the light source and transmitted through the sample, the fluorescence intensity is directly related to the intensity of the light source, where the intensity of emitted light under the form of fluorescence is a fixed percentage of the intensity of the light source. Thus the use of a more intense light source will greatly affect the fluorescent signal, but not the absorbance, resulting in a more sensitive method. In the following sections we will show an overview of the recent advances as reported in the literature (since 2000), categorised by the sensing mechanism underlying their mode of action. The current tutorial review describes the state of the art in water sensors and is not meant to be exhaustive but merely represents what we believe to be to major advances to the field in recent years.

In order to compare the results obtained from the sensors based on various optical detection mechanisms, the limit of detection (LOD) and the limit of quantitation (LOQ) firstly need to be defined. The limit of detection is defined as the lowest concentration at which an analyte can be sensed over the noise with a high degree of certainty. Generally, this condition is said to be fulfilled when an analyte can be sensed with a signal over noise ratio of 3 (or alternatively if the signal is three times as high as the standard deviation of the blank). And the LOQ is analogously defined as the lowest concentration that can confidently be quantified. Practically this is defined as a signal over noise ratio of 10 (thus if the signal is ten times as high as the standard deviation of the blank). These concentrations and their detection classification are, as far as available in their respective primary literature sources, summarised in Table 1 for the probes discussed in this tutorial review.

2. Association based systems (Chemosensors)

A first class of sensors for the water content of organic solvents is based on the reversible association of water with a vital part of the sensor. The association of water will cause a change in either the fluorescence intensity or the wavelength of emission of the probes through a variety of mechanisms as outlined below. This type of sensor, where the fluorophore detects a reversible change in its immediate environment is known as a chemosensor.

2.1 Photo-induced electron transfer (PET)

Photo-induced electron transfer (PET) is a physical quenching process where an electron transfer occurs from the receptor (as a host) to the excited fluorophore in the absence of a guest molecule (*in casu* the analyte). For this process to occur, the energy level of the highest occupied molecular orbital (HOMO) of the receptor needs to have an energy intermediate of the lowest unoccupied molecular orbital (LUMO) and the HOMO of the fluorophore. The molecular architecture of PET-based sensors generally consists of a receptor bound to an energy matched fluorophore through a spacer. Upon excitation, as a result of the electron transfer process, a charge recombination ensues, resulting in the return to the ground state and thus precludes the fluorescence process. Upon host-guest recognition by the receptor and its analyte, the HOMO energy level is shifted outside of the crucial HOMO-LUMO gap of the fluorophore, and the electron transfer becomes energetically unattainable and thus the emission of photons under the form of fluorescence is observed as outlined in Fig. 1. We direct the reader to a recent review for a more in depth discussion of this phenomenon.[4] With the use of this approach, reliable optical water sensors have been designed by controlling suitable receptors and their respective energy levels.

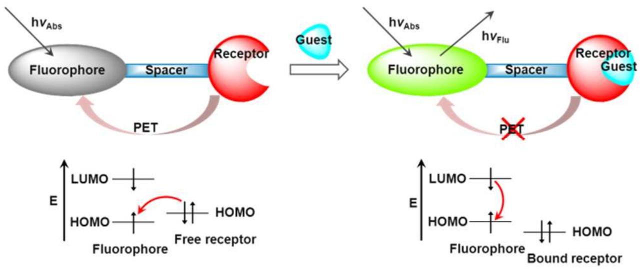

Fig. 1 The general concept of the principle of PET fluorescence sensor.

The scope of PET based water sensing systems in organic solvents has been explored to a great extent by Ooyama *et al.*. The earliest example, probe **1**, displayed a weak fluorescence in pure organic solvents due to a PET mechanism, which occurs from the appended dialkylamino residue to the naphtho[1,2-d]oxazole.[5] An intramolecular proton transfer of the carboxyl proton of **1** to the dialkylamino part occurred after the addition of water, resulting in strong fluorescence of **1** via PET suppression (Fig. 2). The water sensing mechanism of probe **1** was confirmed in their subsequent work through the comparison of semi-empirical molecular orbital calculations with the experimental spectral data.[6]

An exploration of the anthracene–aminobutyric acid system (**2**-**3**) was subsequently performed by Ooyama *et al.*.[7,8] Probe **2**, which consisted of an anthracene fluorophore, a methylene spacer, and a dialkylamino part as the proton binding site, showed a weak fluorescence in pure organic solvents. Probe **2** also bears a carboxyl unit as a proton donor for the initial recognition of water. In organic solvents, the addition of water to **2** enabled the intramolecular proton transfer from the carboxyl proton of **2** to the dialkylamino group resulting in a highly fluorescent zwitter ionic structure (Fig. 2). The LOD and LOQ of **2** for water were, respectively, 0.1 and 0.4 wt% in tetrahydrofuran (THF), 0.1 and 0.3 wt% in 1,4-dioxane, 0.1 and 0.4 wt% in acetonitrile (MeCN) and 0.1 and 0.2 wt% in ethanol (EtOH).[7] An improved response was observed in the case of PET sensor **3**, decorated with two carboxyl groups.[8] Probe **3** exhibited a more efficient sensing behavior than **2**, due to the increased pK_a of the first proton dissociation from the carboxylic acid and thus a more readily formed zwitter ion (Fig. 2). The LOD and LOQ of **3** for water were, respectively, 0.1 and 0.3 wt% in 1,4-dioxane, 0.4 and 1.2 wt% in THF, 0.1 and 0.3 wt% in MeCN and 0.1 and 0.3 wt% in EtOH.

Ooyama *et al.* further explored a structure activity relationship of a series of anthracene–boronic ester systems (**4-8**) for detection of water in organic solvents (Fig. 2).[9-12] In these systems, a boronic pinacol ester moiety was adopted as the proton donor source due to the higher Lewis acidity of boron atoms *vs.* the carboxylic acids used above. Furthermore the more lipophylic pinacol ester exhibited the additional benefit of increased solvent solubility of these probes.

Probe **4**, which serves as a reference structure to illustrate the effect of the structural modifications of the other anthracene-boronic esters in this series, exhibited an increased fluorescence after the addition of increasing amounts of water in organic solvents, resulting from the hydration of the boron ester, succeeded by a proton transfer, thus generating a fluorescent zwitter ionic structure. The LOD and LOQ of **4** for water were, respectively, 0.2 and 0.7 wt% in 1,4-dioxane, 0.2 and 0.5 wt% in THF, 0.04 and 0.1 wt% in MeCN and 0.04 and 0.1 wt% in EtOH.[9]

In a similar approach to the di-substitution of proton donors in the carboxylic acid series (**2-3**) the anthracene–bisboronic ester system **5** showed a better sensing efficacy to water than **4**, due to increase of the Lewis acidity of two boron atoms facilitating a more readily formed zwitter ionic probe.[10] The LOD and LOQ of **5** for water were, respectively, 0.018 and 0.054 wt% in 1,4-dioxane, 0.014 and 0.042 wt% in THF, 0.013 and 0.040 wt% in MeCN and 0.007 and 0.021 wt% in EtOH.

In 2013, anthracene–boronic ester **6** and anthracene–bisboronic ester **7**, with the boronic ester directly attached to the 10-position on the fluorophore core, were reported.[11] In these systems, the addition of water proceeds with the hydration of the boron atom on the 10-position but the formation of the fluorescent zwitter ionic compounds was not observed. Upon the addition of water to probes **6** or **7** negligible fluorescent changes occurred. These results demonstrate the crucial importance of the ability to form zwitter ionic structures as a consequence of proton transfer to the quenching of the PET effect, and thus the sensing of minute concentrations of water.

The importance of the Lewis-acidity of the proton donor was further illustrated by the highly-sensitive fluorescence PET sensor **8** containing a nitrile unit as an electron-withdrawing group at the *para* position of the benzeneboronic ester, stabilizing the anionic boronic species.[12] The LOD and LOQ of **8** for water in organic solvents were, respectively, 0.01 and 0.03 wt% in 1,4-dioxane, 0.008 and 0.026 wt% in THF, 0.009 and 0.026 wt% in MeCN and 0.009 and 0.027 wt% in EtOH, which were much lower than those of the unsubstituted sensor **4** and even lower than the bis-boronic acid probe **5** (see also Table 1).

Kim *et al.* reported a 1,8-naphthalimide derivative **9** linked to a piperazine group and a carboxylic acid, for the detection of a wide range of water contents in organic solvents.[13] A drastic increase in fluorescence was observed subsequent to the addition of water to **9**, induced by PET suppression, after the protonation of the tertiary amine of piperazine (Fig. 2). The probes showed a sigmoidal response to the water content with wider detection ranges, respectively, from 0% to ~80% (*v*/*v*) in EtOH, DMF and dimethyl sulfoxide (DMSO), and from 0% to ~90% (*v*/*v*) in acetone, with fairly broad ranges of a pseudo-linear relationship for intermediate water contents.

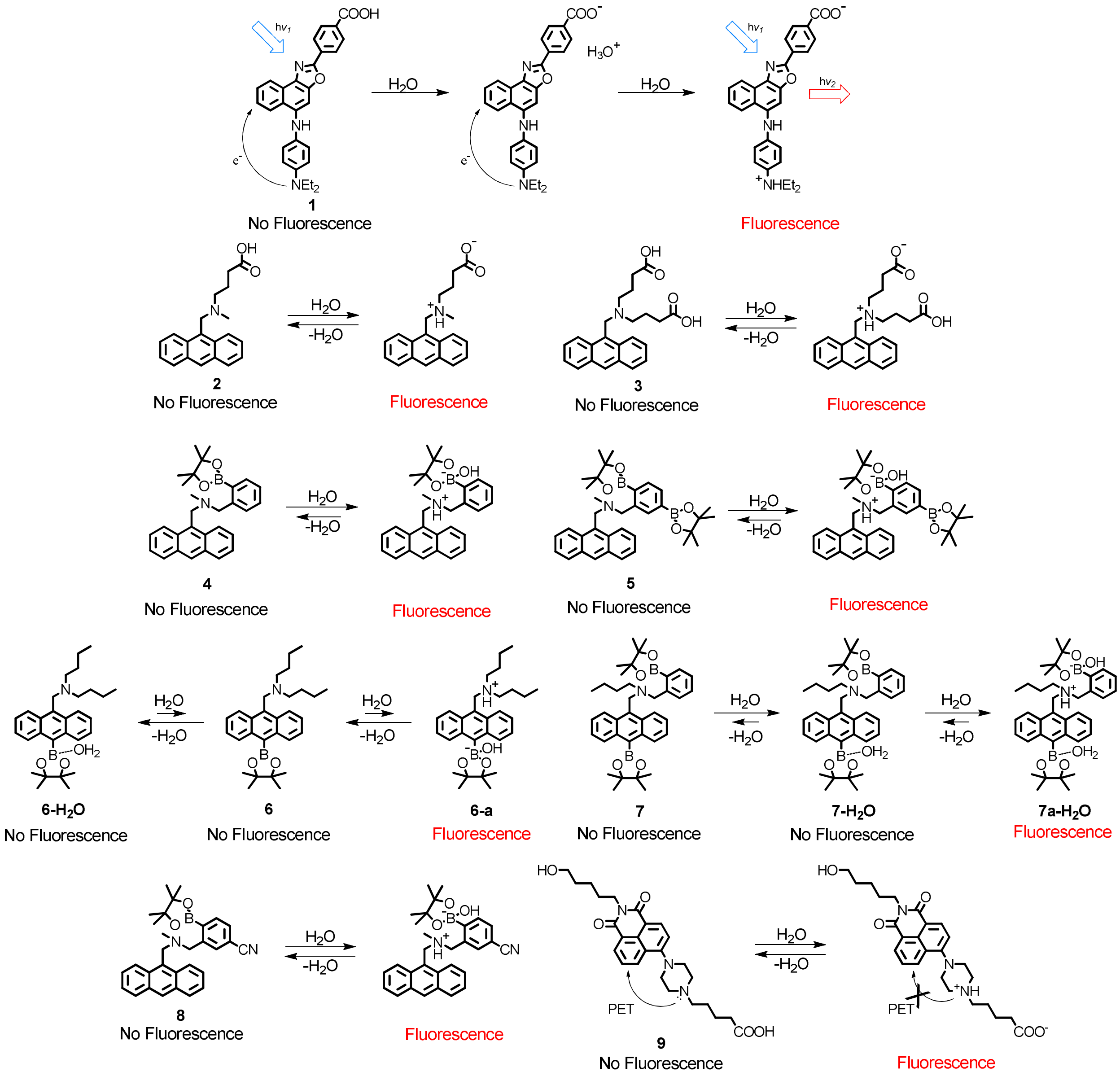

Fig. 2 Proposed mechanisms for fluorescent water-sensors **1-9** by PET.

2.2 Intramolecular charge transfer (ICT)

In intramolecular charge transfer (ICT) sensors, the fluorophore and the receptor are directly connected, thus creating a single entity, with the two functionalities acting as either an electron donor or an electron acceptor generally at opposite ends of the molecule. Whereas the HOMO of the sensor has the highest electron density near the electron-donating moiety, the LUMO has the highest electron density near the acceptor end, thus a strong dipole with charge transfer from the donor to the acceptor is created upon excitation (Fig. 3A). The addition of an analyte (*in casu* water) can result in preferential bonding at either the electron donor or acceptor regions, thus causing an alteration in the dipole strength of the donor-acceptor couple, which is generally associated with changes of intensities and spectral shifts,[14] in contrast to PET-based fluorescent water sensors. The topic has been reviewed in great depth by de Silva *et al.* and we direct the reader to this excellent review for further reading.[15]

Citterio *et al.* reported the fluorescent donor-acceptor acridinyl indicator **10** for water in organic solvents.[16] The fluorescence response of **10** was explained by the formation of an excited state intramolecular charge-transfer *via* a hydrogen bond interaction between the indicator dye (as a H-bond acceptor) and water (as a H-bond donor) (Fig. 3B). A probe **10**-immobilized polymeric membrane was also prepared by a covalent immobilization method, and can be used for the real-time monitoring of the amount of water in a flow-through system. The probe was shown to be very sensitive to water with a LOD of 0.001 wt% in diethyl ether, 0.003 wt% in THF, 0.003 wt% in ethyl acetate (EtOAc) and 0.005 wt% in MeCN, respectively.

Another water sensing membrane was developed by copolymerizing a donor-acceptor probe **11** on a glass slide showing a superior analytical efficacy for water detection in MeCN (Fig. 3B).[17] In the range of 0–6% (*v*/*v*) in organic solvents the fluorescence of this membrane linearly decreased as a function of the water content. Using this membrane, the LOD for water is 0.006 wt% in acetone, 0.008 wt% in EtOH, and 0.002 wt% in MeCN, respectively.

Naphthalimide is another excellent candidate for ICT-based sensors, due to its unique donor-acceptor behavior. This fluorophore, containing an aromatic amine as the electron donor and naphthalimide as the acceptor, shows ICT behavior that is highly dependent upon solvent polarity or water, indicated by fluorescence changes. Hence this class of fluorophores has been studied in a number of recent works.[14]

Niu *et al.* prepared a water sensing membrane with covalently immobilized naphthalimide derivative **12** showing fluorescence quenching behavior (Fig. 3B).[18] The sensor was working within a wide pH range (pH 1~13), showed good reproducibility and reversibility, as well as fast responsive times. The LOD for water is 0.008 wt% in 1,4-dioxane, 0.006 wt% in MeCN, and 0.015% in EtOH, respectively.

The same group subsequently reported ICT-based probe **13** (Fig. 3B), a sensor for which the fluorescence intensity decreased as a linear function of water content, in the range of 0.00 – 4.00% (*v*/*v*).[19] The LOD of **13** for water was 0.019 wt% in 1,4-dioxane, 0.038 wt% in MeCN, and 0.060 wt% in EtOH, respectively.

Li *et al.* studied a small library of different *N*-substituted naphthalimide derivatives **14-16** as ICT-based water-responsive fluorescence probes (Fig. 3B).[20] The introduction of an electron deficient pirimidyl group to this fluorophore, increasing the electron deficiency of the acceptor moiety, induced the enhanced sensitivity of **16** to solvent polarity compared with **14** and **15**, making it a sensitive fluorescent water sensor. The fluorescence intensity at 510 nm decreased linearly as a function of the water content with the LOD of **16** being 0.049 wt% in 1,4-dioxane, 0.020 wt% in THF, 0.016 wt% in acetone, and 0.021 wt% in MeCN, respectively.

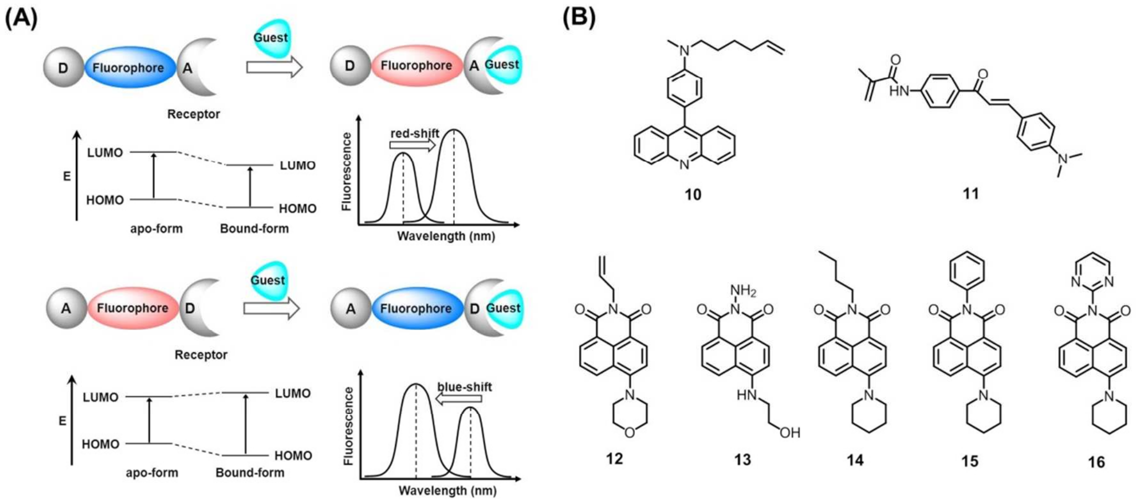

Fig. 3 (A) The general concept of the principle of ICT fluorescence sensors. (B) Molecular structures of water sensors **10**-**16** by ICT.

2.3 Exited state intramolecular proton transfer (ESIPT)

Excited state intramolecular proton transfer (ESIPT) fluorophores are a special class of fluorophores exhibiting the possibility of proton transfer between two sites of the molecule, typically found to be keto-enol tautomers. In these systems the preferred tautomer in the ground state is different from the one in the excited state leading to the transfer of a proton upon excitation. As a result of this, the wavelength of emission is shifted to a longer wavelength than would be expected in the absence of the process, as can be seen from Fig. 4A. We direct the reader to a recent review concerning this type of fluorophores.[21]

Fluorescence sensors based on excited-state intramolecular proton transfer (ESIPT) have increasingly been found to be highly useful due to their unique features such as intense luminescence, significant photostability and the aforementioned large Stokes' shift. As water can act both as a hydrogen bond donor and a hydrogen bond acceptor, as such the addition of water causes a perturbation of the ESIPT process. Applications will however likely be limited to aprotic solvents, as the interference from proton transfer between the probe and the solvent presumptively would inhibit the probe's proper operation.

Mishra *et al.* exploited a salicylic acid doped poly(vinyl alcohol) (PVA) film as a fluorescent water/humidity sensor (Fig. 4B).[22] The film's fluorescence emission at 408 nm originated from the salicylate anion by an ESIPT process. The introduction of water to the film induces the protonation of the salicylic anion in the excited state, followed by a non-radiative decay pathway. The observed detection ranges are fairly large, from 0% to ~60% (*v*/*v*) in 1,4-dioxane/water mixtures and from 5% to ~ 85% (*v*/*v*) relative humidity with a good response time (2 min) and reversibility (<1 min).

Liu *et al.* proposed a solvatochromogenic flavon dye **17** for the determination of water in acetone solutions (Fig. 4C).[23] Probe **17** displays a specific emission band which is attributed to an ESIPT process *via* a pre-existing intramolecular hydrogen bond. The fluorescence enhancement of **17** upon the addition of water was explained by the inhibition of the excited state intramolecular proton transfer process through the formation of intermolecular hydrogen bonds between probe **17** and water molecules. Sensor **17** exhibited a detection range for water in acetone/water mixture from 0.0 wt% to 10.0 wt% with a LOD of 0.02 wt%.

Kim *et al.* proposed a 8-hydroquinoline based ESIPT fluorescent probe **18** for water in polar aprotic organic solutions (Fig. 4D).[24] Probe **18** shows photoinduced tautomerization followed by a relatively poor emission of fluorescence. Upon the exposure to water, a turn-off fluorescence response is observed, presumably due to the suppression of the tautomerization process by the intermolecular proton transfer between fluorophore and surrounding water molecules. The fluorescence response of **18** was linearly proportional to water contents lower than 1 wt% with a LOD as low as 0.006 wt% in THF, 0.05 wt% in 1,4-dioxane and 0.01 wt% in MeCN.

In 2007, Kumar *et al.* reported the application of 1-naphthol doped polyvinyl alcohol film **19** as an ESIPT sensor for water (Fig. 4D). The addition of water to the film showed that an fluorescent intensity decrease at 342 nm (1-naphthol) while a concomitant increase was observed at 464 nm (1-naphtholate). The fluorescence response of **19** with increasing water content was explained by ESIPT perturbation via polymer hydration in the initial stage of swelling. The correlation of the results from differential scanning calorimetry and fluorescence experiments with a model of PVA swelling further supported the proposed mechanism.[25]

Flavilium-based probes **20** and **21** (Fig. 4D) were prepared as solid phase fluorescent sensors for water and humidity.[26] These flavylium compounds exhibit a unique ESIPT fluorescence, correlated to greatly diminished charge densities of the phenolic moieties upon excitation. In the presence of water, a fluorescence quenching response was observed by ESIPT perturbation. These sensors, when encapsulated in polymer hydrogels were observed to perform well as solid phase fluorescent sensors for water. Combining the high sensitivity of the flavylium fluorophores towards water, and the hygroscopic nature of the polymeric system, provides this sensor with a high sensitivity as an ambient humidity sensor.

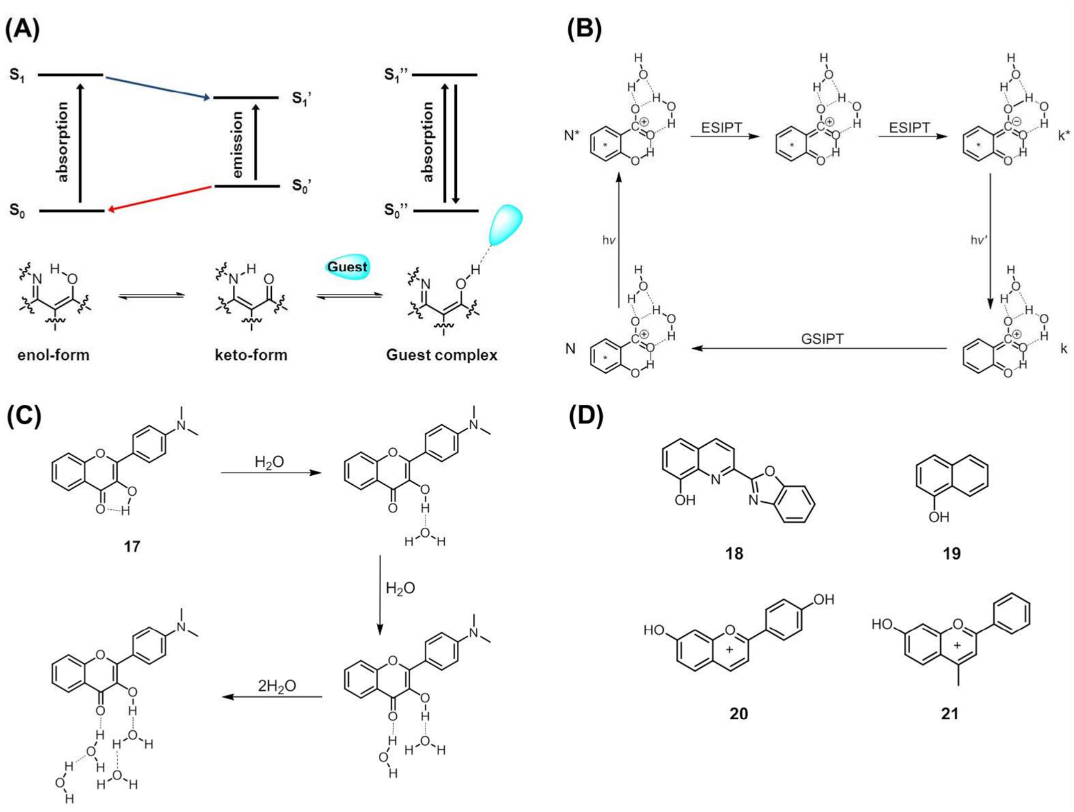

Fig. 4 (A) The general concept of the principle of ESIPT fluorescence sensor. (B) Representative scheme explaining the changes in ESIPT process of a salicylic acid for water (GSIPT: ground state intramolecular proton transfer). (C) Proposed mechanism for flavon water-sensor **17** by ESIPT. (D) Molecular structures of ESIPT-based water sensors **18**-**21**.

2.4 Water as a competitive ligand

The emission from the *f-f* transitions of lanthanide ions cover a broad range from the UV region to the NIR, however these transitions are generally Laporte forbidden and thus very weak. By coordinating these ions with suitable organic ligands, excitation of the ligand and subsequent population of the excited state levels of these lanthanide ions can circumvent this problem, an observation known as the antenna effect.[27] The excited states of the lanthanide ions are nonetheless sensitive to quenching by water and the effect is proportionate to the number of water molecules in the first coordination sphere of the lanthanide ion (*i.e.* the number of water molecules directly bound to the lanthanide ion). We direct the reader to a recent review for a more in depth discussion of the fundamental principles underlying these observations.[27]

This effect has been judiciously utilized by Gao *et al.* to construct water sensors based on the water induced de-excitation of the octa-coordinate Eu(HTTA)$_3$Phen complex **22** (Fig. 5A).[28] In this complex, the ninth coordinate position of the Eu ion is left unoccupied, and the addition of water to **22** leads to a linear decrease in fluorescence intensity in the 0.05–6.0 wt% range. The LOD of **22** for water was found to be 0.002 wt% for EtOH.

Song *et al.* prepared coordination compound **23**, which exhibits a strong red luminescence (Fig. 5A).[29] Increased water contents result in the displacement of two coordinated DAF(4,5-diazafluorene) ligands and one NO_3^-. A weak intraligand transition emission was observed instead of the characteristic strong red emission originating from the sensitized Eu^{3+} ion's *f*-*f* transition. The fluorescence response of **23** upon the addition of water (0.03–6.67 wt%) shows a linear relationship at low water concentrations (0–0.33 wt% in MeCN). The LOD of **23** for water was found to be 0.003 wt% in MeCN.

Water as a competitive agent for coordination/complexation is not only observed in inorganic lanthanide complexes, but can equally be adapted to organic sensors. The first examples were reported by Kim *et al.* and consisted of the dye–anion ensemble systems (**24**-OAc and **25**-OAc) as water sensors that use the water-induced disruption of dye-acetate complexes as a signaling mechanism (Fig. 5B).[30] System **24**-OAc showed a prominent colorimetric signaling change from red (536 nm) to yellow (426 nm) in solvents such as MeCN and THF with the addition of water (up to 1 and 2%). The LOD of **24**-OAc for water in MeCN and THF was 0.037 wt% and 0.071 wt%, respectively. **25**-OAc showed significantly less sensitive signaling behavior, with a respective LOD of 0.12 and 0.63 wt% in MeCN and THF, most likely caused by a stronger dye-acetate anion interaction.

Fluoride ion, being a weak base in aqueous environments, was used by Kim *et al.* to apply the deprotonation (and reversible protonation) of anion receptor **26** to water sensing (Fig. 5B).[31] With increasing water contents, a gradual shift from colorless (**26**·F) to yellow (**26**$^-$) was observed in the absorption spectrum of **26**-F. The sensor has a good water responsibility in the range of 0 to 0.35 wt% in MeCN and 0.2 to 0.5 wt% in DMSO.

Moon *et al.* also reported the fluoride complexes of phenolic dyes (**27**-**28**) for water sensing (Fig. 5B).[32] Dramatic ratiometric changes in the absorption spectra of **27**-F (634 nm to 455 nm) and **28**-F (584 nm to 380 nm) were observed. The LOD for water in MeCN were found to be 0.17 wt% for **27**-F and 0.16 wt% for **28**-F.

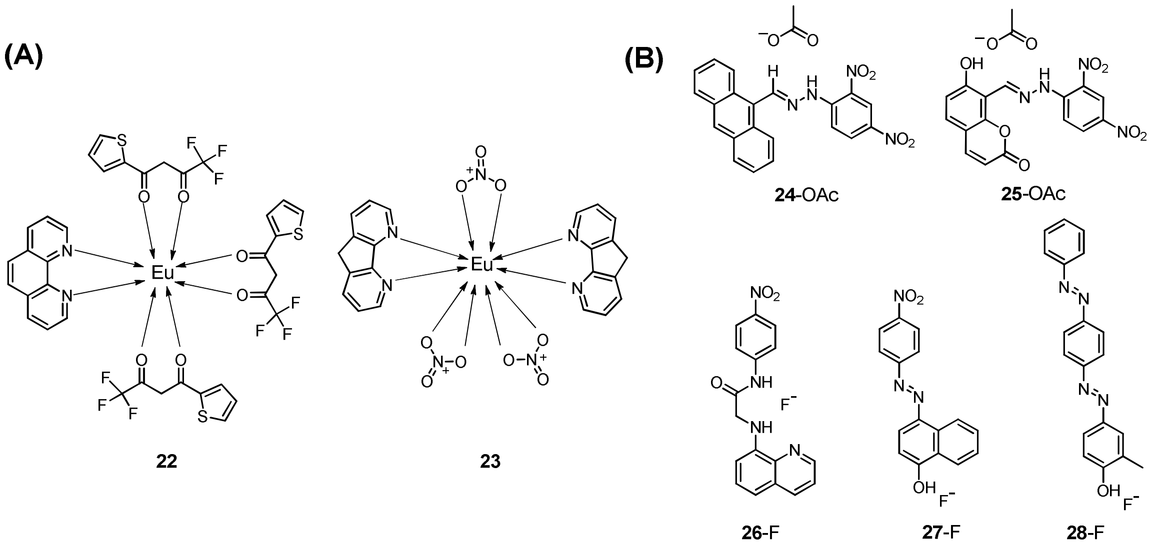

Fig. 5 (A) The structure of water sensors **22**-**23** based on europium ion coordination. (B) Molecular structures of dye–anion ensemble systems **24**-OAc, **25**-OAc, **26**-F, **27**-F and **28**-F.

3. Reaction-based water sensors (Chemodosimeters)

Reaction-based chemosensors (so called chemodosimeters) have emerged as complementary systems to the above described chemosensors, based on a noncovalent host-guest interaction strategy, to detect an specific analyte through a the formation or cleavage of covalent bonds. Since the first report by Czarnik in 1992,[33] reaction-based chemosensors for various analytes have been explored,[34] and we direct the readers to these reviews for further reading. Some chemodosimeters differ in a fundamental way from the chemosensors described above: whereas chemosensors, with their generally reversible non-covalent binding nature, are excellent sensors to detect peak exposure to an analyte, chemodosimeters based on non-reversible reactions find applications as sensors for the cumulative exposure over in a certain time domain. Chemodosimeters based on reversible reactions of course are most useful to measure peak exposure, similarly to chemosensors.

A first example of a water sensing chemodosimeter, based on a reversible reaction, was provided by Choi *et al.*, who studied a fluorescein-anthracene ensemble system **29** for the ratiometric detection of water content in acetone and MeCN (Fig. 6).[35] In response to the increase in water content, fluorescein displays a significant fluorescence response as water triggers the transformation from the relatively non-fluorescent closed from to highly fluorescent the spiro-ring opened structure. As the water content increased, this system exhibits fluorescence enhancement at 520 nm while the unaffected fluorescence of anthracene is used as an internal standard. The system shows appropriate sensing behavior in the aprotic solvents MeCN and acetone, especially in the lower concentration range (less than 2% water). The LOD for water was 0.035 wt% in MeCN and 0.11 wt% in acetone, respectively.

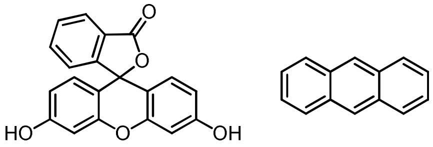

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Fig. 6 Fluorescein-anthracene ensemble system **29** for water.

Poteet *et al.* reported on the hydration reaction of water with quinines (Fig. 7A).[36] Probe **30** exhibited quenched luminescence with the predominant non-radiative decay pathway involving the quinone-based ligand, while the addition of water to **30** induced a long-lived ^{3}MLCT (triplet metal to ligand charge transfer) transition, as the addition of water to the quinone results in a geminal diol with an altered energy level, allowing a luminescent turn on response at 605 nm. Although the luminescence-based system allows for relatively easy and sensitive water detection in aprotic organic solvents, the slow response rate obviously presents a limitation to its utility.

A water-triggered Schiff base chemodosimeter **31** was reported by Men *et al.* (Fig. 7B).[37] Upon the addition of water to **31** (as low as 0.02 volume%) in methanol (MeOH), a Schiff base hydrolysis reaction was induced followed by a 2.23-fold fluorescence emission enhancement. The fluorescence of **31** proportionally increased as a function of the water content in the range of 0–35% for THF and 0–20% (*v*/*v*) for MeCN. The LOD and LOQ of **31** for water were, respectively, 0.0464 and 0.1405 wt% in THF, 0.0298 and 0.0902 wt% in MeCN and 0.0017 and 0.0052 wt% in MeOH.

Pal *et al.* most recently reported a förster resonance energy transfer (FRET) based rhodamine–benzimidazol ensemble system **32**, which can detect minute traces of water in organic solvents (Fig. 7C).[38] Förster resonance energy transfer is a non-radiative effect, where the energy from an excited chromophore is transferred to a second chromophore which can subsequently emit the light under the form of fluorescence, providing that the energy of the two chromophores is matched, a requirement generally fulfilled when the spectral overlap between the light normally emitted by the first fluorophore and the wavelength needed to excite the second chromophore is high. Thus excitation of the first fluorophore will result in light emitted by the second longer wavelength fluorophore (and a concomitant corresponding reduction of the light emitted by the first fluorophore). This process is also highly dependent, on the distance ($1/d^6$) between the FRET donor and the FRET acceptor and thus the second requirement is for the two chromophores to be spatially proximal. Addition of trace amounts of water into a solution of **32** leads to a rearrangement reaction which results in the formation of a spirolactam ring opened rhodamine analogue, conjugated to a 2-amino phenyl benzimidazole moiety. With the benzimidalzole showing a strong FRET effect, resulting in red fluorescence originating from the rhodamine subunit. The FRET efficiency of **32** linearly increased as a function of water content in the range of 1.43–25.7% for MeOH, 1.43–28.6% for DMSO and 1.43–20% *v*/*v* for MeCN. The LOD and LOQ were, respectively, 0.0033 and 0.0105 wt% in THF, 0.0032 and 0.0108 wt% in MeCN, 0.0044 and 0.0147 wt% in DMSO and 0.0026 and 0.0085 wt% in MeOH.

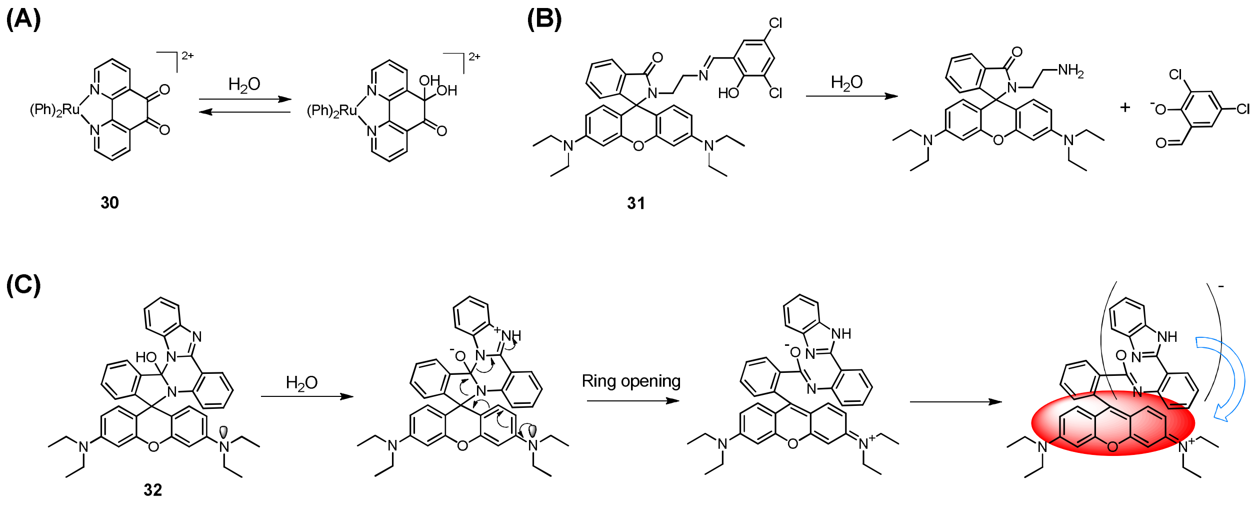

Fig. 7 Proposed water sensing mechanism for sensors (A) **30**, (B) **31**, and (C) **32**.

4. Probes based on physical interactions

4.1 Aggregation induced emission (AIE) of small molecules

Whereas traditional fluorophores, like the ones described above, exhibit fluorescence quenching upon aggregation, one particular class of fluorophores exhibits the inverse effect, *i.e.* upon full solvation of the fluorophore, the quantum yield of emission is extremely low and aggregation induces a turn-ON fluorescent behavior, known as the aggregation induced emission (AIE) effect. Generally speaking, for a compound to exhibit this seemingly contradictory effect, the molecule must consist of a highly conjugated structure with a high degree of rotational freedom, quenching the fluorescence by this mechanism. Aggregation restricts the rotation of the structure, thus eliminating the rotational (non-emissive) de-excitation pathway (also known as RIR, restriction of intramolecular rotation), as can be seen in Fig. 8A for tetraphenylethylene (TPE), one of the earliest known AIE fluorophores. The subject has been reviewed elsewhere and we direct the reader to this tutorial review for further reading.[39]

Zhang *et al.* reported tetraphenylethene (TPE) based donor-acceptor conjugates **33** and **34** containing dicyanovinyl groups as the acceptor (Fig. 8B).[40] Addition of trace amounts of water into a solution of these conjugates leads to significant amount of fluorescence quenching due to the combinational effects of the solvent polarity and the ICT process (see above) with a small red shift in the emission maxima (**33**: 562 nm to 581 nm; **34**: 561 nm to 579 nm) and shows a good linear response below 1 wt%. The LOD of **33** and **34** were determined to be, respectively, 0.0056 wt% for **33** and 0.0097wt% for **34** in THF. Upon the addition of large amounts of water (50 wt% and 40 wt% for **33** and **34**, respectively), the fluorescence emissions were greatly enhanced *via* both the restricted intramolecular rotation (RIR) process and a blocked ICT process, presenting blue-shifted emission bands (**33**: from 598 nm to 547 nm, **34**: from 595 nm to 565 nm).

A similar water sensing strategy using two novel 2,2’-biindenyl-based AIE probes **35** and **36** (Fig. 8B) was studied by Chen *et al.*.[41] A small fraction of water in an organic solution leads to fluorescence quenching of **35** and **36** along with a red shift from 597 nm to 617 nm. In contrast, large amounts of water (40% for **35** and **36**) resulted in aggregated environments, causative of restricted intramolecular rotations of *C*-*C* bond rotors of the probes and thus showed significant fluorescence emission. The fluorescence quenching behavior of **35** and **36** as a function of water content exhibited a good linear response below 1% (*v*/*v*), and the LOD of **35** for water was, respectively, 0.010 wt% in THF and 0.019 wt% in 1,4-dioxane.

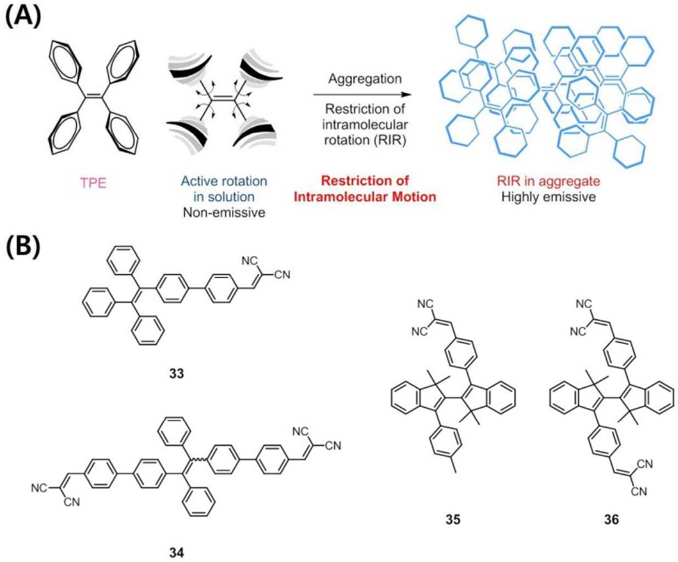

Fig. 8 (A) The general view of the principle of AIE. (B) Molecular structures of AIE probes **33**-**36** for water.

4.2 Aggregation based monomer-excimer/exciplex switching

Certain molecules, usually flat polycyclic aromatic hydrocarbons such as anthracene and pyrene, can exhibit the formation of excimers. That is, when one molecule is excited, this increases the affinity for an identical molecule in the ground state forming an excited dimer structure. After the emission of a photon, the affinity of the two ground state molecules for each other is lowered and the complex dissipates. Excimers only form under high monomer concentrations and their emission profile differs from that of the emission of only the monomeric species (*i.e.* under low concentrations) in that the fine structure is lost, resulting in a broad unstructured emission band with a considerably longer wavelength. Similarly, when the monomers are part of the same molecule, conformational changes can, in some cases, increase or decrease the intramolecular distance between the monomers thus affecting the ratios of monomer and excimer emission.

Zhao *et al.* prepared a butterfly shaped pyrene derivative **37** of cholesterol for the determination of water contents.[42] It was observed that this butterfly shaped molecule **37** responded to both a change in the polarity and the viscosity upon increasing amounts of water (Fig. 9A) as a solution in organic solvents, showed a greater extent of incorporation into aggregates, hence leading to a decreased intra- or intermolecular pyrene – pyrene distances in the aggregates and thus a higher degree of excimer *vs.* monomer emission with increasing amounts of water. The LOD of **37** for water in in MeCN, EtOH, MeOH and 1,4-dioxane is 0.0007, 0.06, 0.2, and 0.4% (*v*/*v*), respectively. Moreover, **37** also can be used to monitor viscosity.

Cho *et al.* recently described 1,8-naphtalimide based fluorophores **38** and **39** (Fig. 9B), whereas **38** is appended by an aliphatic chain only, **39** is further decorated with an electron rich phenothiazine unit.[43] The addition of incremental amounts of water into solutions of **38** or **39** in THF results in a fairly complex behavior (Fig. 9B), whereas initially the fluorescence arising from the naphtalimide unit increases with increasing amounts of water (up to 70% water for **38** and 50% for **39**) further addition of water decreases the fluorescence intensity of the emission at 350–450 nm. In the case of **38**, a concomitant increase in intermolecular excimer emission of the aggregated probe (with a fluorescent emission band centred around 475 nm) can be observed up to 94% water content. In the case of **39**, an increased emission band centred around 625 nm can be observed. Here, the emission is arising from the intramolecular exciplex emission of the probe. Similarly to excimers, exciplexes originate from the excited state coordination between two chromophores, but unlike the excimers, exciplexes arise between two non-identical chromophores. *In casu*, the excited state of the electron poor naphtalimide coordinates with the electron rich phenothiazine in the aggregated form of the dye at high water contents, resulting in a red-shifted emission. The initial nearly linear increase in monomer emission was explained by a polarity dependent ordering of the singlet and triplet excited state energies of napthalimide with the more polar (and protic) solvent conditions making the triplet state energetically inaccessible and thus increasing the fluorescence emission.

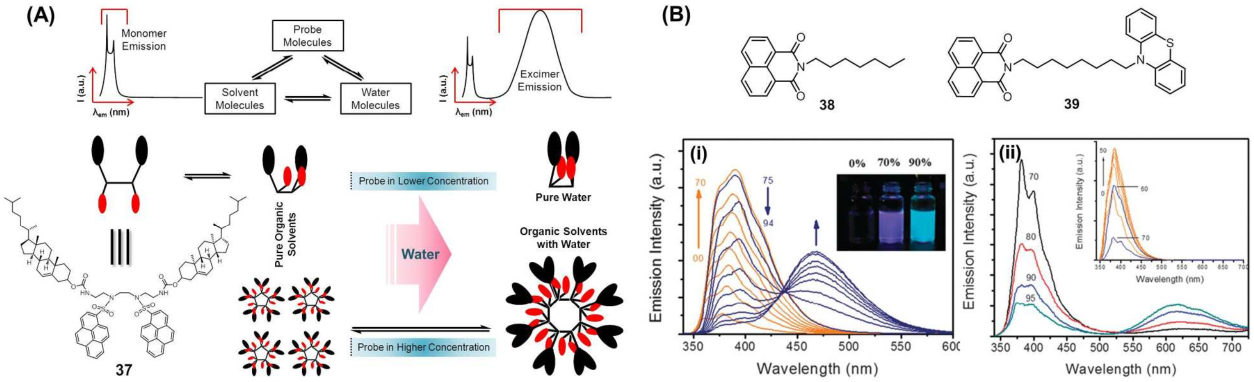

Fig. 9 (A) Schemetic diagram of water sensor **37**. (B) Structures of sensors **38** and **39** (top) and their response to increasing amounts of water ((i) **38** and (ii) **39**). (B) is reproduced with permission from ref. 43. Copyright 2014 the Royal Society of Chemistry.

4.3 Water induced interpolymer π-stacking aggregation

Highly π-conjugated polymers are responsive to their environment and their physical properties differs when organic solvents are added from the solid state (non-solvated) in a number of ways, both determined by their own structure and the physical properties of the materials they are joined with (if any). A first example was provided by Deng *et al.*, who prepared a highly sensitive fluorogenic polymer, poly(3-aminobenzoic acid) as a water sensing probe.[44] **40** (Fig. 10A) showed a strong fluorescence band at 402 nm, while the addition of water leads to fluorescence quenching in various organic solvents. The effect of **40** with water content was rationalized to be a result of interchain hydrogen bonding between water and **40** leading to increasing amounts of polymer aggregation, which in turn caused a perturbation of the conjugation and thus quenched the emission. Probe **40** exhibits a good linear response as a function water content in organic solvents (0–8.86 wt%). The LOD and LOQ of **40** for water were, respectively, 0.1 and 0.3 wt% in EtOH, 0.02 and 0.07 wt% in MeCN, 0.008 and 0.03 wt% in DMF and 0.009 and 0.03 wt% in *N*-methyl-2-pyrrolidone (NMP).

Poly[1-phenyl-2-(p-trimethylsilyl)phenylacetylene] (PTMSDPA) films exhibit an intramolecular stacked structure in the bulk solid state, the addition of various organic solvents leads to increased polymer swelling, and lesser amounts of intramolecular stacking, as witnessed by increased fluorescence intensities. An opposite effect (a decrease of fluorescence efficiency) is observed when water is added, due to a leaching of the organic solvents out of the polymer film and an associated deswelling of the polymers Lee *et al.* reported on a microporous PTMSDPA conjugated polymer based fluorescent actuator, responsive to the water concentration in a mixture of alcohol and water (Fig. 10B).[45] The actuator was composed of an active layer of PTMSDPA and a supporting layer of biaxially oriented polypropylene (BOPP), which was uncurled in pure EtOH, associated with a strong fluorescence intensity (by the mechanism described above). In contrast, the addition of water to the polymer gradually produced a curled film by polymer aggregation (and the associated decrease in the PTMSDPA thickness) with decreasing fluorescence intensities. The process was quite fast (1.2 s to uncurl completely and 2.0 s to re-curl), and reversible without the observation of fatigue.

A fluidic channel coated with a PTMSDPA based polymeric film for real-time monitoring of water in this flow based system was reported by same group (Fig. 10C).[46] The water-responsive fluorescence change was quite fast, reaching its equilibrium within several seconds in various organic solvents, showing a decreased fluorescence intensity. The authors successfully demonstrated the system’s utility as a convenient microfluidic lab-on-chip system for the on-line monitoring of trace amounts of water.

A recent remarkable addition to the field by Lee *et al.* reported on hydrochromic conjugated polydiacetylene target materials for detection of water (Fig. 10D).[47] This system was composed of a fluorogenic skeleton of conjugated polydiacetlylene (PDA) containing alkali metal salts of carboxylate head groups. These metal salts, in particular the cesium salt, introduced a hygroscopic element to the periphery of the conjugated PDAs, resulting in a hydrochromic conjugate polymer that is rapidly responsive to water because it leads to the formation of isolated domains of the conjugated backbone with significant electronic changes Whereas the exact mechanism underlying these observations is as yet not fully understood, a likely cause for the observed phenomena is the dissolution of unreacted monomers trapped in the polymer matrix upon the addition of water, thus relaxing the polymer's packing, resulting in the above mentioned isolated domains of the conjugated backbone. Interestingly, this system was employed to map human sweat pores as a novel way of fingerprint scanning. The very small amounts of water (sub-nanoliter) secreted from sweat pores is sufficient to promote an instantaneous color change, which is reversible upon heating the polymer film. As a result, this sensing system can be used to construct a precise map of active sweat pores on finger tips, complementing the traditional finger print recognition technique based on the analysis of ridge patterns.

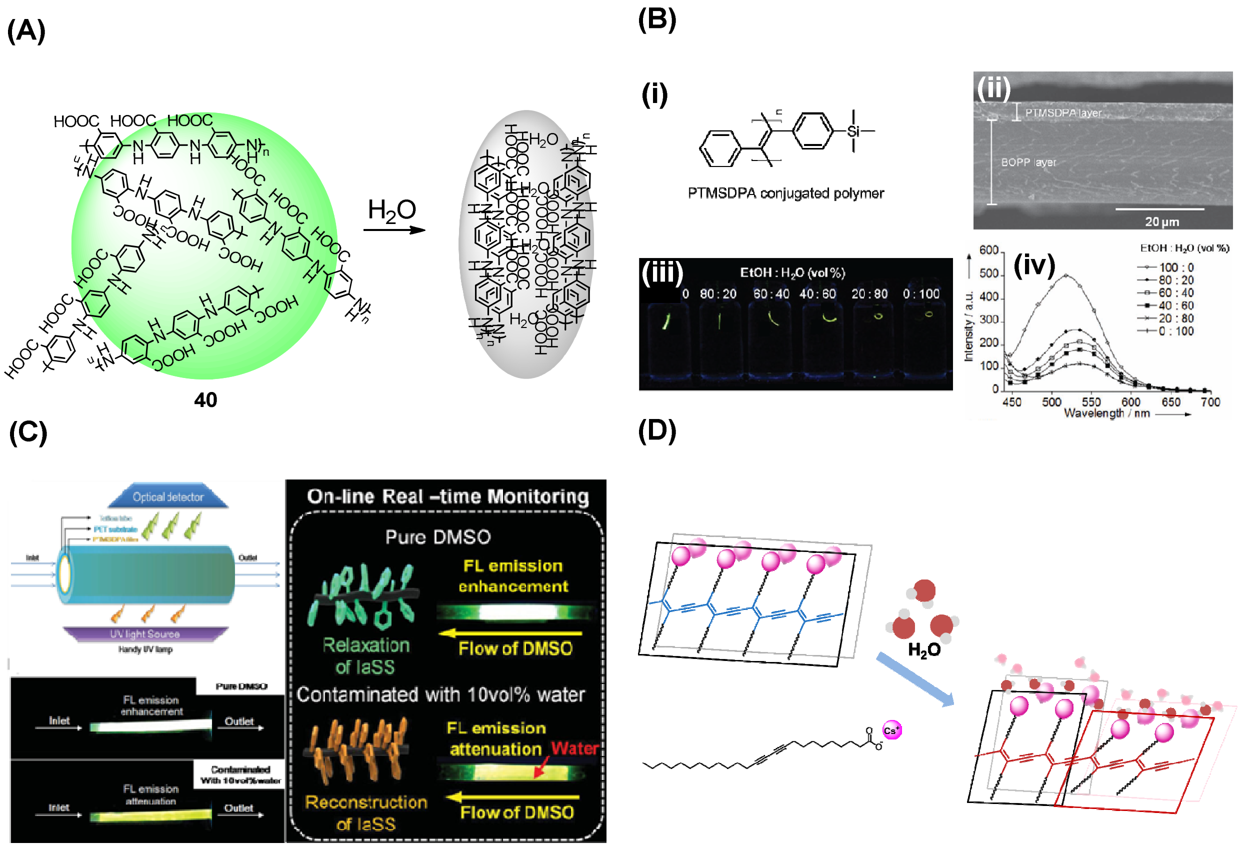

Fig. 10 (A) Schemetic diagram of water sensor **40**. (B) Microporous PTMSDPA conjugated polymer based fluorescent actuator responsive to the water concentration. (i) Chemical structure of PTMSDPA, and (ii) cross-sectional SEM image of PTMSDPA/BOPP bilayer film. (iii) Actuation and (iv) fluorescence spectra of a PTMSDPA/BOPP bilayer film in an EtOH/water mixture. (C) Proposed diagram of fluidic channel water sensor device using PTMSDPA. (D) Schemetic diagram of water-promoted morphological change using PDAs. (B) and (C) are reproduced with permission from ref. 47 and 48, respectively, Copyright 2012 and 2014 Wiley-VCH.

A benzothioxanthene derivative **41** was used as a fluorescent water sensor by Li *et al.* (Fig. 11).[48] **41**, bearing a terminal Michael type olefin, was photocopolymerized on a glass surface, pre-treated with a silanizing agent. When the film was subjected to immersion in solutions with water contents ranging from 0.00 to 100.0% (*v*/*v*), the fluorescence intensity gradually decreased. The water response ranges of the film were from 0.00 to 20.00% (*v*/*v*) for MeCN and acetone, and 0.00 to 12.00% (*v*/*v*) for EtOH and the LOD of **41** was, respectively, 0.088 in MeCN, 0.144 in acetone, and 0.019 wt% in EtOH.

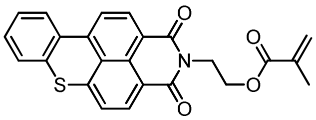

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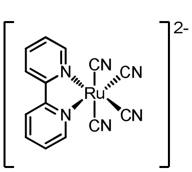
Fig. 11 Molecular structure of a benzothioxanthene derivative **41** for water.

4.4 Sensors based on hydrogen-bond interactions

Pinheiro *et al.* reported on a Ru(bpy)$(CN)_4^{2-}$ complex **42**, which exhibits strong solvatochromic properties (Fig 12).[49] The nitrile group of **42** acts as hydrogen bond acceptor towards protic solvents (H-bond donor), such as water. Increased water contents in organic solvents (MeCN, THF, DMF, DCM and toluene) result in second-sphere donor-acceptor interactions, leading to blue shifted absorption band maxima with linear behaviour in function of the water content in the 5–70 ppm range.

Cha *et al.* described two 7-hydroxycoumarin based merocyanine dyes **43** and **44** for the detection of water in organic solvents (Fig. 12).[50] A dramatic blue-shifted change in the absorption wavelength of both **43** and **44** was observed subsequent to the addition of incremental amounts water, induced by the formation of hydrogen bonds between the oxygen atom of the coumarin dyes and water molecules. The LOD of **43** and **44** for water in organic solvents were, respectively, 0.21 and 0.038 wt% in MeCN, 0.26 and 0.74 wt% in acetone, 0.30 and 0.98 wt% in THF, 0.63 and 1.1 wt% in DMSO and 2.1 and 1.3 wt% in MeOH. Although the probes were fully responsive in the 0-100% water content range, they were particularly sensitive in the sub-10% water content range.



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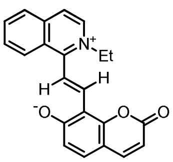

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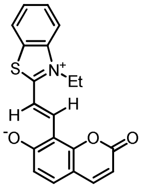

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Fig. 12 Molecular structures of Sensors **42**-**44** based on hydrogen-bond interactions.

Table 1 Comparison the limit of detection and quantitation and their mode of action for the molecules discussed in this work

Comp. #	Solvent	LOD (wt%)	LOQ (wt%)	Sensing strategy	Ref.
2	1,4-Dioxane	0.1	0.3	PET	7
	THF	0.1	0.4		
	MeCN	0.1	0.4		
	EtOH	0.1	0.2		
3	1,4-Dioxane	0.1	0.3	PET	8
	THF	0.4	1.2		
	MeCN	0.1	0.3		
	EtOH	0.1	0.3		
4	1,4-Dioxane	0.2	0.7	PET	9
	THF	0.2	0.5		
	MeCN	0.04	0.1		
	EtOH	0.04	0.1		
5	1,4-Dioxane	0.018	0.054	PET	10
	THF	0.014	0.042		
	MeCN	0.013	0.040		
	EtOH	0.007	0.021		
6	1,4-Dioxane	[a]	[a]	PET	11
	THF	[a]	[a]		
	MeCN	[a]	[a]		
	EtOH	[a]	[a]		
7	1,4-Dioxane	[a]	[a]	PET	11
	THF	[a]	[a]		
	MeCN	0.4	[a]		
	EtOH	0.04	0.12		
8	1,4-Dioxane	0.01	0.03	PET	12
	THF	0.008	0.026		
	MeCN	0.009	0.026		
	EtOH	0.009	0.027		
10[b]	Diethyl ether	0.001	NA	ICT	16
	THF	0.003	NA		
	EtOAc	0.003	NA		
	MeCN	0.005	NA		
11[b]	Acetone	0.006	NA	ICT	17
	MeCN	0.002	NA		
	EtOH	0.008	NA		
12	1,4-Dioxane	0.008	NA	ICT	18
	MeCN	0.006	NA		
	EtOH	0.015	NA		
13	1,4-Dioxane	0.019	NA	ICT	19
	MeCN	0.038	NA		
	EtOH	0.060	NA		
14	1,4-Dioxane	0.049	NA	ICT	20
	MeCN	0.021	NA		
	Acetone	0.016	NA		
	THF	0.020	NA		
17	Acetone	0.02	NA	ESIPT	23
18	1,4-Dioxane	0.05	NA	ESIPT	24
	MeCN	0.01	NA		

	THF	0.006	NA		
22	EtOH	0.002	NA	Water as a competitive ligand	28
23	MeCN	0.003	NA	Water as a competitive ligand	29
24	MeCN	0.037	NA	Water as a competitive ligand	30
	THF	0.071	NA		
25	MeCN	0.12	NA	Water as a competitive ligand	30
	THF	0.63	NA		
26	MeCN	0.17	NA	Water as a competitive ligand	31
28	MeCN	0.16	NA	Water as a competitive ligand	32
29	Acetone	0.11	NA	Chemical Reaction	35
	MeCN	0.035	NA		
31	THF	0.0464	0.1405	Chemical Reaction	37
	MeCN	0.0298	0.0902		
	MeOH	0.0017	0.0052		
32	THF	0.0033	0.0105	Chemical Reaction	38
	MeCN	0.0032	0.0108		
	MeOH	0.0026	0.0085		
	DMSO	0.0044	0.0147		
33	THF	0.0056	NA	ICT and AIEE	40
34	THF	0.0097	NA	ICT and AIEE	40
35	THF	0.010	NA	ICT and AIEE	41
	1,4-Dioxane	0.019	NA		
37	MeCN	0.0007	NA	Aggregation based monomer-excimer switching	42
	EtOH	0.06	NA		
	MeOH	0.2	NA		
	1,4-Dioxane	0.4	NA		
38	EtOH	0.1	0.3	Water induced interpolymer π-stacking aggregation	44
	MeCN	0.02	0.07		
	DMF	0.008	0.03		
	NMP	0.009	0.03		
39	MeCN	0.088	NA	Water induced interpolymer π-stacking aggregation	48
	Acetone	0.144	NA		
	EtOH	0.019	NA		
43	MeCN	0.21	NA	Hydrogen-bond interactions	50
	Acetone	0.26	NA		
	THF	0.30	NA		
	DMSO	0.63	NA		
	MeOH	2.1	NA		
44	MeCN	0.038	NA	Hydrogen-bond interactions	50
	Acetone	0.74	NA		
	THF	0.98	NA		
	DMSO	1.1	NA		
	MeOH	1.3	NA		

Abbreviations: [tetrahydrofuran (THF)], [acetonitrile (MeCN)], [ethanol (EtOH)], [methanol (MeOH)], [dimethyl sulfoxide (DMSO)], [*N*,*N*-dimethylformamide (DMF)], [ethyl acetate (EtOAc)], [*N*-methyl-2-pyrrolidone (NMP)], [not available (NA)]. [a] Over 1.0 wt%, [b] Immobilized to polymeric membrane.

5. Concluding remarks

As we have outlined above, water sensing in organic solvents can be achieved via a plethora of techniques, each with its own advantages and disadvantages, and different potential applications. The chemosensor based probes can be easily applied to measure the exposure level of organic solvent to water, with LODs and LOQ's in the sub 0.01 wt% and 0.02 wt% regions, respectively. These systems could be applied to flow based systems with relative ease, when appended to polymer surfaces.

Whereas it can easily be seen how the construction of PET systems with highly mobile protons (as influenced by the pK_a of the proton donor) are superior to the first generation of PET indicators, much less attention has been given to the proton acceptor abilities of the PET-quenching amines (that is their pK_b). Therefore, optimizing both the proton donating and accepting parts of the molecule might lead to further improvements of these probes. Caution must be given in these designs to the charge density of the probes, as the solubility of the zwitter ionic structures after the addition of very small amounts of water may be compromised, leading to precipitation for the solution containing them. The behavior of ICT based probes is somewhat less predictable, as water may influence both the donor and acceptor parts, yet it was clear that the more electron poor acceptor type ICT dyes show a greater promise, due to increased sensitivities. ESIPT probes show very small LOD's in certain solvents, but because their effect is caused by hydrogen bonding, the application in protic solvents likely will result in far smaller sensitivities, furthermore the specificity of these probes for water over other analytes capable of hydrogen bonding (*e.g.* alcohols) is not clear.

Water as fluorescence quencher in unsaturated lanthanides complexes, has been shown to be highly sensitive in the case of europium complexes. Future analogues with different lanthanide ions could lead to a higher variation in sensitivity and wavelength domains. Whereas analogous organic sensors with water as a competitive ligand for fluorescent anion sensors are currently less sensitive, the introduction of more hygroscopic anions could close the observed sensitivity gap. Other future research endeavors related to analogues cation-dye complexes, of which the sensitivity to water has yet to be reported, are likely to appear.

Chemodosimeters, which generally have a slower response time to water, but equally competitive as far as sensitivity is concerned, have been discussed as well. Particularly the irreversible reactions, and their cumulative sensing modes are as yet underrepresented in this research field. Yet potential applications as self-indicating smart coatings, could include the detection of (hairline) cracks in water-containing ducts. Another application that could be anticipated, is a dosimeter for the quantitation of the cumulative exposure to moisture of water-sensitive products included in its packaging. As these and many other examples demonstrate, the current underrepresentation of these types of dyes is not likely to persist much longer.

The final reported sensor category, utilizing physical interaction between molecules and between polymers, shows competitive LOD's as well. Furthermore some of these examples discussed above represent the fastest water indication systems to date. Studying the judicious combination of the water responsive polymer systems with supporting materials, could allow further amelioration of these systems and could lead to miscellaneous applications, including the incorporation in electronic systems.

In view of this large variety of sensing mechanisms and their properties, a case-by-case analysis of the potential advantages and disadvantages and their implications for the envisioned application is of crucial importance. We hope this review entices the scientific community into designing ever more sensitive and tailor-made water sensors and hope this review might educate students new to the field as well as provide guidance in the selection of appropriate sensing modes for future applications.

Acknowledgements

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References

1. R. Nussbaum, D. Lischke, H. Paxmann and B. Wolf, *Chromatographia,* 2000, **51**, 119.
2. E. D. Tsamis and J. N. Avaritsiotis, *Sensor Actuat. A-Phys.*, 2005, **118**, 202.
3. J. Mitchell, Jr. and D. M. Smith, *Aquametry: A Treatise on Methods for the Determination of Water*, *Pt. 1*, 2nd ed., Wiley, New York, 1977.
4. A. P. de Silva, T. S. Moody and G. D. Wrighta, *Analyst*, 2009, **134**, 2385.
5. Y. Ooyama, H. Egawa and K. Yoshida, *Eur. J. Org. Chem.,* 2008, **31**, 5239.
6. Y. Ooyama, H. Egawa and K. Yoshida, *Dyes Pigm.,* 2009, **82**, 58.
7. Y. Ooyama, M. Sumomogi, T. Nagano, K. Kushimoto, K. Komaguchi, I. Imae and Y. Harima, *Org. Biomol. Chem.*, 2011, **9**, 1314.
8. Y. Ooyama, A. Matsugasako, T. Nagano, K. Oka, K. Kushimoto, K. Komaguchi, I. Imae and Y. Harima, *J. Photochem. Photobiol. A: Chem.*, 2011, **222**, 52.
9. Y. Ooyama, A. Matsugasako, K. Oka, T. Nagano, M. Sumomogi, K. Komaguchi, I. Imae and Y. Harima, *Chem. Commun.*, 2011, **47**, 4448.
10. Y. Ooyama, A. Matsugasako, Y. Hagiwara, J. Ohshita and Y. Harima, *RSC Adv.*, 2012, **2**, 7666.
11. Y. Ooyama, K. Uenaka, A. Matsugasako, Y. Harima and J. Ohshita, *RSC Adv.*, 2013, **3**, 23255.
12. Y. Ooyama, K. Furue, K. Uenaka and J. Ohshita, *RSC Adv.*, 2014, **4**, 25330.
13. K.-H. Kim, W.-J. Lee, J. N. Kim and H. J. Kim, *Bull. Korean Chem. Soc.,* 2013, **34**, 2261.
14. M. H. Lee, J. S. Kim and J. L. Sessler, *Chem. Soc. Rev.*, 2015, **44**, 4185.

15. A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
16. D. Citterio, K. Minamihashi, Y. Kuniyoshi, H. Hisamoto, S. Sasaki and K. Suzuki, *Anal. Chem.*, 2001, **73**, 5339.
17. C.-G. Niu, A.-L. Guan, G.-M. Zeng, Y.-G. Liu and Z.-W. Li, *Anal. Chim. Acta*, 2006, **577**, 264.
18. C.-G, Niu, P.-Z. Qin, G.-M. Zeng, X.-Q. Gui and A.-L. Guan, *Anal. Bioanal. Chem.*, 2007, **387**, 1067.
19. C. Niu, L. Li, P. Qin, G. Zeng and Y. Zhang, *Anal. Sci.*, 2010, **26**, 671.
20. Z. Li, Q. Yang, R. Chang, G. Ma, M. Chen and W. Zhang, *Dyes Pigm.*, 2011, **88**, 307.
21. J. Zhao, S. Ji, Y. Chen, H. Guo and P. Yang*, Phys. Chem. Chem. Phys*., 2012, **14**, 8803.
22. H. Mishra, V. Misra, M. S. Mehata, T. C. Pant and H. B. Tripathi, *J. Phys. Chem. A*, 2004, **108**, 2346.
23. W. Liu, Y. Wang, W. Jin, G. Shen and R. Yu, *Anal. Chim. Acta*, 1999, **383**, 299.
24. J. S. Kim, M. G. Choi, Y. Huh, M. H. Kim, S. H. Kim, S. Y. Wang and S.-K. Chang, *Bull. Korean Chem. Soc.,* 2006, **27**, 2058.
25. A. C. Kumar and A. K. Mishra, *Talanta*, 2007, **71**, 2003.
26. F. Galindo, J. C. Lima, S. V. Luis, M. J. Melo, A. J. Parola and F. Pina, *J. Mater. Chem.*, 2005, **15**, 2840.
27. S. V. Eliseeva and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 2010, **39**, 189.
28. F. Gao, F. Luo, X. Chen, W. Yao, J. Yin, Z. Yao and L. Wang, *Microchim. Acta,* 2009, **166**, 163.
29. L. Song, Y.-W. Wu, W.-X. Chai, Y.-S. Tao, C. Jiang and Q.-H. Wang, *Eur. J. Inorg. Chem.*, 2015, **13**, 2264.
30. Y. H. Kim, M. G. Choi, H. G. Im, S. Ahn, I. W. Shim and S.-K. Chang, *Dyes Pigm.*, 2012, **92**, 1199.
31. Y.-H. Kim, Y. K. Han and J. Kang, *Bull. Korean Chem. Soc.*, 2011, **32**, 4244.
32. J. O. Moon, Y. H. Kim, M. G. Choi and S.-K. Chang, *Bull. Korean Chem. Soc.*, 2011, **32**, 3517.
33. J. Yoon and A. W. Czarnik, *J. Am. Chem. Soc.*, 1992, **114**, 5874.
34. X. Chen, Y. Zhou, X. Peng and J. Yoon, *Chem. Soc. Rev.*, 2010, **39**, 2120.

35. M. G. Choi, M. H. Kim, H. J. Kim, J.-E. Park and S.-K. Chang, *Bull. Korean Chem. Soc.*, 2007, **28**, 1818.
36. S. A. Poteet and F. M. MacDonnell, *Dalton Trans.*, 2013, **42**, 13305.
37. G. Men, G. Zhang, C. Liang, H. Liu, B. Yang, Y. Pan, Z. Wang and S. Jiang, *Analyst*, 2013, **138**, 2847.
38. S. Pal, M. Mukherjee, B. Sen, S. Lohar and P. Chattopadhyay, *RSC Adv.*, 2014, **4**, 21608.
39. J. Wu, W. Liu, J. Ge, H. Zhang and P. Wang, *Chem. Soc. Rev.*, 2011, **40**, 3483.
40. Y. Zhang, D. Li, Y. Li and J. Yu, *Chem. Sci.*, 2014, **5**, 2710.
41. W. Chen, Z. Zhang, X. Li, H. Ågren and J. Su, *RSC Adv.*, 2015, **5**, 12191.
42. K. Zhao, T. Liu, G. Wang, X. Chang, D. Xue, K. D. Belfield and Y. Fang, *J. Phys. Chem. B*, 2013, **117**, 5659.
43. D. W. Cho and D. W. Cho, *New J. Chem.*, 2014, **38**, 2233.
44. Q. Deng, Y. Li, J. Wu, Y. Liu, G. Fang, S. Wang and Y. Zhang, *Chem. Commun.*, 2012, **48**, 3009.
45. W.-E. Lee, Y.-J. Jin, L.-S. Park and G. Kwak, *Adv. Mater.*, 2012, **24**, 5604.
46. D.-C. Han, Y.-J. Jin, J.-H. Lee, S.-I. Kim, H.-J. Kim, K.-H. Song and G. Kwak, *Macromol. Chem. Phys.*, 2014, **215**, 1068.
47. J. Lee, M. Pyo, S. Lee, J. Kim, M. Ra, W.-Y. Kim, B. J. Park, C. W. Lee and J.-M. Kim, *Nat. Commun.,* 2014, **5**, 3736.
48. Z.-Z. Li, C.-G. Niu, G.-M. Zeng and P.-Z. Qin, *Chem. Lett.*, 2009, **38**, 698.
49. C. Pinheiro, J. C. Lima and A. J. Parola, *Sensor Actuat. B-Chem.*, 2006, **114**, 978.
50. S. Cha, M. G. Choi, H. R. Jeon and S.-K. Chang, *Sensor Actuat. B-Chem.*, 2011, **157**, 14.