Talanta 100 (2012) 229–238

Contents lists available at SciVerse ScienceDirect

Talanta

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

Synthesis, characterization of conjugated oligo-phenylene-ethynylenes and their supramolecular interaction with β-cyclodextrin for salicylaldehyde detection

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ARTICLE INFO

Article history:
Received 25 April 2012
Received in revised form
7 August 2012
Accepted 9 August 2012
Available online 17 August 2012

Keywords:
Functional oligo-phenylene-ethynylenes
β-cyclodextrin
Supramolecular interaction
Spectroscopy
Salicylaldehyde

ABSTRACT

Four new conjugated oligo-phenylene-ethynylenes derivatives, *N*-methyl-4-(4-acetylthiophenylethynyl)-1,8-naphthalimide (**1**), thioacetic acid *S*-[4-(4-aminophenyl-ethynyl)phenyl]ester (**2**), 4-methylthiophenylethynylbenzenamine (**3**), *N*-methyl-4-(4-methyl-thiophenyl-ethynyl)-1,8-naphthalimide (**4**), were synthesized by Sonogashira and Eglinton cross-coupling reactions. The structures of the four compounds were confirmed by ^{1}HNMR, ^{13}CNMR, MS and IR and their spectral characteristics were studied by ultraviolet and visible (UV) spectroscopy as well as fluorescence spectroscopy in different medium. It was found that the fluorescence properties of compounds **2** and **3** were notably improved in aqueous solutions in the presence of β-cyclodextrin (β-CD). Spectral analysis supported the suppositions that the fluorescence intensity enhancement was due to the formation of inclusion complex with β-CD. The supramolecular interaction was investigated in detail and the reaction mechanism was provided. A salicylaldehyde determination method in aqueous medium was established based on the supramolecular complex of compound **3**. Under the optimum conditions, the supramolecular complex exhibited a dynamic fluorescence response range for salicylaldehyde from 0.6 to 240×10^{-6} molL^{-1}, with a detection limit of 1×10^{-8} molL^{-1}.

1. Introduction

The molecular assembly of alkanethiols and supramolecules has provided a facile approach to novel molecular materials for applications in separation, catalysis and molecular recognition [1]. Alkanethiols containing terminal carboxylic or amino groups can be used in fabrication of self-assembled bio-molecular monolayers [2]. However, the electroactivity and sensitivity of the alkanethiols modified biosensors or bioelectronics were low due to the poor electrical conductivity and the flexible nature of carbon chains [3]. While for the aromatic thiols, the electrical conductivity and physical properties are greatly improved due to their π-conjugated backbone systems [4]. Rigid rod conjugated oligo(phenylene ethynylene)s (OPEs) are one family of molecules having interesting molecular electronic and optical properties. If the OPEs are modified with some functional groups, a variety of electronic properties, such as negative differential resistance (NDR) [5] and molecular memory devices [6] can be achieved. Changes in the molecular functionality [7] and conformation [8] are thought to generate alterations in the conductivity of the molecular devices, thus producing the molecular scale switching behavior. Modifying the linear rigid rod conjugated OPEs with thiols, thioesters or amino groups on the terminal, favorable new molecules can be obtained.

One drawback of the linear conjugated OPEs is their poor solubility in polarity solvents. Their fluorescence properties are very weak in water if there are not any hydrophilic side chains in the conjugated molecules. It was reported that the formation of supramolecular complexes with cyclodextrins (CDs) can alter the photochemical and photophysical properties of the guest molecules, such as enhancement of the solubility, stability, and bioavailability [9]. β-cyclodextrin (β-CD) is a torus-shaped cyclic oligosaccharide composed of seven *D*-glucopyranose units and has a hollow truncated cone with hydrophobic cavity and hydrophilic wall to form inclusion complexes with organic or inorganic

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http://dx.doi.org/10.1016/j.talanta.2012.08.008

molecules if the guest possess suitable polarity and dimension [10]. It has also been proved that β-CD is a suitable candidate for target drug delivery and release in human bodies, which can promote the digestion, absorption and therapeutic effect of drugs. Highly sensitive and selective methods for determination of drugs in aqueous solution have been established based on the significant enhancement in absorbance or fluorescence intensity of drug molecules owing to the formation of complexes with CDs [11–17]. The β-CD complexes are attractive for sensing applications if the supramolecular structures can be assembled or dissembled in the presence of some specific analytes. For example, some applications are based on the β-CD complexes [18] and β-CD derivative complexes [19,20]. Recently, colorimetric and fluorescence sensing of Cu^{2+} in aqueous have been realized using 1,8-dihydroxyanthraquinone-β-cyclodextrin complex with the assistance of ammonia [21]. The supramolecular complex of cyclodextrin and a chromophoric dye was prepared by Sooyeon Jeong et al. and it exhibited selectively and efficiently quenching by lead ions [22].

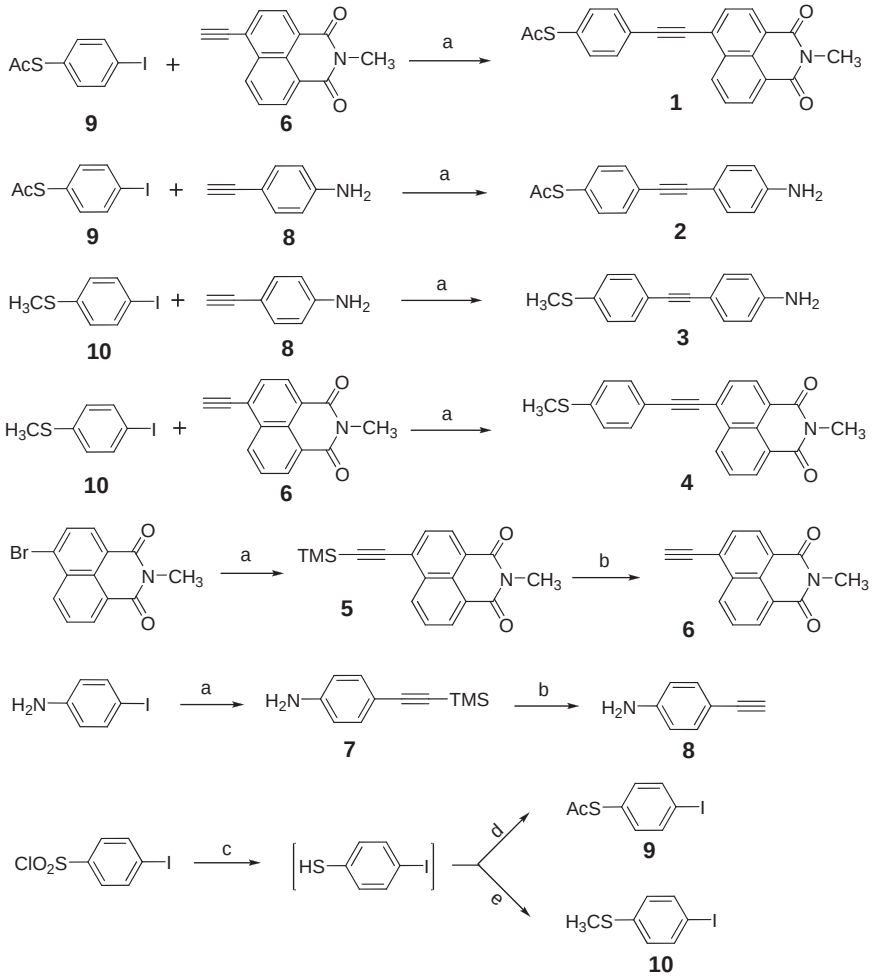
In the present work, four new oligo-phenylene-ethynylenes derivatives, *N*-methyl-4-(4-acetylthiophenylethynyl)-1,8-naphthalimide (**1**), thioacetic acid *S*-[4-(4-aminophenyl-ethynyl)phenyl]ester (**2**), 4-methyl-thiophenyl-ethynylbenzenamine (**3**), *N*-methyl-4-(4-methyl-thiophenyl-ethynyl)-1,8-naphthalimide (**4**), were firstly synthesized and characterized, and the supramolecular interactions of them with β-CD were studied in detail and the possible mechanism was discussed. The supramolecular complex of compound **3** exhibits fluorescence quenching with the addition of salicylaldehyde, which could be utilized as a selective fluorescence probe for salicylaldehyde detection in aqueous solutions.

2. Experimental section

2.1. Instruments and chemicals

Varian-500 high resolution NMR spectrometer (Bruker AVANCE DRX500, Switzerland) and Thermo-Finnigan LCQ-Advantage Mass-spectrometer (GCMS-QP2010, Japan) were used to confirm the structure of the compounds. All absorbance measurements were carried out on a UV-2450 spectrophotometer equipped with a 1.0 mL quartz cells (Shimadzu, Japan). Fluorescence spectra were conducted on an F-4500 fluorophotometer (Hitachi, Japan). The FTIR spectra were obtained from a Nicolet 670 IR spectrophotometer (Nicolet, USA). pH values were measured with a pHs-3C digital pH-meter (Shanghai Lei Ci Device Works, China).

Trimethyl silyl acetylene (TMSA), triphenylphosphine (PPh_3), bis(triphenylphosphine) Palladium (II) chloride ($Pd(PPh_3)_2Cl_2$), cuprous iodide, dichlorodimethylsilane, pipsyl chloride, methyl iodide, petroleum ether (PE), ethyl acetate (EA) were purchased from Aladdin. Reagent grade tetrahydrofuran (THF) and



a: $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF/TEA b: K_2C0_3, THF/CH_3OH

c: Zn + Me_2SiCl_2 /DMA. d: i) K_2C0_3, ii)AcCl e: i)K_2C0_3, ii) ICH_3,acetone

Scheme 1. The synthetic route of target compounds and intermediates.

triethylamine were distilled under nitrogen from sodium benzophenone ketyl. β-CD was obtained from China Medicine Shanghai Chemical Reagent Corp. and was purified by two recrystallizations in doubly distilled water, followed by vacuum drying at 60 °C for 12 h. 0.1 molL^{-1} of β-CD stock solution was prepared with Milli-Q water. Britton–Robinson (BR) solutions of different pH were prepared by mixing appropriate amounts of phosphoric, acetic and boric acids in the same concentration (0.04 molL^{-1}) and then adjusted to desired pH with 0.2 molL^{-1} sodium hydroxide. All other reagents were of analytical grade and used as received without further purification.

2.2. Experimental procedures

2.2.1. Synthesis and characterization of the new compounds of 1–4

The target compounds were synthesized by palladium catalyzed Sonogashira coupling reactions and all reactions were performed under nitrogen atmosphere. And the synthesis processes were shown in Scheme 1. *N*-methyl-4-bromo-1,8-naphthalimide was synthesized from 4-bromo-1,8-naphthalimide and 30% aq. methylamine. 4-iodophenyl aniline was synthesized according to the literature [23]. The target compounds were confirmed by ^{1}HNMR, ^{13}CNMR, MS and IR.

2.2.1.1. N-methyl-4-(4-acetylthiophenylethynyl)-1,8-naphthalimide (1). A 50 mL two-necked flask was charged with *N*-methyl-4-ethynyl-1,8-naphthalimide (470 mg, 2 mmol), 4-iodo-1-thioacetybenzene (556 mg, 2 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol), PPh_3 (52.4 mg, 0.2 mmol) and cuprous iodide (37.5 mg, 0.2 mmol). The flask was then sealed with a serum cap, evacuated and backfilled with nitrogen several times. Dry THF (25 mL) and triethylamine (6 mL) were added via a syringe through the serum cap. After being stirred at 70 °C for 10 h, the reaction solution was poured into saturated ammonium chloride solution and extracted with dichloromethane. The extract was then washed with brine, dried over magnesium sulfate, and filtered. The solvent was evaporated *in vacuo*, and the residue was purified by flash chromatography (PE: EA=10:1, silica gel) to give **1** (0.524 g, 68%) as yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.72 (dd, 1H, J=8.5 Hz; 1.0 Hz), 8.67 (dd, 1H, J=7.25 Hz; 1.0 Hz), 8.58 (d, 1H, J=7.5 Hz), 7.97 (d, 1H, J=7.5 Hz), 7.86 (t, 1H, J=7.5 Hz), 7.70 (d, 2H, J=8.5 Hz), 7.49 (d, 2H, J=8.5 Hz), 3.58 (s, 3H), 2.47 (s, H).^{13}C NMR ($CDCl_3$, 126 MHz): δ 195.1 (1C=O), 160.7 (2C=O), 139.5 (1CH), 137.7 (1CH), 137.8 (1CH), 136.7 (1C), 135.8 (1C), 133.6 (2CH), 125.7 (1C), 126.9 (1C), 123.8 (1C), 120.5 (1C), 93.2 (2C), 30.1 (C), 27.9 (C). *m/z* (%): 385 (M^+, 100). IR (KBr): 2960, 2830, 2208, 1719, 1682, 1399, 1355, 1285, 1175, 836 cm^{-1}.

2.2.1.2. Thioacetic acid S-[4-(4-aminophenylethynyl)phenyl]ester (2). The synthesis of **2** was similar to **1**. 4-ethyynylaniline (166 mg, 1.42 mmol), 4-iodo-1-thioacetybenzene (395 mg, 1.42 mmol), $Pd(PPh_3)_2Cl_2$ (91 mg, 0.13 mmol), PPh_3 (35 mg, 0.13 mmol) and cuprous iodide (25 mg, 0.13 mmol), THF (15 mL), triethylamine (4 mL) were used. After being stirred at 50 °C for 5 h, the reaction residue was purified by silica gel flash chromatography using dichloromethane: PE (1:4, then 1:1) to provide a light yellow solid **2** (0.334 g, 88%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (d, 2H, J=8.5 Hz), 7.36 (d, 2H, J=8.5 Hz), 7.33 (d, 2H, J=8.5 Hz), 6.63 (d, 2H, J=8.5 Hz), 3.84 (s, 2H), 2.42(s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz,): δ 193.8, 146.9, 134.2, 133.1, 131.9, 127.1, 125.3, 114.7, 112.2, 92.0, 86.7, 30.2. *m/z* (%): 267 (M^+, 100). IR (KBr): 3474, 3375, 3034, 2921, 2210, 1690, 1622, 1588, 1517, 1483, 1399, 1355, 1290, 1177, 1115, 831 cm^{-1}.

2.2.1.3. 4-methylthiophenylethynylbenzenamine (3). The synthesis process of **3** was similar to what described for **1**. 4-iodothioanisole (250 mg, 1 mmol), 4-ethyynylaniline (128 mg, 1.1 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), PPh_3 (26 mg, 0.1 mmol) and cuprous iodide (19 mg, 0.1 mmol), THF (12 mL), triethylamine (4 mL) were used. After being stirred at 60 °C for 10 h, the reaction residue was purified by silica gel flash chromatography by using dichloromethane: PE (1:3, then 1:1) to provide yellow solid of **3** (0.222 g, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43(d, 2H, J=8.0 Hz), 7.35 (d, 2H, J=8.0 Hz), 7.21 (d, 2H, J=8.0 Hz), 6.65 (d, 2H, J=8.5 Hz), 3.84 (s, 2H), 2.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 146.6, 138.4, 132.9, 131.6, 126.0, 120.3, 114.8, 112.7, 90.2, 87.1, 15.5. *m/z* (%): 239 (M^+, 100). IR (KBr): 3472, 3372, 2921, 2845, 1615, 1517, 1489, 1294, 1140, 1086, 828, 809 cm^{-1}.

2.2.1.4. N-methyl-4-(4-methylthiophenylethynyl)-1, 8-naphthalimides (4). *N*-methyl-4-ethynyl-8-naphthalimides (235 mg, 1 mmol), 4-iodothioanisole (250 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), PPh_3 (26.2 mg, 0.1 mmol) and cuprous iodide (19 mg, 0.1 mmol) were used. After being stirred at 70 °C for 6 h, the reaction residue was purified by flash chromatography (PE: EA 10:1, silica gel) to give **4** (0.267 g, 75%) as yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.73 (dd, 1H, J=7.5 Hz; 1.0 Hz), 8.67 (dd, 1H, J=7.0 Hz; 1.0 Hz), 7.56 (d, 1H, J=7.5 Hz), 7.94 (d, 1H, J=8.0 Hz), 7.83 (t, 1H, J=8.0 Hz), 7.57 (d, 2H, J=8.5 Hz), 7.28(d, 2H, J=8.0 Hz), 3.57(s, 3H), 2.54 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 160.1, 139.4, 137.8 137.1, 136.4, 135.2, 133.3, 132.5, 131.9, 129.0, 125.9, 125.5, 125.2, 121.7, 119.2, 94.2, 27.5, 14.8. *m/z* (%): 357 (M^+, 100). IR (KBr): 3034, 2960, 2830, 2208, 1719, 1682, 1399, 1355, 1285, 1175, 836 cm^{-1}.

2.2.1.5. N-methyl-4-trimethylsilanylethynyl-1,8-naphthalimides (5). A 100 mL flask was charged with *N*-methyl-4-bromo-1,8-naphthalimide (2.72 g, 9.4 mmol), $Pd(PPh_3)_2Cl_2$ (330 mg, 0.47 mmol), cuprous iodide (89 mg, 0.47 mmol). The flask was then sealed with a serum cap, evacuated and backfilled with nitrogen several times. Triethylamine (7 mL), THF (30 mL) and TMSA (1.5 mL, 10.3 mmol) were added. After being stirred at 40 °C for 10 h, the reaction solution was poured into aqueous ammonium chloride and extracted with EA. The extract was then washed with brine, dried over magnesium sulfate, and filtered. The solvent was evaporated *in vacuo*, and the residue was purified by flash chromatography (PE: EA=10:1, silica gel) to give **5** (2.82 g, 98%) as brown solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.63 (m, 2H), 8.5 (d, 1H, J=7.5 Hz), 7.89 (d, 1H, J=8.0 Hz), 7.82 (t, 1H, J=7.5 Hz), 3.56 (s, 3H), 0.37 (s, 9H).

2.2.1.6. N-methyl-4-ethynyl-1,8-naphthalimides (6). A 250 mL flask was charged with 5 (2.82 g, 9.2 mmol), potassium carbonate (9.1 g, 66 mmol), THF (20 mL) and methanol (20 mL). After being stirred for 2 h, the purify process was the same as that of **5**, to give **6** (1.731 g, 80%) as yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.65 (d, 1H, J=8.25 Hz), 8.63 (d, 1H, J=7.25 Hz), 8.53 (d, 1H, J=7.5 Hz), 7.93 (d, 1H, J=7.5 Hz), 7.82 (t, 1H, J=7.5 Hz), 3.75 (s, 1H), 3.56 (s, 3H).

2.2.1.7. 4-[(trimethylsilyl)ethynyl]aniline (7). A 100 mL flask was charged with 4-iodophenyl aniline (3.44 g, 15.7 mmol), $Pd(PPh_3)_2Cl_2$ (0.55 g, 0.78 mmol), cuprous iodide (0.14 g, 0.78 mmol). The flask was then sealed with a serum cap, evacuated and backfilled with nitrogen several times. Triethylamine (10 mL), THF (40 mL) and TMSA (2.4 mL, 16.5 mmol) were added. After being stirred at 60 °C for 5 h, the reaction solution was processed similar to compound **5** except the residue was purified by flash chromatography (PE: EA=4:1, silica gel) to give **7** (2.62 g, 88%) as brown solid. ^{1}H NMR

($CDCl_3$, 500 MHz): δ 7.27 (dd, 2H, J=8.5 Hz), 6.57 (dt, 2H, J=9.0 Hz), 3.80 (s, 2H), 0.23 (s, 9H).

2.2.1.8. 4-ethyynylaniline (8). A 250 mL flask was charged with **7** (2.5 g, 13.2 mmol), potassium carbonate (18.3 g, 132 mmol), THF (30 mL) and methanol (30 mL). After being stirred for 2 h, the reaction was ended. And purify process was the same as that of **7**, to give **8** (1.43 g, 92%) as brown-yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (dd, 2H, J=6.8 Hz), 6.59 (dd, 2H, J=6.8 Hz), 3.82 (s, 2H), 2.96 (s, 1H).

2.2.1.9. 4-iodo-1-thioacetybenzene (9). A solution of pipsyl chloride (6.05 g, 20.0 mmol) and *N,N*-dimethylacetamide (5.224 mL, 60.0 mmol) in dichloroethane (130 mL) was added in a stirred suspension of zinc powder (4.55 g, 70.0 mmol) and dichlorodimethylsilane (8.41 mL, 70.0 mmol) in 1,2-dichloroethane (130 mL) [23]. The mixture was stirred at 75 °C for 2 h until the zinc powder almost disappeared, then potassium carbonate powder (1.518 g, 11.0 mmol) was added and the mixture was stirred for another 30 min. The mixture was cooled to room temperature, and then acetyl chloride (5.68 mL, 80.0 mmol) was added to react overnight under stirring. The mixture was poured into water and extracted with dichloromethane. The organic layers were combined and dried over magnesium sulfate, filtered, concentrated *in vacuo,* and purified by flash chromatography (PE, silica gel) to give **9** (4.56 g, 82%) as white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.73 (d, 2H, J=8.5 Hz), 7.12 (d, 2H, J=8.5 Hz), 2.42 (s, 3H).

2.2.1.10. 4-iodothioanisole (10). The synthesis procedure was similar to that of *S*-acetyl-4-iodothiophenol except that 4-iodothioanisole was synthesized in two steps instead of the one-pot procedure. 4-iodothiophenol was prepared and used immediately without further purification. Potassium carbonate powder (1.81 g, 13.0 mmol) and methyl iodide (4.39 g, 18.6 mmol) were dissolved in 40 mL acetone, and then methyl iodide was added dropwise under stirring. The mixture was allowed to stir at 50 °C for 4 h. The purifying process was the same as that of **9** to give **10** (3.71 g, 79.6%) as white-yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57 (dd, 2H, J=7.0 Hz; 2 Hz), 7.37 (dd, 2H, J=8.0 Hz; 2 Hz), 2.45 (s, 3H).

2.2.2. Spectra properties of compounds 1–4

The absorption and fluorescence spectra of compounds **1**–**4** in different solvents were investigated. The absorbance spectra of the compounds were measured against a reagent blank. The excitation and emission silts were set at 5 nm and the photomultiplier voltage was 700 V in the fluorescence measurements.

2.2.3. Supramolecular interaction of the new compounds with β-CD

The 10 mmolL^{-1} stock solutions of the novel conjugated OPEs **1**–**4** were prepared in ethanol and kept in dark. Then they were diluted with water and buffer solution to the corresponding concentration for the supramolecular interaction with β-CD. That is, a certain volume of the stock solution of compounds **1**–**4** was transferred into a 4 mL volumetric flask, then appropriate amount of 0.01 molL^{-1} β-CD solution was added in. The pH was controlled by BR buffer solution (2 mL) and the mixed solution was diluted to 4 mL with water and shaken thoroughly at 20 °C.

2.2.4. Detection of salicylaldehyde based on the complex of compound 3 and β-CD

The fluorescence titrations of the supramolecular complex of compound **3** with salicylaldehyde were performed as follows: fixed volume of the supramolecular complex stock solution and different volumes of salicylaldehyde stock solution were mixed. The final volume was adjusted to 4.5 mL with water and was shaken thoroughly. The mixture was allowed to react for 5 min before the fluorescence spectra were measured. The effect of various interferences on the determination of salicylaldehyde was investigated by analyzing the sample solutions in the presence of 1×10^{-4} molL^{-1} interfering compounds.

3. Results and discussion

3.1. The optical properties of compounds 1–4

The optical properties of compounds **1**–**4** were studied, the results are shown in Fig. 1. They all display obvious absorption bands in UV region in dichloromethane or THF. It can be seen that the maximum absorption wavelength (λ_{max}) of compounds **1**–**4** exists in the range of 350–400 nm and these bands can be attributed to n–π^* transition of the OPEs compounds. And another band near 300 nm is ascribed to the π–π^* transition of each compound owing to the conjugation structure. Table 1 gives the maximum absorbance wavelength of each compound in different solvents. The λ_{max} of the compounds shifted to longer wavelength with increase of the solvent polarity. Compounds **2** and **3** show similar spectra properties in organic solvents though the intensity of compound **2** is somewhat lower than compound 3 in the same solvent. For compounds **1** and **4**, there are two obvious bands in organic solvents and the λ_{max} are red-shifted compared with compounds **2** and **3**, which may result from the larger conjugation structure of naphthalimide ring in **1** and **4**.

In aqueous solution, the UV intensity decreased notably and this may come from the salvation of water. There is only a large peak near 320 nm which may be attributed to π–π^* transition of each compound and the peak is blue-shifted compared with that

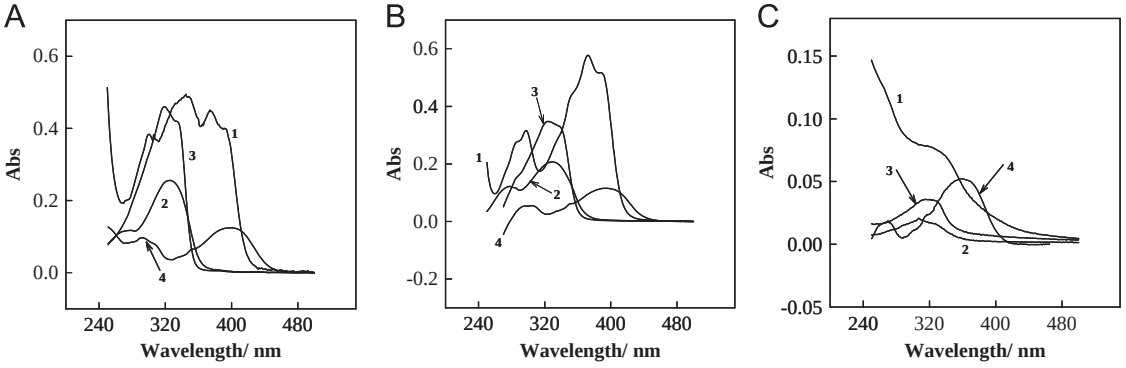


Fig. 1. The UV spectra of compounds 1–4 in dichloromethane (A), THF (B), and water (C). The concentrations of the compounds were 1.0×10^{-5} mol L^{-1}.

Table 1
The maximum UV absorbance peak (λ_{ab}), molar absorptivity (ε), fluroscence emission wavelength (λ_{em}) and the fluorescent quantum yield value (φ) of each compound in different solvents.

Compound	CH_2Cl_2				THF				Water			
	λ_{ab}	ε	λ_{em}	φ	λ_{ab}	ε	λ_{em}	φ	λ_{ab}	ε	λ_{em}	φ
1	372	1.8×10^5	460	0.72	374	2.8×10^5	460	0.65	345	3.5×10^4	473	0.57
2	325	1.6×10^5	418	0.70	329	1.1×10^5	421	0.54	319	1.3×10^4	492	0.26
3	320	3.0×10^5	402	0.56	325	2.6×10^5	408	0.66	315	1.8×10^4	453	0.22
4	392	1.2×10^5	521	0.68	393	8.0×10^4	532	0.53	393	3.2×10^4	495	0.41

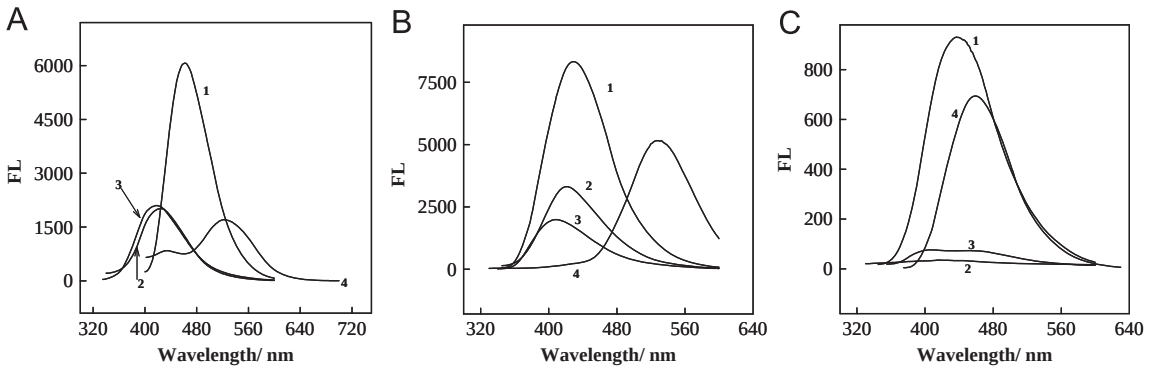


Fig. 2. The FL spectra of compounds **1**–**4** in dichloromethane (A), THF (B), and water (C). The concentrations of the compounds were 1.0×10^{-5} mol L^{-1}.

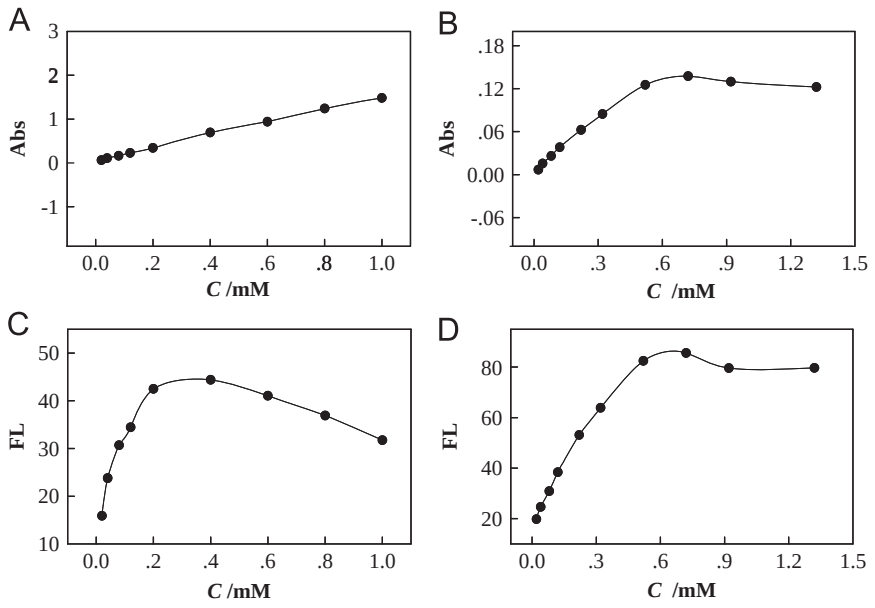


Fig. 3. The dependence of UV (A, B) and fluorescence (C, D) on the concentrations of compounds **2** (A, C) and **3** (B, D) in aqueous solution.

of in organic solvent except for compound **4**. According to the Lambert–Beer law, the molar absorption coefficients of these compounds are determined, and the results are shown in Table 1.

The compounds show high fluorescent intensity in the range of 400–550 nm in organic solvents though the maximum emission wavelength and intensity are different among them (Fig. 2). The OPEs chromophores induce a larger stokes shift about 100 nm. The quantum yields were about 0.5 in organic solvent, such as dichloromethane and THF using sulfatequilion as a standard. It is noteworthy that the emission wavelength of compounds **1** and **4** was red-shifted than compounds **2** and **3**. This may result from the different molecular structure of them. The fluorescence intensities of these compounds were larger in dichloromethane or THF and quickly quenched in water. It is found that compounds **1** and **4** have relatively better optical property than the other two compounds in water and this may attribute to the difference of the salvation and solubility between them in aqueous. The donor and acceptor moieties of compounds **2** and **3** are in close proximity, which can result in the emissions of the fluorophores quenched in the linear OPEs derivatives [24].

Considering that the optical properties of **2** and **3** in aqueous solution are poor, the dependence of the concentration on UV and fluorescence intensity was studied as shown in Fig. 3. It can be seen that the absorbance (A, B) and fluorescence (C, D) intensity of them increased with the concentration. When the concentration arrived at a certain value, the absorbance and fluorescence intensity reached to its maximum. This may be attributed to the super-saturation of compounds **2** and **3** owing to the small

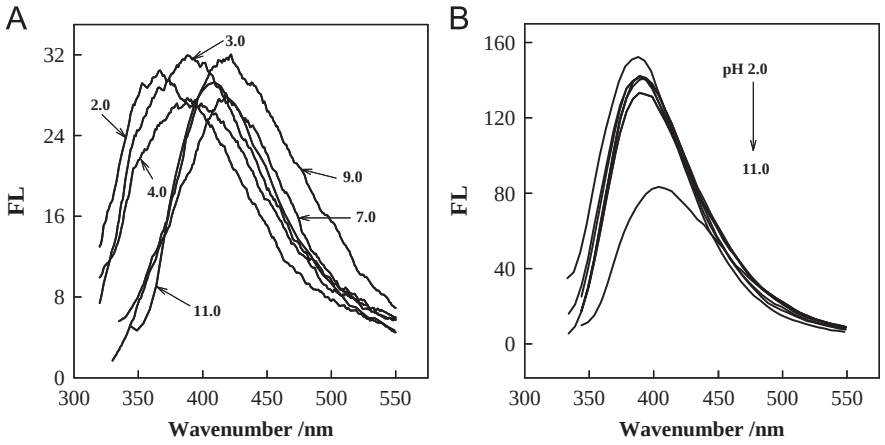


Fig. 4. The fluroscence spectra of compound **2** in different pH in the absence (A) or presence of β-CD (B). The concentrations of **2** and β-CD were 1.3×10^{-5} and 3.3×10^{-3} mol L^{-1}.

solubility of them in water. Due to their inherent rigid and linear structure, they inevitably exhibit limited solubility in polar solvent, which leads to a consideration decrease in emission intensity [19]. And in aqueous solutions, the efficient transfer between the nitrogen lone pair electrons of the amino/thiol groups and the phenylene–ethynylenes is low, which can also cause the fluorescence quenched.

3.2. The supramolecular interaction of compounds 1–4 and β-CDs

A variety of organic compounds can be included in β-CD central cavities in aqueous solution. Therefore, in the section below, β-CD is utilized as a candidate for the supramolecular interaction with compounds **1**–**4**. And it is reported that different inclusion models have been observed during interaction of β-CDs with guest molecules, *e.g.* inclusion within the cavity or binding to the rim or penetrating partially into the β-CD [25]. Alcohol may not compete with the hydrophobic cavity of β-CD preferentially because of its high polarity, and therefore it is chosen as an organic solvent to prepare the stock solutions of compounds **1**–**4**. The corresponding solutions of compounds **1**–**4** were prepared by injecting a certain volume (smaller than 100 μL) of the stock solutions via a Gilsone microliter syringe into a 4 mL colorimetric tube. Hence, the sample solutions were almost entirely aqueous. And the percentage of alcohol present in the experimental solution was considered to be too low to have any significant influence on the acid–base behavior of the compounds.

Fluorescence spectra of compounds **1** and **4** show slight enhancement in fluorescence emission (not shown) when adding β-CD in various pH value solutions. And this can be explained as follows: compounds **1** and **4** have larger size and cannot enter into the cavity of β-CD in our experiment condition owing to the stereo-hindrance effect of naphthalene ring. While for compounds **2** and **3**, the intensity of UV and fluorescence intensity were greatly enhanced. And in the section below, the interaction between compound **2** or **3** and β-CD will be discussed in detail.

3.2.1. The effect of pH

Compounds **2** and **3** contained amino, thioacetyl group, and therefore the properties will be changed with the pH value. Because of the instability of CDs at very low pH, the use of a strongly acidic solution was avoided [26]. Thus, the influence of pH on the system was studied in the range of 2.0–11.0. The concentrations of the guest molecules (compounds **2** or **3**) and β-CD in the experiment were kept at 1.3×10^{-5} and 3.3×10^{-3} mol L^{-1}, respectively. The reaction temperature was maintained at 20 °C. The measurements were performed thrice. Fig. 4A shows the fluorescence spectra of compounds **2** at different pH values and it was found that compound **2** can emit relatively weak fluorescence in the absence of β-CD. The fluorescence intensity was not basically varied at different pH values but the maximum emission wavelength was red-shifted from acidic media to basic media. The emission intensity of compound **2** was notably enhanced and the maximum emission wavelength was red-shifted when adding β-CD. It was noteworthy that in the presence of β-CD, the fluorescence intensity enhanced more obviously in acid media. In pH=2, the fluorescence intensity increased about five times and the maximum emission wavelength shifted from 357 to 389 nm. It may suggest that the acid media is propitious to the supramolecular interaction of compound **2** with β-CD. This is because the acidic form of compound **2** has more affinity than the basic form when forming an inclusion complex with β-CD. And at the same time, the acidic form of compound **2** (thiol, –SH) is more hydrophobic than that of the basic form (thioacetyl, $-SOCH_3$). It can be concluded that hydrophobic interactions may play an important role in the stabilization of supramolecular complex of 2 with β-CD in acid media.

For compound **3**, as seen in Fig. 5, pH affects the fluorescence intensity more obviously. The fluorescence intensity decreased with pH (Fig. 5A) and it changed more notably in the presence of β-CD (Fig. 5B) compared to Fig. 5A. In pH=2, 3 and 4, the fluorescence intensity increased about 11, 5 and 3 times in the presence of β-CD. And the fluorescence intensity almost remained unchanged in the basic media. The maximum emission wavelength shifted from 404 to 398 nm, which may suggest that the supramolecular interaction took place and the complex between compound **3** and β-CD successfully formed. Therefore, we also choose pH=2 BR solution as the inclusion reaction medium in the study.

It can be seen that the fluorescence intensity of **2** or **3** almost keep unchanged in the presence of β-CD in strong basic media but obviously enhance in acid media. Hence, the optimum pH value for the inclusion complex formation is in acid medium, where the compounds are in their acid forms. The conjugate base forms of compounds **2** or **3** have higher polarity and therefore they are relatively difficult to enter into the hydrophobic cavity of β-CD. We also found that the fluorescence intensity of compound **3** increased 11 times in pH=2 BR solution and the intensity of compound **2** increased five times at the same condition. It is reported that the hydrophobic/hydrophilic plays an important role in the inclusion process, and therefore, the phenomenon may

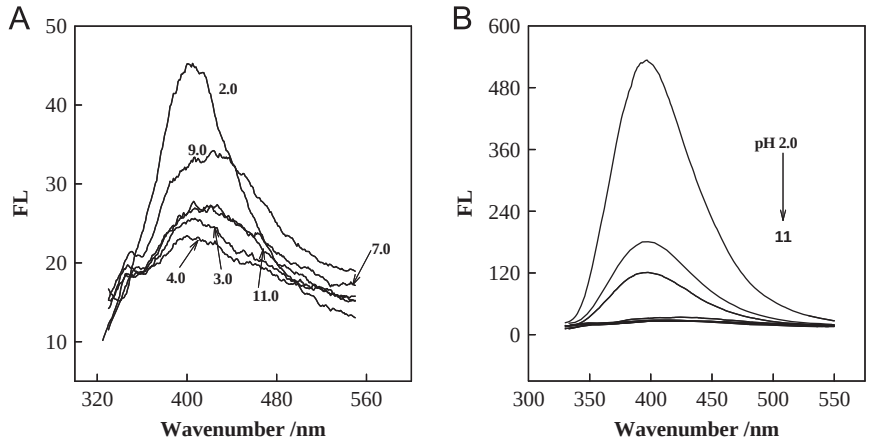


Fig. 5. The fluroscence spectra of compound **3** in different pH in the absence (A) or presence of β-CD (B). The concentrations of **3** and β-CD were 1.3×10^{-5} and 3.3×10^{-3} mol L^{-1}.

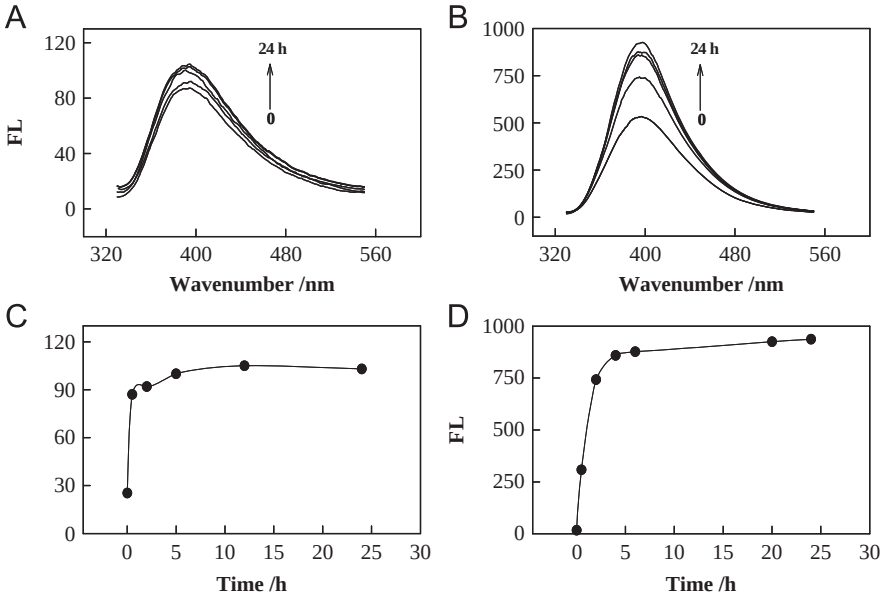


Fig. 6. The dependence of the reaction time on the fluorescence of **2** (A, C) and **3** (B, D) in pH=2 BR solution. The concentrations of **2** or **3** and β-CD were 1.3×10^{-4} and 3.3×10^{-3} mol L^{-1}.

result from the different hydrophilic property of compounds **3** and **2**. The methylthio group may exhibit larger hydrophobic property than the thioacetyl group, which may make compound **3** enter into the cavity easier.

3.2.2. *Effect of reaction time*

We also investigated the dependent of reaction time on the fluorescence intensity in the inclusion process. Fig. 6 shows the fluorescence intensity of the system in condition of the concentrations of β-CD and guest compounds hold constant at 3.3×10^{-3} and 1.3×10^{-4} mol L^{-1}. The reaction was faster at the beginning and then slowed to a level. The fluorescence intensities of **2** and **3** gradually enhanced with increase of β-CD in different concentrations until stable inclusion complexes were formed. It was found that they reached their saturation states at about 5 h though the maximum values were different.

3.2.3. *Effect of β-CD concentration*

Fig. 7 shows the fluorescence of **2** and **3** in various concentrations in the absence and presence of β-CD. The concentration of β-CD held constant at 3.3×10^{-3} mol L^{-1}, while concentrations of 2 and 3 were varied from 1.3×10^{-5} to 6.6×10^{-4} mol L^{-1}. The spectra were obtained by exciting at 305 nm and 309 nm, which were near the maximum absorption wavelength. In the absence of β–CD, compounds **2** and **3** exhibit relatively slow increase in fluorescence intensity with increase of concentrations. In the presence of β-CD, the fluorescence was greatly enhanced. These results demonstrated that the energy transfer between the amino group moiety and the OPE moiety can efficiently proceed after adding β–CD.

To demonstrate that these spectral changes did not result from the solvent effect caused by high concentration of β–CD, the effect of glucose on the spectra of the compounds was tested. When adding glucose (in an equivalent concentration of β–CD, 3.3×10^{-3} mol L^{-1}) in a 1.3×10^{-4} mol L^{-1} of object compounds aqueous solutions, neither spectral shifts nor intensity change in the spectra of **2** or **3** (see Fig. 8) were observed. And these phenomena were different from those of adding β–CD. Therefore, we concluded that the β-CD-induced changes observed in the absorption spectra of **2** and **3** resulted from the formation of supramolecular complexes between the guest molecules and β-CD [27].

Because the polarity of the hydrophobic cavity of β–CD was similar to that of alcohols, we used alcohol/water as media to

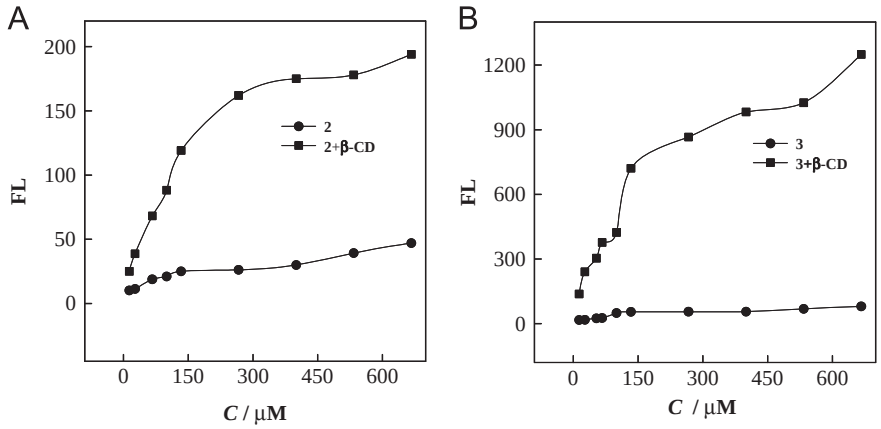


Fig. 7. The fluorescence of **2** (A) and **3** (B) in various concentrations in the absence and presence of β-CD in pH=2 BR solutions. The concentration of β-CD was held constant at 3.3×10^{-3} mol L^{-1}, the object compounds were varied from 1.3×10^{-5} to $6.6\times/10^{-4}$ mol L^{-1}.

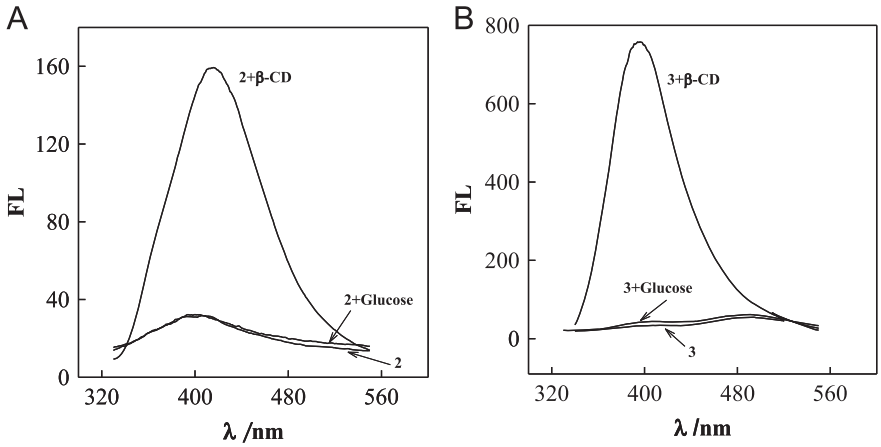


Fig. 8. Fluorescence spectra of 1.3×10^{-4} mol L^{-1} compounds **2** (A) and **3** (B) in aqueous solution in the absence or presence of β-CDs and glucose. The concentrations of β-CDs and glucose are 3.3×10^{-3} mol L^{-1}.

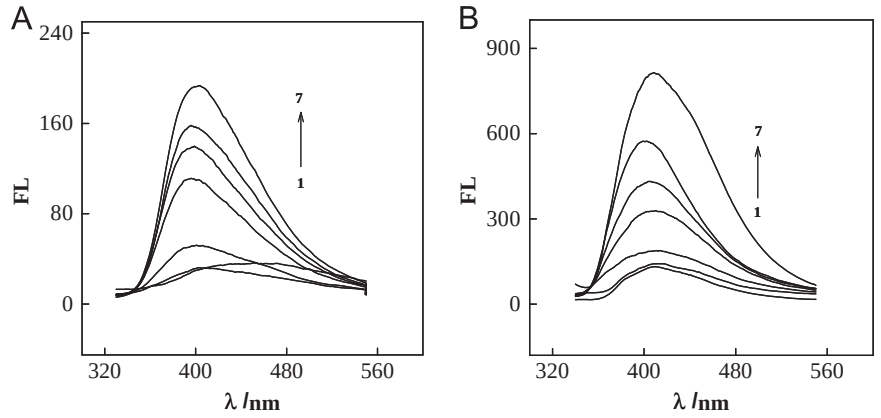


Fig. 9. Fluorescence spectra of compounds **2** (A) and **3** (B) at different ratios of alcohol/water, 1–7, are respected to 1/9, 1/4, 3/7, 1/1, 3/2, 4/1, 9/1. Concentrations of **2** or **3** were 1.3×10^{-4} mol L^{-1}.

obtain the spectra of the object compounds at different alcohol/water ratios. It was found that the maximum emission wavelength of **2** and **3** shifted from 352 to 404 nm and 409 to 403 nm, respectively. The fluorescence intensity was gradually enhanced with the increase of the percentage of alcohol in the mixed solvent (Fig. 9). That is, the spectra of **2** and **3** in different alcohol/water ratios were similar to that of adding β–CD in their aqueous solutions. The facts suggested that, in the presence of β–CD, the microenvironment around the object molecules was similar to those of in the alcohols, thus it indicated the formation of inclusion complexes between β–CD and compounds **2** or **3**.

3.2.4. *The reaction mechanism*

The fluorescence emission spectra of **2** and **3** in pH=2 BR solutions containing various concentrations of β-CDs are shown in Fig. 10. The concentrations of compounds **2** and **3** were held constant at 1.3×10^{-4} mol L^{-1}, and reaction time was kept at 5 h.

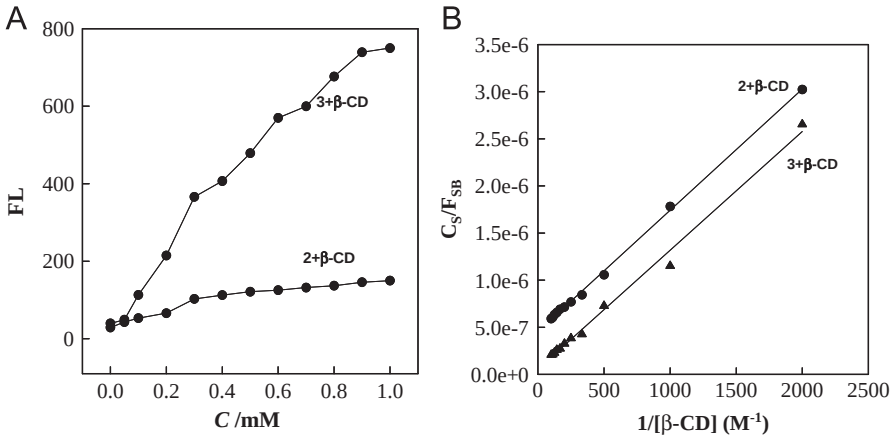


Fig. 10. (A) Fluorescence spectra of compounds **2** and **3** in various β-CDs concentrations in pH=2 BR solutions. (B) Double reciprocal plot for the compounds **2** and **3** and β-CD complexes. The plot is linear, indicating 1:1 complexion throughout the concentration range of β-CD used. Concentrations **2** or **3** were 1.3×10^{-4} mol L^{-1}.

And it was found that the fluorescence intensity was gradually enhanced with the increase of β–CD concentrations until stable complex was formed.

The enhancement of fluorescence intensity was due to the interaction between the compounds **2**, **3** and β–CD, implying the formation of inclusion complexes. The fluorescence intensity increased, owing to the increase of the solubility and fluorescence quantum yield in the presence of β–CD. This may result from the electronic density increased after the guest molecule entering into the hydrophobic cavity of β–CD [19]. β–CD has the peculiar 'interior hydrophobic, exterior hydrophilic' structure and can form a 1:1 or 1:2 inclusion complex with the guest molecule. The hydrophobic cavity of β–CD can provide the microenvironment of high electronic density for the guest molecule. It is known that the characteristic IR absorption frequency of β–CD covered 400–3800 cm^{-1}, and some of the peaks for guest molecules are covered up and hard to be recognized. However, some characteristic peaks of the guest in the complex shifted compared with the guest or the physical mixture. There are apparent difference between the complex and the mixture, and some characteristic peaks of the compounds **2** and **3** are changed obviously: C≡C in 2210 cm^{-1} was shifted to 2215 cm^{-1}; the benzene ring skeleton vibration absorption peak at 1600 was shifted to 1612 cm^{-1}; the C=N vibration band in 1500 cm^{-1} was shifted to 1480 cm^{-1}.

It is generally believed that dipole–dipole, van der Walls forces, electrostatic, hydrogen bonding, hydrophobic interaction and the release of distortion energy of β-CD ring upon guest binding cooperatively govern the stability of an inclusion complex [28,29]. The hydrophobic substituent introduced at the rim of the cavity of β-CD upon guest accommodation, and the molecular recognition by chromophoric β-CD is achieved through the induced-fit mechanism. Compounds **2** and **3** are ionic species with positive electric charge in acid condition. The β-CD is not charged in pH 2–11 and there is no electrostatic reaction between β-CD and the guest compounds. The major inclusion interactions are hydrophobic interactions between the guests and β-CD cavity and hydrogen bonding of the guests to hydroxyl groups of β-CDs ring. This can explain why β-CD can easily include the guest compound **3** in acid media. The underlying theory for employing fluorescence spectra to calculate equilibrium constant has been previously reported [30] and for a simple 1:1 (host:guest) complex, the inclusion process should be

$$S + B \rightarrow SB$$

where S, B and SB represent the guest compound, β–CD and the complex, respectively. And the equilibrium constant can be obtained according to the following equation [31]:

$$\frac{C_S}{F_{SB}} = \frac{1}{Kk_{SB}Q_{SB}}\frac{1}{C_B} + \frac{1}{k_{SB}Q_{SB}}$$

where a reasonable estimate of K can be obtained by simply dividing the intercept by the slope from the plot of C_S/F_{SB} *versus* $1/C_B$ in Fig. 10.

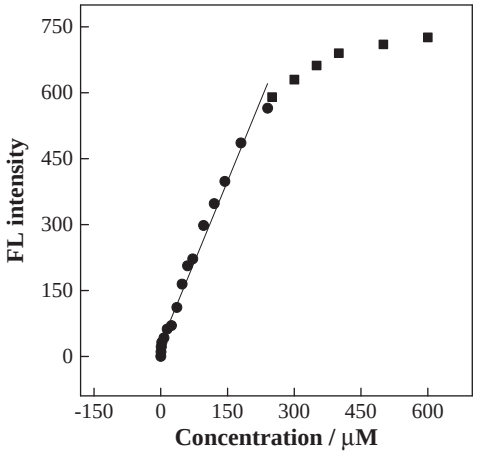


Fig. 11. Fluorescence spectra of 3-β-CDs complex (formed in Fig. 7 in 1.3×10^{-4} mol L^{-1} 3 and 3.3×10^{-3} mol L^{-1}) in various concentrations of salicylaldehyde in pH=2 BR solution.

Fig. 10 B illustrates the double reciprocal plots for complexes of 2 and β–CD or 3 and β–CD, and the completely linear region for them indicated 1:1 complexes were obtained. And calculated from the plots, K was estimated to be 46 and 350 for 2-β–CD and 3-β–CD, respectively.

3.2.5. *The β–CD complex application in detection of salicylaldehyde*

The applicability of the β-CD complex was used for the salicyladehyde detection as an example. It is found that the fluorescence intensity of the complex of compound **3** and β–CD was quickly quenched with the addition of salicylaldehyde. The results may result from the interaction between salicylaldehyde and compound **3** and replace the interaction between **3** and β-CD. The inclusion complex of 3 and β-CD was dissembled while compound **3** was pulled out from the β-CD cavity when adding salicylaldehyde. Therefore, the microenvironment around compound **3** returned to water again, resulting in the decrease of

fluorescence intensity. Under the optimum conditions, the supramolecular complex exhibited a dynamic fluorescence response range for salicylaldehyde from 0.6 to 240×10^{-6} mol L^{-1} as shown in Fig. 11, with a detection limit of 1×10^{-8} mol L^{-1}. These results are superior to the capillary electrophoresis method reported elsewhere [32]. Other aldehydes, such as formaldehyde and glutaraldehyde were investigated, and the fluorescence changed little. And the presence of 1×10^{-4} mol L^{-1} metal ions and the phenols did not interfere the detection of salicylaldehyde in aqueous solution.

The method was applied to measure the industrial waste water by using the standard addition method. In order to avoid the interferences of the real samples matrix and to fit into the linear range of salicylaldehyde, only low concentration of waste water was added to the reaction cell and the diluted sample was spiked with certain amount of salicylaldehyde and then was detected. The recovery of the spiked samples ranged between 97.5% and 103.0%.

4. Conclusion

Four novel conjugated oligo-phenylene-ethynylenes with good optical properties in organic solvents were synthesized and characterized. The supramolecular interaction between compounds **2** or **3** and β-CD has been studied by fluorescence spectroscopy. The inclusion capacity depends on the molecular species in aqueous solution except for the size-match and hydrophobicity. β–CD interacts with compounds **2** and **3** to form host–guest complexes and alter the physical and chemical properties of them. The β–CD complex can be dissembled in the presence of special analyte and shows good prospective in analytical detection.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20975037, 21075037 and 21275051) and the Scientific Research Fund of Hunan Provincial Education Department (10C0926 and CX2010b218) and the Aid program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province.

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