Dyes and Pigments 123 (2015) 248–253

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Fluorescence sensor for water based on PET (photo-induced electron transfer): Anthracene-bis(aminomethyl)phenylboronic acid ester

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ARTICLE INFO

Article history:
Received 4 June 2015
Received in revised form
1 July 2015
Accepted 23 July 2015
Available online 14 August 2015

Keywords:
Dyes
Sensors
Water
Fluorescence
Photo-induced electron transfer
Anthracene–phenylboronic acid

ABSTRACT

In order to provide a direction in molecular design toward creating a highly-sensitive fluorescence PET (photo-induced electron transfer) sensor for a trace amount of water in organic solvents, we have designed and synthesized anthracene-bis(aminomethyl)phenylboronic acid ester **OA-1** and **OA-2**, without substituent and with cyano group, respectively, on the phenylboronic acid ester. It was found that the introduction of bis(aminomethyl)phenylboronic acid ester on the fluorophore such as anthracene activates significantly the PET compared with that of an (aminomethyl)phenylboronic acid ester. On the basis of the proposed mechanisms of fluorescence PET sensors for detection of water, a key point for creating a highly-sensitive fluorescence PET sensor based on fluorophore–phenylboronic acid ester for a trace amount of water is to effectively facilitate the formation of fluorescent ionic structure by the addition of water molecules.

1. Introduction

Fluorescent sensors for detection and quantification of a trace amount of water in solutions, solids, the atmosphere and the products have received considerable attention in recent years from the viewpoint of not only fundamental study in analytical chemistry, photochemistry and photophysics, but also their potential applications to the environmental and medical materials, and quality control monitoring system in industry [1–23]. Most of fluorescent sensors for water developed so far are based on fluorescent conjugated polymer and organic fluorescent dyes, and their fluorescence intensities decrease with an increase in the amount of water in organic solvents. This feature can be attributed to the solvatochromic property of sensors, the aggregation of sensors or the formation of hydrogen bonding between the sensor and water molecules with the increase in the water content [5–13]. However, this fluorescence quenching system makes it difficult to detect trace amounts of water. Thus, recently, some research groups reported the fluorescence enhancement system [1–4,13–15] based on decomposition reaction [14] and spirolactone ring opening reaction [15] of sensor, or metal-organic framework [2]. On the other hand, the fluorescence sensors based on photo-induced electron transfer (PET) concept have been generally developed for detecting cations such as H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} as well as neutral organic species in biochemical analyses [24–33]. They are composed of fluorophore skeleton linked to cation binding site such as an amino moiety via a methylene spacer (fluorophore–spacer–receptor structure). The PET takes place from the nitrogen atom of amino moiety to fluorophore skeleton, leading to fluorescence quenching of the fluorophore. When the nitrogen atom of amino moiety is protonated or strongly interacts with a cation, a drastic enhancement of fluorescence is observed because of the inhibition of PET. On the basis of PET concept, an anthracene–phenylboronic acid system has been developed by Shinkai group [34–37] and Wang group [38–40] as the fluorescence PET sensor for saccharides. On the other hand, their anthracene–phenylboronic acid system inspired us to conceive an anthracene–phenylboronic acid ester **OM-1** and **OF-2** as a new fluorescence PET sensor for water (Scheme 1) [20–23]. Boronic acid ester plays an important role in enhancement of the solubility of the sensor in organic solvents. Our previous study demonstrated that for both an unsubstituted sensor **OM-1** and a cyano-substituted sensor **OF-2**, the addition of water to organic solvents containing the sensor causes the efficient formation of the fluorescent ionic structure **OM-1a** or **OF-2a**, resulting in the suppression of PET (occurrence of fluorescence) due to the protonation of the tertiary amino group

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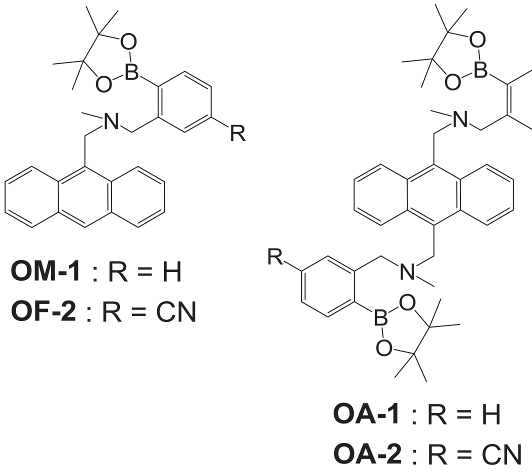
http://dx.doi.org/10.1016/j.dyepig.2015.07.042



Scheme 1. Fluorescence PET sensors **OM-1**, **OF-2**, **OA-1** and **OA-2** for detection of water in organic solvents.

(Scheme 3a). It was found that the detection limit (DL) and quantitation limit (QL) of **OF-2** are 0.008 and 0.026 wt%, respectively, for water in THF, which are superior to those (0.2 and 0.5 wt%) of **OM-1** and are equivalent to or superior to those of the reported fluorescence water sensors based on not only a fluorescence enhancement system (Refs. [21,23] in Table 1) by the decomposition reaction [14] and the spirolactone ring opening reaction [15] of sensor, but also a fluorescence quenching system (Refs. [5,10] in Table 1) by the aggregation of sensors or the formation of hydrogen bonding between sensor and water molecules. This implies that the introduction of electron-withdrawing substituent such as cyano group on the phenylboronic acid ester can enhance the Lewis acidity of the boron atom, effectively leading to formation of fluorescent ionic structure by the addition of water molecules. Consequently, we demonstrated that the fluorescence enhancement system based on PET concept is useful for detection and quantification of a trace amount of water in organic solvents.

In this work, to provide a direction in molecular design toward creating a highly-sensitive fluorescence PET sensor for a trace amount of water in organic solvents, we have designed and synthesized anthracene-bis(aminomethyl)phenylboronic acid ester **OA-1** and **OA-2**, without a substituent and with a cyano group, respectively, on the phenylboronic acid ester (Scheme 1). On the basis of the proposed mechanisms of fluorescence PET sensors for detection of water, the influences of bis(aminomethyl)phenylboronic acid ester on the PET and the detection of water in organic solvents are discussed.

Table 1
DL and QL of **OM-1**, **OF-2**, **OA-1** and **OA-2**, and of previously reported fluorescence sensors for water determination in organic solvents.

Sensor	Solvent	m_s	DL	QL
OM-1 [21]	1,4-Dioxane	14	0.2 wt%	0.7 wt%
	THF	19	0.2 wt%	0.5 wt%
OF-2 [23]	1,4-Dioxane	334	0.01 wt%	0.03 wt%
	THF	390	0.008 wt%	0.026 wt%
OA-1	1,4-Dioxane	23[a]	–[b]	–[b]
	THF	42[a]	–[b]	–[b]
OA-2	1,4-Dioxane	220[a]	–[b]	–[b]
	THF	257[a]	–[b]	–[b]
Ref. [14]	THF	16	0.0464 wt%	0.1405 wt%
	Acetonitrile	13	0.0298 wt%	0.0902 wt%
Ref. [15]	THF	7771	0.0033 wt%	0.0105 wt%
Ref. [5]	NMP	−610.2	0.009 wt%	0.03 wt%
	Acetonitrile	−275.4	0.02 wt%	0.07 wt%
Ref. [10]	1,4-Dioxane	−40.23	0.008 wt%	No data
	Acetonitrile	−52.10	0.006 wt%	No data

[a] The water content range is 0.4–0.97 wt% for **OA-1** in 1,4-dioxane, 0.38–0.93 wt% for **OA-1** in THF, 0.11–0.65 wt% for **OA-2** in 1,4-dioxane and 0.11–0.5 wt% for **OA-2** in THF, respectively.

[b] The plots of changes in the fluorescence peak intensity against the water fraction are not a linear system in the water content region below 1.0 wt%.

2. Experimental section

2.1. General

Melting points were measured with a Yanaco micro melting point apparatus MP model. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. Absorption spectra were observed with a Shimadzu UV-2910 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian-400 (400 MHz) FT NMR spectrometer. High-resolution mass spectral data by ESI were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. Elemental analyses were measured with a Perkin–Elmer 2400 II CHN analyzer. The addition of water to organic solvents containing **OA-1** or **OA-2** was made by weight percent (wt%). The determination of water in 1,4-dioxane and THF was done with an MKC-610 and MKA-610 Karl Fischer moisture titrator (Kyoto Electronics manufacturing Co., Ltd.) based on Karl Fischer coulometric titration (relative standard deviation is below 0.3% in a measurement of methanol containing 1 mg H_2O) for below 1.0 wt% and volumetric titration for above 1.0 wt%, respectively.

2.2. Synthesis

2.2.1. Synthesis of 1,1′-(anthracene-9,10-diyl)bis(N-methyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)methanamine) (*OA-1*)

A solution of 9,10-bis(methylaminomethyl)anthracene (0.3 g, 1.1 mmol) [37], **1** (1.0 g, 3.4 mmol), Na_2CO_3 (0.48 g, 4.5 mmol) and DMF (40 ml) was stirred for 2 days at 80 °C under an argon atmosphere. The water was added to the reaction mixture and the aqueous layer was extracted with dichloromethane. The organic extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was dissolved in toluene, and HPLC was performed to give **OA-1** (0.05 g, yield 7%) as a light yellow solid; m.p. 201–203 °C; IR (ATR): $\tilde{\nu} = 2978, 1602, 1342, 1310, 1145$ cm^{-1}; ^{1}H NMR (400 MHz, [D$_2$]Dichloromethane) $\delta = 1.26$ (s, 24H), 2.16 (s, 6H), 3.97 (s, 4H), 4.35 (s, 4H), 7.28 (dd, $J = 1.4$ and 7.3 Hz, 2H), 7.37–7.43 (m, 8H), 7.78 (d, $J = 7.4$ Hz, 2H), 8.34–8.37 (m, 4H) ppm; HRMS (ESI): m/z (%): [M + H$^+$] calcd for $C_{44}H_{55}B_2N_2O_4$, 697.43425; found 697.43555; Anal. calcd for $C_{44}H_{54}B_2N_2O_4$: C 75.87, H 7.81, N 4.02; found C 75.58, H 7.94, N 3.86.

2.2.2. Synthesis of 3,3′-(((anthracene-9,10-diylbis(methylene))bis(methylazanediyl))bis(methylene))bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile) (*OA-2*)

A solution of 9,10-bis(methylaminomethyl)anthracene (0.3 g, 1.1 mmol) [37], **2** [23] (0.91 g, 2.8 mmol), Na_2CO_3 (0.48 g, 4.5 mmol) and DMF (40 ml) was stirred for 2 days at 80 °C under an argon atmosphere. The water was added to the reaction mixture and the aqueous layer was extracted with dichloromethane. The organic extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was recrystallized form 1,4-dioxane to give **OA-2** (0.11 g, yield 14%) as a light yellow solid; m.p. 258–259 °C; IR (ATR): $\tilde{\nu} = 2982, 2230, 1608, 1362, 1347, 1139$ cm^{-1}; ^{1}H NMR (400 MHz, [D$_2$]Dichloromethane) $\delta = 1.26$ (s, 24H), 2.45 (s, 6H), 3.92 (s, 4H), 4.36 (s, 4H), 7.46–7.49 (m, 6H), 7.62 (s, 2H), 7.79 (d, $J = 7.7$ Hz, 2H), 8.35–8.38 (m, 4H) ppm; HRMS (ESI): m/z (%): [M + H$^+$] calcd for