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Development of highly sensitive fluorescent sensor and fluorescent sensor-doped polymer films for trace amounts of water based on photo-induced electron transfer

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Anthracene-(aminomethyl)phenylboronic acid pinacol ester (AminoMePhenylBPin) SM-1 having a cyano group as an electron-withdrawing substituent and a hydroxymethyl group has been adopted as an electron-withdrawing group for water. SM-1 shows enhancement of fluorescence with the increase in water content in various solvents (polar, less polar, protic, and aprotic solvents), which is attributed to the suppression of PET due to the formation of the PET inactive (fluorescent) species SM-1a by interaction with water molecules. In fact, the formation of SM-1a by interaction with water molecules has been successfully detected by 1H NMR spectral measurements. The detection limits (DLs) and quantification limits (QLS) of SM-1 for water in solvents are, respectively, 0.006 and 0.018 wt% in 1,4-dioxane, 0.004 and 0.012 wt% in THF, 0.004 and 0.013 wt% in acetonitrile, and 0.007 and 0.021 wt% in ethanol, which are superior to those of OF-2 without a hydroxymethyl group. This result is attributed to the improvement of fluorescence emission property by the introduction of hydroxymethyl group to an anthracene fluorophore. Actually, fluorescence quantum yields (Φfl) of OF-2 and SM-1 in absolute acetonitrile are below 2%, but in acetonitrile with 1 wt% water content the Φfl (20%) of SM-1 is higher than that (13%) of OF-2. Moreover, we have achieved the preparation of various types of polymer films (polystyrene (PS), poly(4-vinylphenol) (PVP), polyvinyl alcohol (PVA), and polyethylene glycol (PEG)) doped with SM-1, and investigated the optical sensing properties of the SM-1-doped polymer films for water. It was found that the SM-1-doped polymer films produce a reversible switching in fluorescent color between the green excimer emission in the PET active state under a drying process and the blue monomer emission in the PET inactive state upon exposure to moisture. Herein we propose that PET-type fluorescent sensor-doped polymer films based on a fluorescence enhancement system are one of the most promising and convenient functional materials for not only environmental and quality control monitoring systems and industry, but also visualizing the droplet on material surfaces.

Introduction

Development of fluorescent sensors for the visualization as well as detection and quantification of a trace amount of water in solutions, solids, and gas or on material surfaces, has been of considerable scientific and practical concern in recent years, with the objective of not only fundamental study in analytical chemistry, photochemistry, and photophysics, but also their potential applications to environmental and quality control monitoring systems and industry. Consequently, fluorescent sensors for water are one of the most promising functional materials contributing to the achievement of the 2030 agenda for Sustainable Development Goals (SDGs), which has been adopted by all United Nations Member States in 2015 and provides a shared blueprint for peace and prosperity for people and the planet now and in the future. Actually, some kinds of organic fluorescent sensors and polymers for the determination of water content based on ICT (intramolecular charge transfer), ESIP (excited state intramolecular proton transfer), PET (photo-induced electron transfer), and solvatochromism have been designed and synthesized. The optical sensing properties of these fluorescent sensors for the detection and quantification of water content were investigated from the viewpoints of the relationship between ICT, ESIP, PET, or solvatochromatic characteristics and the intermolecular interaction of the sensors with water molecules. As a result, it was found that most of the previous fluorescent sensors for water, including fluorescent conjugated polymers and organic fluorescent dyes with ICT and ESIP characteristics, are based on a fluorescence quenching (turn-off) system, that is, the fluorescence intensity of the sensors decreases as a function of water content in organic solvents. This fluorescence quenching system makes it difficult to detect a trace amount of water. In contrast, a fluorescence enhancement (turn-on) system exhibiting a fluorescence response with an increase in water content in organic solvents is useful for the visualization,
detection, and quantification of a trace amount of water in organic solvents. In particular, the fluorescence enhancement system based on the PET-type fluorescent sensors for water can detect a reversible change in its immediate environment due to the reversible intermolecular interactions between the sensors and water molecules. Thus, during the past decade, we have designed and developed anthracene-(aminomethyl)phenylboronic acid pinacol esters (AminoMePhenylBPin) OM-1, OF-1, and OF-2 (Fig. 1a) as PET-type fluorescent sensors for the determination of a trace amount of water. OF-1 and OF-2 have a methoxy group as an electron-donating substituent and a cyano group as an electron-withdrawing substituent, respectively, at the para position on PhenylBPin. In each sensor, the PET takes place from the nitrogen atom of the amino moiety to the photoexcited fluorophore (anthracene) skeleton in the absence of water, leading to fluorescence quenching. The addition of water to organic solvents containing the PET-type fluorescent sensors causes a drastic and linear enhancement of fluorescence emission as a function of water content, which is attributed to the suppression of PET; that is, the nitrogen atom of the amino moiety is protonated or strongly interacts with water molecules, leading to the formation of the PET inactive (fluorescent) species such as OM-1a, OF-1a, or OF-2a. Moreover, it was found that the fluorescent sensing ability of the cyano-substituted sensor OF-2 for water is superior to that of the unsubstituted sensor OM-1 and the methoxy-substituted sensor OF-1. This result can be attributed to the fact that for OF-2, the cyano group at the para position on PhenylBPin enhances the Lewis acidity of the boron atom due to its electron-withdrawing effect, leading to the facilitation of the formation of the PET inactive (fluorescent) species by interaction with water molecules. In contrast, for OF-1, the electron-donating methoxy group at the para position on PhenylBPin diminishes the Lewis acidity of the boron atom, leading to the retardation of the formation of the PET inactive (fluorescent) species by addition of water. Indeed, the detection limits (DLs) and quantitation limits (QLs) of OF-2 for water were, respectively, 0.01 wt% and 0.03 wt% in 1,4-dioxane, 0.008 wt% and 0.026 wt% in THF, 0.009 wt% and 0.026 wt% in acetonitrile, and 0.009 wt% and 0.027 wt% in ethanol, which are superior to those of OM-1 and OF-1, and are equivalent or superior to those of the fluorescent quenching systems (turn-off) based on the reported ICT-type and ESIPT-type fluorescent sensors. Thus, the PET method based on the fluorescence enhancement (turn-on) system makes it possible to visualize, detect, and determine a trace amount of water.

Meanwhile, a novel coronavirus, severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) that causes the Coronavirus Disease 2019 (COVID-19), dramatically changed the world to give people a sense of fear of death. Infectious viruses are generally released into the atmosphere through droplet spread from coughing and sneezing by an infected person. Thus, the infection route from an infected person to an uninfected person is predominately due to the droplet. Actually, face shields made of polyester or polycarbonate films and partitions made of acrylic resin are commercially available for reducing the risk of droplet infection. Therefore, if we can visually confirm the droplet on the face shields and partitions, this allows us to accurately remove the viruses by wiping away the droplet. However, because the virus-containing droplet is generally 5 μm or more, it is practically difficult for us to visually confirm the droplet. Meanwhile, over 90% of the droplet is composed of water, and thus, techniques and methods capable of visualizing water are undoubtedly useful for detecting the virus-containing droplet. For this purpose, in our previous work, in order to develop fluorescent polymeric materials for visualization and detection of water, we have achieved the preparation of various types of polymer films (polystyrene (PS), poly(4-vinylphenol) (PVP), polystyrene alcohol (PVA), and polylethylene glycol (PEG)) doped with the PET-type fluorescent sensor OF-2, and investigated the optical sensing properties of the OF-2-doped polymer films for water. It was found that the OF-2-doped polymer films exhibit a reversible switching in fluorescent color between the green excimer emission in the PET active state under a drying process and the blue monomer emission in the PET inactive state upon exposure to moisture or water droplets. To the best of our knowledge, our previous work is the first to achieve the preparation of PET-type fluorescent sensor-doped polymer films for water, although some fluorescent conjugated polymers and ICT-type and ESIPT-type fluorescent sensor-doped polymer films for water based on a fluorescence quenching (turn-off) system have been prepared. Nevertheless, in order to put the visualization of moisture and water droplets based on the PET method into practical applications, the development of a highly sensitive PET-type fluorescence sensor for a trace amount of water is required.

![Fig. 1 Mechanisms of PET-type fluorescent sensors (a) OM-1, OF-1, OF-2, and (b) SM-1 for detection of water in organic solvents.](image-url)}
In this work, the formation of the PET inactive species OF-2a and SM-1a by interaction with water molecules has been successfully detected by $^1$H NMR spectral measurements. Furthermore, in order to develop fluorescent polymeric materials for visualization and detection of water, we have achieved the preparation of various types of polymer films (PS, PVP, PVA, and PEG) doped with SM-1, and investigated the optical sensing properties of the SM-1-doped polymer films for water. Herein we propose that the PET-type fluorescent sensor-doped polymer films based on a fluorescence enhancement system are one of the most promising and convenient functional materials for visualizing the virus-containing droplet on the surfaces of face shields and partitions, that is, contributing to post-COVID19 society.

**Results and discussion**

A PET-type fluorescent sensor SM-1 was prepared by the reaction of (10-((methylamino)methyl)anthracen-9-yl)methanol$^{18,49}$ with 3-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (Scheme 1).

![Scheme 1 Synthesis of SM-1.](image)

In order to investigate the optical sensing ability of SM-1 for water in 1,4-dioxane and THF as less polar solvents, acetonitrile as a polar solvent, and ethanol as a protic solvent, the photoabsorption and fluorescence spectra of SM-1 were measured in the solvents containing various concentrations of water (Fig. 2). As with the case of OF-2,$^{32}$ in all the four solvents, the photoabsorption spectra of SM-1 show a vibronically-structured photoabsorption band in the range of 300 nm to 400 nm originating from the anthracene skeleton and did not undergo appreciable changes in the absorbance and shape upon the addition of water to the solution (Fig. 2a,c,e,g). In the corresponding fluorescence spectra, SM-1 in the absolute solvents exhibits a feeble and vibronically-structured fluorescence band with a fluorescence maximum wavelength ($\lambda_{\text{max}}$) at around 420 nm in the range of 400 nm to 500 nm in the PET active state, which is attributed to the monomer emission originating from the anthracene skeleton (Fig. 2b,d,f,h). On the other hand, with the increase in the water content in the solutions, the fluorescence spectra exhibited an enhancement of the monomer emission band with a negligible change in their spectral shapes due to the suppression of PET (the PET inactive state). As shown in Fig. 3a, the acetonitrile solution of SM-1 did not show visual fluorescence emission, but exhibited the blue fluorescence emission upon the addition of water.

![Fig. 2](image)

**Fig. 2** (a) Photoabsorption and (b) fluorescence spectra ($\lambda_{\text{ex}} = 375$ nm) of SM-1 (2.0 \times 10^{-5} M) in 1,4-dioxane containing water (0.0044–9.7 wt%). (c) Photoabsorption and (d) fluorescence spectra ($\lambda_{\text{ex}} = 375$ nm) of SM-1 (2.0 \times 10^{-5} M) in THF containing water (0.0058–10 wt%). (e) Photoabsorption and (f) fluorescence spectra ($\lambda_{\text{ex}} = 375$ nm) of SM-1 (2.0 \times 10^{-5} M) in acetonitrile containing water (0.0103–9.1 wt%). (g) Photoabsorption and (h) fluorescence spectra ($\lambda_{\text{ex}} = 375$ nm) of SM-1 (2.0 \times 10^{-5} M) in ethanol containing water (0.009–10 wt%).

![Fig. 3](image)

**Fig. 3** Photographs (under 254 nm irradiation) of (a) acetonitrile solution of SM-1 before and after addition of water and (b) 50 wt% SM-1-doped PVA film before and after exposure to moisture.
In order to estimate the sensitivity and accuracy of SM-1 for the detection of water in solvent, the changes in the fluorescence peak intensity at around 420 nm were plotted against the water fraction in solvent (Fig. 4). As with the case of OF-2 (Fig. S2, ESI†), the plots of SM-1 demonstrated that the fluorescence peak intensity increased linearly as a function of the water content in all four solvents (Fig. 4a). Thus, the DLs and QLs of SM-1 for water in the solvents were determined based on the following equations: DL = 3.3σ/mc and QL = 10σ/mc, where σ is the standard deviation of blank sample and mc is the slope of a calibration curve obtained from the plot of the fluorescence peak intensity at around 420 nm versus the water fraction in the low water content region below 1.0 wt% (Fig. 4b). The results are as follows:

1,4-Dioxane: \[F = 564.2[H_2O] + 43.8 \quad (R^2 = 0.983, [H_2O] = 0.0044–0.58 \text{ wt\%})\] (1)

THF: \[F = 819.6[H_2O] + 31.5 \quad (R^2 = 0.989, [H_2O] = 0.0058–0.36 \text{ wt\%})\] (2)

Acetonitrile: \[F = 753.5[H_2O] + 13.1 \quad (R^2 = 0.975, [H_2O] = 0.0103–0.28 \text{ wt\%})\] (3)

Ethanol: \[F = 484.2[H_2O] + 12.6 \quad (R^2 = 0.979, [H_2O] = 0.009–0.30 \text{ wt\%})\] (4)

Indeed, the correlation coefficient \((R^2)\) values for the calibration curves of SM-1 are 0.975–0.989, which indicates good linearity, as with case of OF-2. However, a large difference in the mc values between SM-1 and OF-2 was observed; that is, the mc values for SM-1 are, respectively, 564 in 1,4-dioxane, 819 in THF, 753 in acetonitrile, and 484 in ethanol and much larger than those of OF-2 (Table 1). The large mc values for SM-1 relative to OF-2 can be attributed to the improvement of fluorescence emission property by the introduction of hydroxymethyl group to an anthracene fluorophore. Actually, fluorescence quantum yields (\(\Phi_f\)) of OF-2 and SM-1 in absolute acetonitrile are below 2%, but in acetonitrile with 1 wt% water content the \(\Phi_f\) (20%) of SM-1 is higher than that (13%) of OF-2. The DLs and QLs of SM-1 for water are, respectively, 0.006 and 0.018 wt% in 1,4-dioxane, 0.004 and 0.012 wt% in THF, 0.004 and 0.013 wt% in acetonitrile, and 0.007 and 0.021 wt% in ethanol, which are superior to those of OF-2. Consequently, it was found that the anthracene-AminoMePheny1BPin-based sensor SM-1 having a cyan group as an electron-withdrawing substituent and a hydroxymethyl group is a highly sensitive PET-type fluorescence sensor for the detection and quantification of a trace amount of water in polar, less polar, protic, and aprotic solvents.

| Sensor | Solvent | mč | DLc | QLc |
|--------|---------|----|-----|-----|
| OF-2   | 1,4-Dioxane | 334 | 0.010 wt% | 0.03 wt% |
|        | THF     | 390 | 0.008 wt% | 0.026 wt% |
|        | Acetonitrile | 382 | 0.009 wt% | 0.026 wt% |
|        | ethanol | 362 | 0.009 wt% | 0.027 wt% |
| SM-1   | 1,4-Dioxane | 564 | 0.006 wt% | 0.018 wt% |
|        | THF     | 819 | 0.004 wt% | 0.012 wt% |
|        | Acetonitrile | 753 | 0.004 wt% | 0.013 wt% |
|        | ethanol | 484 | 0.007 wt% | 0.021 wt% |
| ICT-type | 1,4-Dioxane | -40.23 | 0.008 wt% | No data |
|        | Acetonitrile | -52.10 | 0.006 wt% | No data |
|        | ethanol | -22.42 | 0.015 wt% | No data |
| ESIPT-type | 1,4-Dioxane | -5.46 | 0.053 wt% | No data |
|        | THF     | -10.38 | 0.006 wt% | No data |
|        | Acetonitrile | -7.63 | 0.011 wt% | No data |

Table 1 DL and QL of OF-2, SM-1, and previously reported ICT-type and ESIPT-type fluorescent sensors for water in various organic solvents

In order to confirm the mechanism of PET-type fluorescent sensor based on anthracene-AminoMePheny1BPin structure for the detection of water, we performed \(^1\)H NMR spectral measurements of OF-2 and SM-1 with and without the addition of water in the acetonitrile-d\(_6\) solution (2.0 × 10\(^{-2}\) M) (Fig. 5 and 6). Both the \(^1\)H NMR spectra of OF-2 and SM-1 solution (containing water content of 0.46 wt% and 0.18 wt%, respectively) without the addition of water show an obvious signals which can be assigned to a single chemical species with OF-2 and SM-1 structure. On the other hand, for both the \(^1\)H NMR spectra of OF-2 and SM-1 solution with water content of 2.6 wt% and 2.8 wt%, respectively, some additional signals appear at both the aliphatic and aromatic regions, compared to that of the solution without the addition of water. Indeed, the \(^1\)H NMR spectra in the solutions with water content of 2.6–2.8 wt% clearly indicate the existence of another chemical species as well as OF-2 and SM-1. Moreover, both the \(^1\)H NMR spectra of OF-2 and SM-1 solution with water content of 11 wt% and 13 wt%, respectively can be assigned to a single chemical species which is quite different from OF-2 and SM-1 structure, that is, the PET inactive species OF-2a and SM-1a (Fig. 1) occur upon addition of water to the OF-2 and SM-1 solution, respectively. Consequently, upon the addition of water to OF-2 and SM-1 solution, the chemical shifts of the methyl protons H\(_e\) of boronic acid pinacol ester and the aromatic protons H\(_b\) of the
anthracene skeleton show considerably upfield shift, but the chemical shifts of H_2, H_4 and H_6 of the phenyl group and the methylene protons H_3 of the anthracene skeleton show considerably downfield shift. Furthermore, for the ^1H NMR spectrum of SM-1 solution with the addition of water, it is worth noting here that there is no appreciable change in chemical shifts for the methylene protons H_3 of hydroxymethyl group on an anthracene skeleton (Fig. 6). The fact indicates that for SM-1 the hydroxymethyl group does not act as a proton donor or acceptor which may affect the formation of the PET inactive species SM-1a by interaction with water molecules.

Next, in order to investigate the optical properties of SM-1 in the aggregate state, the spin-coated SM-1 film was prepared on a glass substrate, and the photoabsorption and fluorescence spectra of the spin-coated SM-1 film before and after exposure to moisture were repeatedly measured several times (Fig. 7). As with the case of OF-2 (Fig. S3, ESI†), the as-prepared spin-coated SM-1 film (in dry process) shows a vibronically-structured photoabsorption band in the range of 300 nm to 400 nm originating from the anthracene skeleton (Fig. 7a). The photoabsorption spectral shape of the spin-coated SM-1 film did not undergo appreciable changes upon exposure to moisture, although a slight change in the absorbance during the repeated cycles was observed due to the disturbance of baseline in the photoabsorption spectra. In the corresponding fluorescence spectra, the as-prepared spin-coated SM-1 film shows a broad fluorescence band in the range of 400 nm to 600 nm, which is assigned to the excimer emission originating from the anthracene skeleton in the PET active state (Fig. 7b). Interestingly, the spin-coated SM-1 film underwent a change in the fluorescence spectra upon exposure to moisture (in wet process), which caused the vibronically-structured monomer emission (λ_{max} = ca. 420 nm) in the range of 400 nm to 500 nm arising from the PET inactive state. Moreover, it was found that when the spin-coated SM-1 film after exposure to moisture was dried in the atmosphere, the photoabsorption and fluorescence spectra showed the original spectral shapes before exposure to moisture, as with the case of OF-2. However, there is a difference in the ratio (F_{mon}/F_{exm}) of the intensity of the monomer to excimer emission between the spin-coated SM-1 and OF-2 film. The F_{mon}/F_{exm} of the spin-coated OF-2 film is higher than that of the spin-coated SM-1 film, that is, for the spin-coated OF-2 film, the F_{mon} is much larger than F_{exm}, but for the spin-coated SM-1 film, the F_{mon} is almost equal to F_{exm}. This result might be attributed to the idea that for SM-1 in the aggregate state, the excimer formation is facilitated by intermolecular hydrogen bonding between the hydroxymethyl groups. Thus, for the spin-coated SM-1 film, the reversibility of the fluorescence intensity between the excimer and monomer emissions in the dry-wet (moisture) process was investigated (Fig. 7b inset). The dry-wet cycle shows that the monomer emission disappeared almost completely in the second wet process, as with the case of OF-2 (Fig. S3b inset, ESI†). The poor reversibility of the fluorescence intensity of the spin-coated SM-1 and OF-2 films between the excimer and monomer emissions may be attributed to destruction of the film during the dry-wet process.
In order to investigate the possibility for SM-1 to function in polymeric materials for visualization and detection of water, we prepared various types of polymer films (PS, PVP, PVA, and PEG) doped with SM-1 at 50 wt%, and the photoabsorption and fluorescence spectra of the SM-1-doped polymer films before and after exposure to moisture were repeatedly measured several times (Fig. 8). As with the case of the OF-2 (Fig. S4, ES1F), the as-prepared SM-1-doped polymer films (in dry process) show a vibronically-structured photoabsorption band in the range of 300 nm to 400 nm and a broad fluorescence band in the range of 400 nm to 600 nm attributable to the excimer emission originating from the anthracene skeleton in the PET active state (Fig. 8). When the OF-2-doped polymer films were exposed to moisture (in wet process), the photoabsorption spectral shape did not undergo appreciable changes, although a slight change in the absorbance was observed due to the disturbance of baseline in the photoabsorption spectra. The corresponding fluorescence spectra show a change in spectral shape from the broad excimer emission to the vibronically-structured monomer emission (\( \lambda_{\text{max}}^{\text{ex}} = 415 \text{ nm} \)) arising from the PET inactive state upon exposure to moisture. In fact, one can see that an as-prepared SM-1-doped PVA film initially exhibits the green excimer emission in the PET active state, but the blue monomer emission in the PET inactive state upon exposure to moisture or water droplets (Fig. 3b). It is worth mentioning here that there are differences in the \( \text{Fl}_{\text{ex}}/\text{Fl}_{\text{mon}} \) of the intensity of the monomer to excimer emission between the four types of polymer films. For the SM-1-doped PS and PVP films, the \( \text{Fl}_{\text{ex}} \) is larger than \( \text{Fl}_{\text{mon}} \), but for the SM-1-doped PVA and PEG films, the \( \text{Fl}_{\text{mon}} \) is larger than \( \text{Fl}_{\text{ex}} \). In contrast, for all the four OF-2-doped polymer films, the \( \text{Fl}_{\text{mon}} \) is larger than \( \text{Fl}_{\text{ex}} \). This result suggests that for SM-1 in the polymer films, the excimer formation is facilitated in the hydrophobic PS and PVP films suitable for the formation of intermolecular hydrogen bonding between the hydroxymethyl groups, rather than in the hydrophilic PVA and PEG films. Indeed, for the fluorescence spectra of the SM-1-doped PS and PVP films, it is practically difficult to distinguish between the monomer and excimer emissions before and after exposure to moisture. The dry-wet cycles of the SM-1-doped polymer films show that for the SM-1-doped PVA and PEG films, a reversible switching in fluorescent intensity between the excimer and monomer emissions was obviously still observed in the third dry-wet process (Fig. 9). This result might be attributed to the idea that SM-1 has a good compatibility with the hydrophilic PVA and PEG films rather than the hydrophobic PS and PVP films. In addition, the reversibility of the fluorescence intensity of the SM-1-doped PVA and PEG films is superior to that of the spin-coated SM-1 film (Fig. 7b inset). Therefore, it was found that for SM-1, the hydrophilic PVA and PEG films produce a good reversibility and a large change in the intensity between the excimer and monomer emissions during the dry-wet process, that is, enable the visualization and detection of moisture and water droplets.

Fig. 8 (a) Photoabsorption and (b) fluorescence spectra (\( \lambda_{\text{ex}} = 360 \text{ nm} \)) of spin-coated PS film with 50 wt% SM-1 before (in dry process) and after (in wet process) exposure to moisture. (c) Photoabsorption and (d) fluorescence spectra (\( \lambda_{\text{ex}} = 360 \text{ nm} \)) of spin-coated PVP film with 50 wt% SM-1 before (in dry process) and after (in wet process) exposure to moisture. (e) Photoabsorption and (f) fluorescence spectra (\( \lambda_{\text{ex}} = 360 \text{ nm} \)) of spin-coated PVA film with 50 wt% SM-1 before (in dry process) and after (in wet process) exposure to moisture. (g) Photoabsorption and (h) fluorescence spectra (\( \lambda_{\text{ex}} = 360 \text{ nm} \)) of spin-coated PEG film with 50 wt% SM-1 before (in dry process) and after (in wet process) exposure to moisture. For all the photoabsorption spectra, baseline-correction has been made to be the same absorbance at 425 nm.
sensor based on anthracene-AminoMePhenylBPin structure, J. Name

Melting points were measured with AS ONE ATM-02.

We have developed a highly sensitive PET-type fluorescent sensor based on anthracene-AminoMePhenylBPin structure, SM-1 having a cyano group as an electron-withdrawing substituent and a hydroxymethyl group, for visualization, SM-1a by interaction with water molecules has been successfully detected by 1H NMR spectral measurements. It was found that the introduction of a cyano group and a hydroxymethyl group to anthracene-AminoMePhenylBPin structure can improve the sensitivity and accuracy of PET-type fluorescent sensor for water. Moreover, we have achieved the preparation of various types of polymer films (PS, PVP, PVA, and PEG) doped with SM-1, and demonstrated that the SM-1-doped polymer films produce a reversible switching in fluorescent color between the green excimer emission in the PET active state upon exposure to moisture. Consequently, this work proposes that highly sensitive PET-type fluorescent sensor-doped polymer films are one of the most promising and convenient fluorescent polymeric materials for visualization and detection of moisture and water droplets.

Experimental

General

Melting points were measured with AS ONE ATM-02. IR spectra were recorded on a SHIMADZU IRTracer-100 spectrometer by the ATR method. 1H and 13C NMR spectra were recorded on a Varian-400 or Varian-500 FT NMR spectrometer. High-resolution mass spectral data obtained by APCI were recorded on a Varian-400 or Varian-500 FT NMR spectrometer. 1H NMR (400 MHz, acetone-6): δ = 25.14, 42.95, 52.33, 57.52, 60.70, 83.95, 113.35, 119.21, 124.54, 125.50, 125.74, 125.93, 129.68, 129.94, 130.98, 131.34, 131.78, 131.87, 135.36, 146.18 ppm; HRMS (APCI): m/z (%): [M+•] calcd for C33H32N2O8B, 492.25787; found 492.25879.

Preparation of SM-1-doped polymer films

Polystyrene (PS), poly(4-vinylphenol) (PVP), or polyethylene glycol (PEG) (5 mg) was dissolved in a THF solution (1 mL) of SM-1 (5 mg) to form a 50 wt% stock solution. On the other hand, a THF solution (0.5 mL) of SM-1 (5 mg) was added to a polyvinyl alcohol (PVA) (5 mg) aqueous solution (0.5 mL) around 50 °C to form a 50 wt% stock solution. To prepare a polymer film, 300 μL of an SM-1-polymer solution was directly spin-coated (3000 rpm for 30 s) on a glass substrate (Mikasa MS-A-100 Opticoat Spincoater). The spin-coated films were dried in air. The resulting SM-1-doped polymer films were exposed to moisture for 60 s using a humidifier.

Conclusions

We have developed a highly sensitive PET-type fluorescent sensor based on anthracene-AminoMePhenylBPin structure, SM-1 having a cyano group as an electron-withdrawing substituent and a hydroxymethyl group, for visualization, detection, and quantification of a trace amount of water. In fact, the formation of the PET inactive species SM-1a by interaction with water molecules has been successfully detected by 1H NMR spectral measurements. It was found that the introduction of a cyano group and a hydroxymethyl group to anthracene-AminoMePhenylBPin structure can improve the sensitivity and accuracy of PET-type fluorescent sensor for water. Moreover, we have achieved the preparation of various types of polymer films (PS, PVP, PVA, and PEG) doped with SM-1, and demonstrated that the SM-1-doped polymer films produce a reversible switching in fluorescent color between the green excimer emission in the PET active state upon exposure to moisture. Consequently, this work proposes that highly sensitive PET-type fluorescent sensor-doped polymer films are one of the most promising and convenient fluorescent polymeric materials for visualization and detection of moisture and water droplets.

Conflicts of interest

There are no conflicts to declare.

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