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ORIGINAL PAPER

Enantioselective Recognition of Tartaric Acids with Ethynylated Carbazole-Based Chiral Bisboronic Acid Chemosensors with Improved Response at Acidic pH

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Abstract Chiral bisboronic acid chemosensors based on ethynylated carbazole were prepared. The chiral chemosensors show red-shifted emission than the chemosensors with unsubstituted carbazole fluorophore. a-PET effect was found for the chemosensors, which is different from our previous observation of the d-PET effect for boronic acid chemosensors based on carbazole. Enantioselective recognition of tartaric acids was implicated with these chemosensors. Consecutive fluorescence emission enhancement/diminishment were observed with increasing the concentration of the tartaric acids, which is tentatively assigned to the transition of the binding stoichiometry from 1:1 binding to 1:2 binding. In particularly interesting is the improved fluorescence response at acidic pH for recognition of tartaric acids, which is rarely observed for a-PET chemosensors. We propose that the sensing is due to hybrid mechanism of a-PET/d-PET and conformational restriction upon binding. Our results will be useful for design of chiral boronic acid chemosensors with improved fluorescence response at acidic pH, which are rarely reported.

Keywords Chiral boronic acid · Enantioselective · Fluorescent chemosensors · Tartaric acid · PET

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Introduction

Fluorescent molecular chemosensors have attracted much attention due to their applications in chemical, biological and environmental science [1–13]. Boronic acid chemosensors for selective detection of sugars or hydroxyl acids, such as tartaric acid, are of particular interesting due to the covalent bonding nature of the interaction between the boronic acid chemosensors and the analytes, thus the chemosensors can be used in aqueous media [14–22]. It should be pointed out that a large amount of chiral molecular chemosensors are based on hydrogen bonding, thus the recognition can only be carried out in non-protic organic solvents [23].

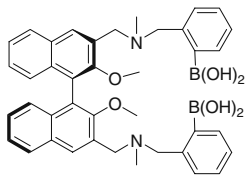
We have been interested in study of boronic acid chemosensors for a while [24–32]. Besides the binding sites and the fluorophore of the molecular chemosensors, the sensing mechanism is also critical for a successful chemosensor design [31]. One of the most popular sensing mechanism of the molecular chemosensors, including boronic acid chemosensors, is the photo-induced electron transfer (PET), usually with fluorophore as the electron acceptor and a proximate alkyl *N* atom (not conjugated to the fluorophore) as the electron donor, and the switch of the fluorescence [8]. This kind of PET is termed as a-PET (a for *a*cceptor of the PET process). Quenched emission at basic media is usually observed for a-PET chemosensors because the PET effect (quenching effect) at neutral and basic pH is significant [8]. At acidic pH, however, the *N* atom is protonated and the otherwise transferable electron on the *N* atom is fixed, thus PET is inhibited, and the fluorescence of the fluorophore is switched on. As a result, the recognition of analytes with a-PET chemosensors, especially the Wulff type of boronic acid chemosensors, is

only effective at neutral or basic pH region [8]. Serious interference exists in the acidic media due to the protonation of the *N* atom, i.e. the background emission of the chemosensors is strong, and as a result, the fluorescence transduction at acidic pH upon binding with analytes is small [24–27] (chemosensor **7** and **8**, Scheme 1). However, some analytes, such as tartaric acid or mandelic acid, require recognition at acidic pH because the binding of the boronic acid chemosensors with these analytes at acidic pH is much stronger than that at neutral or basic pH. Unfortunately, the fluorescence relay of the normal a-PET boronic acid chemosensors upon binding with hydroxyl acid analytes is poor at acidic pH [25].

Recently we devised the d-PET boronic acid chemosensors with carbazole as the fluorophore (chemosensor **9**, **10**, and **11**, Scheme 1) [30–32]. In this kind of chemosensors, the fluorophore serves as the electron donor and the protonated amine/boronic acid groups as the electron acceptor of the PET process. This is in stark contrast to the normal a-PET chemosensors. d-PET chemosensors give emission intensity-pH profiles which are opposite to the normal a-PET chemosensors, i.e. d-PET chemosensors show relatively diminished emission at acidic pH (due to the quenching effect of the d-PET) and intensified emission at neutral/basic pH. The chiral recognition of tartaric acid is achieved with the d-PET boronic acid chemosensors [30]. The fluorescence response is significant at acid pH [30]. However, up to date the number of the d-PET boronic acid chemosensors is very limited and little is known on the fluorophores that can induce the d-PET effect [30–32].

Herein we prepared ethynylated carbazole based chiral bisboronic acid chemosensors (*S,S*-**1** and *R,R*-**1**, Scheme 2). The emission of the chemosensors is red-shifted compared to the chemosensors that based on carbazole [30–32]. Different from our previous d-PET chemosensors based on carbazole [30–32], these new chemosensors show the normal a-PET profile. We found that the recognition of tartaric acid is enantioselective, i.e. the chiral chemosensors give different fluorescence response to the enantiomers of the tartaric acids. Interestingly, we found that the fluorescence response at acidic pH range is significant. This kind of response is rare and the only reported example is boronic acid chemosensors based on anthracene [35]. We propose that the sensing mechanism of the chemosensor is hybrid a-PET/d-PET mechanism, and the conformational restriction upon binding with analytes. Furthermore, we found a consecutive fluorescence enhancement/diminishment upon increasing the tartaric acid concentration, which is proposed to be due to the transition of the binding stoichiometry from 1:1 binding to 1:2 binding. The binding complex of the chemosensor with tartaric acid was optimized by DFT calculations. Our result will be useful for the design of chiral boronic acid chemosensors with improved fluorescence response at acidic pH, which is rarely reported [8].

Scheme 1 Typical a-PET (**7**, **8**, **12**) and d-PET (**9**, **10** and **11**) fluorescent boronic acid chemosensors



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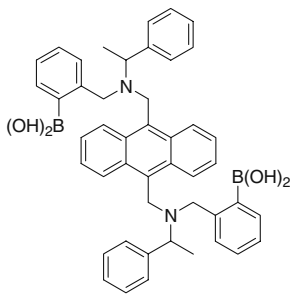
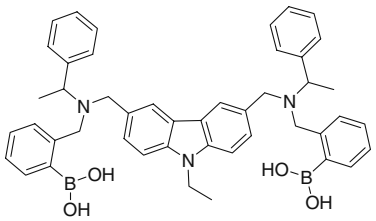
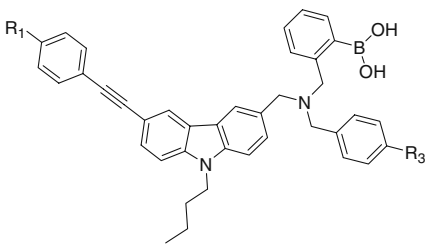


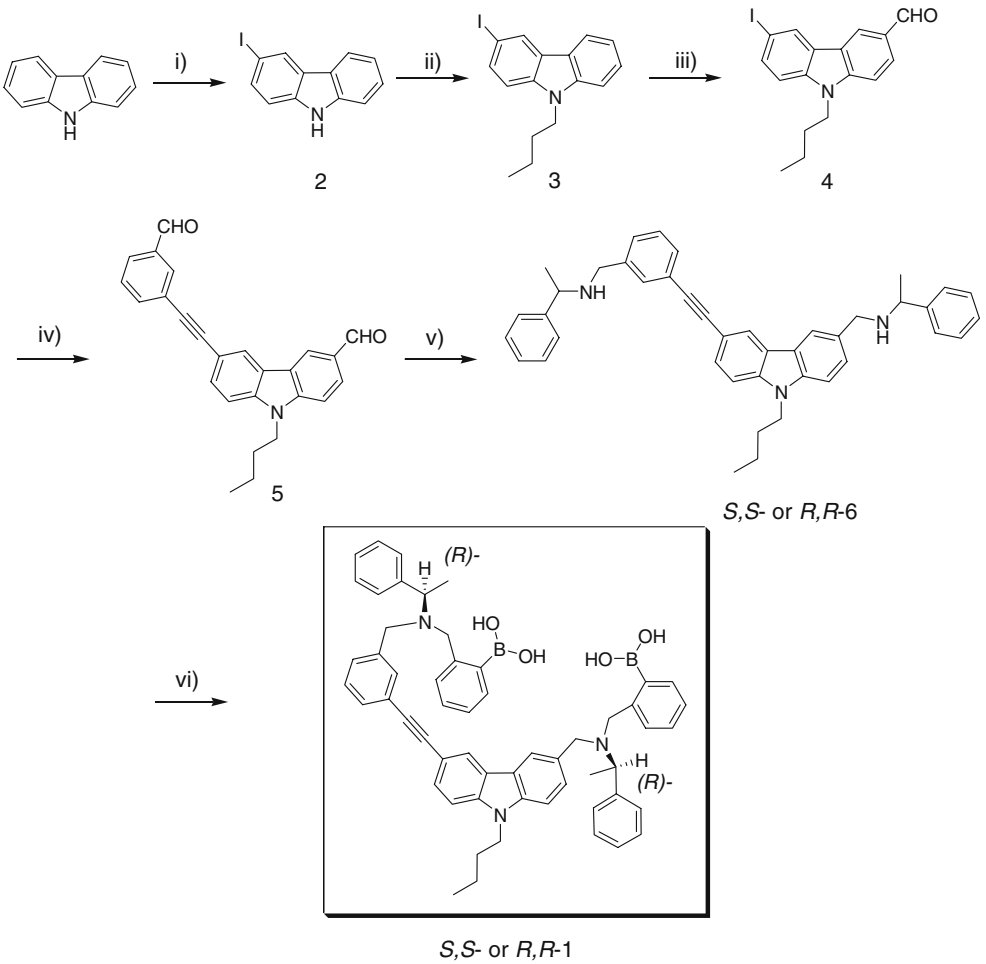
***S,S*-8 and *R,R*-8**



***S,S*-9 and *R,R*-9**



10: R_1 = -NMe_2, R_2 = F
11: R_1 = -NMe_2, R_2 = H
12: R_1 = H, R_2 = F



Scheme 2 Synthesis of the *S,S-* and *R,R-* fluorescent boronic acid chemosensor **1**. i) KI, KIO_3, CH_3COOH, reflux, 10 min, 45%; ii) NaH, DMF, n-C_4H_9Br, room temperature, 1 h, 72% iii) $POCl_3$, DMF, CH_2Cl_2, reflux, 8 h, 63%. iv) $Pd(PPh_3)_4$, CuI, NEt_3, 3-ethynylbenzaldehyde, argon atmosphere, 60 °C, 8 h, 79.8%; v) ethanol, THF, *S*-1-phenylethylamine or ***R***-1-phenylethylamine, reflux, 6 h, then methanol, THF, $NaBH_3CN$, room temperature, 1 h; vi) acetonitrile, K_2CO_3, 2-(2-bromomethylphenyl)-1,3, 2-dioxaborinane, reflux, 10 h, 11.7-12.6%

Experimental

Materials and General Methods

All the chemicals are analytical pure and were used as received. NMR spectra were taken on a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were recorded with Q-TOF Micro MS spectrometer. Fluorescence spectra were recorded on a JASCO FP-6500 or on a Sanco 970 CRT spectrofluorometer.

*3-Iodocarbazole (**2**)*

3-Iodocarbazole was synthesized according to a literature procedure [33].

*9-Butyl-3-iodocarbazole (**3**) and 9-Butyl-6-iodocarbazole-3-carbaldehyde (**4**)*

9-Butyl-3-iodocarbazole and 9-Butyl-6-iodocarbazole-3-carbaldehyde were prepared by a literature procedure [34].

*9-butyl-6-[2-(3-formylphenyl)ethynyl]-9H-carbazole-3-carbaldehyde (**5**)*

9-Butyl-6-iodocarbazole-3-carbaldehyde (400.0 mg, 1.06 mmol) and $Pd(PPh_3)_4$ (120.0 mg, 0.1 mmol) were dissolved in triethylamine (8 mL) under argon atmosphere. 3-ethynylbenzaldehyde (198 mg, 1.52 mmol) was added to the above solution and CuI (29.0 mg, 0.15 mmol) was added. The mixture was stirred at 60 °C for 8 h. After removal of triethylamine in vacuo, the residue was purified with column chromatography (silica gel; dichloromethane/methanol, 100:1, V/V) to give 320.0 mg (yield: 79.8 %) yellow solid. M. p. 122.9-123.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 10.05 (s, 1H), 8.62 (s, 1H), 8.37 (s, 1H), 8.04-8.09 (m, 2H), 7.82-7.87 (m, 2H), 7.71 (d, 1H, *J*=8.4 Hz), 7.56 (t, 1H, *J*=7.6 Hz), 7.50 (d, 2H, *J*=8.4 Hz), 7.45 (d, 1H, *J*=8.4 Hz), 4.36 (t, 2H, *J*=6.8 Hz), 1.86-1.93 (m, 2H), 1.40-1.45 (m, 2H), 0.98 (t, 3H, *J*=7.2 Hz). ESI-HRMS ($C_{26}H_{21}NO_2^+$): calcd 379.1572, found 379.1577.

*N-((3-(2-(3-((1-phenylethylamino)methyl)-9-butyl-9H-carbazol-6-yl)ethynyl)phenyl)methyl)-1-phenylethanamine (S, S-**6** or R, R-**6**)*

5 (150.0 mg, 0.4 mmol) and *S*-1-phenylethylamine (288.0 mg, 3.2 mmol) were dissolved in ethanol/THF (3:2, V/V). The mixture was refluxed with stirring for 6 h under N_2. The solvent was removed under reduced pressure, the residue was dissolved in 10 mL of MeOH/THF, $NaBH_3CN$ (252.0 mg, 4.0 mmol) was added in several portions and the mixture was stirred for 1 h at room temperature. The solvent was removed and the residue was taken up with dichloromethane (DCM), the organic phase was washed with brine and dried over Na_2SO_4, DCM was removed and the residue was purified with column chromatography (silica gel, DCM/MeOH, 20:1, v/v). A light yellow oil of ***S,S-6*** was obtained in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.00 (s, 1H), 7.53 (s, 1H), 7.46-7.50 (m, 6H), 7.40-7.43 (m, 7H), 7.28-7.30 (m, 2H), 7.14-7.17 (m, 2H), 4.13-4.17 (q, 1H), 4.09 (t, 2H, *J*=7.6 Hz), 4.01 (d, 1H, *J*=6.8 Hz), 3.85-3.96 (m, 2H), 3.60-3.68 (m, 2H), 1.70-1.76 (m, 2H), 1.66 (d, 3H, *J*=6.8 Hz), 1.58 (d, 3H, *J*=6.8 Hz), 1.30-1.38 (m, 2H), 0.91 (t, 3H, *J*=7.6 Hz). ESI-HRMS ($[C_{42}H_{43}N_3 + H]^+$): calcd 590.3535, found 590.3518.

R, R-6 was prepared with same method of *S,S*-**6**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.95 (s, 1 H), 7.50 (s, 1H), 7.40-7.50 (m, 7H), 7.32-7.39 (m, 6H), 7.24-7.28 (m, 2H), 7.14-7.19 (m, 2H), 4.12-4.17 (q, 1H), 4.05 (t, 2H, *J*=7.2 Hz), 4.00 (d, 1H, *J*=6.8 Hz), 3.84-3.92 (m, 2H), 3.61-3.69 (m, 2H), 1.68-1.74 (m, 2H), 1.66 (d, 3H, *J*=6.8 Hz), 1.52 (d, 3H, *J*=6.8 Hz), 1.24-1.33 (m, 2H), 0.87 (t, 3H, *J*=7.2 Hz). ESI-HRMS ($[C_{42}H_{43}N_3 + 2H]^{2+}$): calcd 295.6807, found 295.6812.

*S, S-**1** or R, R-**1***

S,S-**6** (140.0 mg, 0.24 mmol), 2-(2-bromomethylphenyl)-1,3,2-dioxaborinane (390.0 mg, 1.31 mmol) and K_2CO_3 (620.0 mg, 3.86 mmol) were mixed in acetonitrile (15 mL), the mixture was refluxed for 10 h under N_2. The mixture was cooled and DCM was added. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified with column chromatography (Al_2O_3, DCM/MeOH, 15:1, V/V). 26.0 mg of yellow powder (*S,S*-**1**) was obtained, yield: 12.6 %. M.p. 116.5-117.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD) δ 8.27 (s, 1H), 7.88 (s, 1H), 7.81 (d, 2H, *J*=6.0 Hz), 7.61 (d, 1H, *J*=8.8 Hz), 7.39-7.45 (m, 6H), 7.31-7.37 (m, 12H), 7.16-7.27 (m, 5H), 4.28 (t, 2H, *J*=7.2 Hz), 4.07-4.16 (m, 2H), 3.93-4.00 (m, 2H), 3.84 (d, 1H, *J*=13.2 Hz), 3.59-3.69 (m, 3H), 3.51 (d, 1H, *J*=12.4 Hz), 3.33 (d, 1H, *J*=13.6 Hz), 1.81-1.88 (m, 2H), 1.59 (d, 6H, *J*=7.2 Hz), 1.34-1.43 (m, 2H), 0.95 (t, 3H, *J*=7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD) δ 141.9, 141.6, 140.5, 140.3, 137.8, 136.2, 132.7, 131.4, 130.4, 130.0, 129.3, 129.2, 129.1, 128.8, 128.5, 128.4, 128.0, 127.8, 127.7, 127.4, 127.2, 124.1, 123.9, 122.8, 121.8, 113.3, 109.0, 108.9, 91.0, 87.6, 54.0, 53.6, 43.2, 31.3, 29.5, 20.7, 15.7, 14.0. ESI-HRMS ($[C_{58}H_{61}B_2N_3O_4 + 2H]^{2+}$): calcd 443.7503, found 443.7483.

*R,R-**1*** was prepared with the same method of *S,S*-**1**. 24.0 mg of yellow powder (*R,R*-**1**) was obtained, yield: 11.7 %. m.p. 118.9-119.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD) δ 8.25 (s, 1H), 7.86 (s,1H), 7.81 (s, 2H), 7.61 (d, 1H, *J*=8.4 Hz), 7.40-7.45 (m, 6H), 7.33-7.39 (m, 12H), 7.17-7.28 (m, 5H), 4.30 (t, 2H, *J*=7.2 Hz), 3.93-4.16 (m, 5H), 3.61-3.71 (m, 5H), 1.81-1.89 (m, 2H), 1.60 (d, 6H, *J*=7.2 Hz), 1.37-1.42 (m, 2H), 0.95 (t, 3H, *J*=7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD) δ 142.0, 141.6, 140.7, 140.4, 137.1, 136.5, 132.9, 131.6, 130.5, 130.1, 129.7, 129.6, 129.4, 129.0, 128.6, 128.5, 128.0, 127.8, 127.7, 127.5, 127.2, 124.2, 124.0, 122.5, 122.0, 113.5, 109.0, 108.9, 91.1, 87.7, 54.0, 53.7, 43.3, 31.3, 29.9, 20.7, 16.1, 14.0. ESI-HRMS ($[C_{58}H_{61}B_2N_3O_4 + 2H]^{2+}$): calcd 443.7503, found 443.7501.

Results and Discussions

Synthesis Previously we devised chiral d-PET chemosensor **9** with unsubstituted carbazole as the fluorophore (Scheme 1) [30]. In a later study we designed chemosensors **10**–**12** (Scheme 1) [31]. Interestingly, with introduce of ethynylene subunit to the carbazole fluorophore, the d-PET effect was switched to a-PET effect, which is probably due to the electron-deficient feature of the ethynylene moiety. Herein we design the bisboronic acid chemosensors based on the scaffold of ethynylated carbazole. The binding pocket of the new chiral chemosensor is larger than the previous chiral bisboronic acid chemosensors [31].

The synthesis is with carbazole as the starting material (Scheme 2), with iodination and formylation, the iodo-aldehyde **4** was obtained. Then with Sonogashira coupling reaction, the bis-aldehyde **5** was obtained. With reductive amination and introduce of the binding moiety of boronic acid moieties, the chiral chemosensor **1** (*S,S*-**1** and *R,R*-**1**) was obtained in moderate yields.

Fluorescence of the Chemosensors The excitation and the emission spectra of *S,S*-**1** were studied (Fig. 1). Broad structureless excitation and emission bands were observed, which are different from the structured excitation/emission bands of the previously reported carbazole-based chemosensor [30, 31]. Furthermore, the emission is red-shifted by ca. 15 nm compared to a previously reported boronic acid

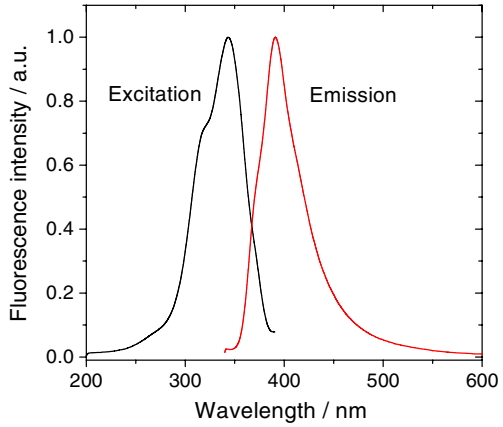


Fig. 1 Normalized excitation and emission spectra of *S,S*-**1**. λ_{ex}=343 nm, λ_{em}=391 nm. 1.0×10^{-6} mol dm^{-3} of chemosensor in 0.05 mol dm^{-3} NaCl ionic buffer (52.0% methanol in water). pH 7.5, 20 °C

chemosensor based on the non-ethynylated carbazole [30]. These results demonstrated that the electron communication between the periphery phenyl subunit and the carbazole core is efficient.

The pH titration of the chemosensors in the absence and presence of tartaric acids were studied (Fig. 2). Enhanced emission at acid pH but diminished emission at neutral and basic pH were observed. Thus the chemosensors can be identified as a-PET chemosensors [25, 31]. The pK_a of *S,S*-**1** is 5.71±0.08. similar p*K*a was observed for *R,R*-**2** (5.81±0.05). The pK_a of the chemosensors changed in the presence of tartaric acid. For example, the pK_a of *S,S*-**1** changed to 7.03±0.06 (D-tartaric acid) or 7.15±0.08 (D-tartaric acid). For *R,R*-**1**, the p*K*a changed to 7.33±0.04 (D-tartaric acid) or 6.99±0.06 (L-tartaric acid).

We noticed that the contrast ratio of the chemosensors are relatively smaller (only ca. 2.0-fold) compared to the typical a-PET chemosensors based on anthracene fluorophore (ca. 8-fold) [25, 35]. The pH titration of the chemosensors in the presence of D- and L-tartaric acid shows that the recognition at acidic pH region is significant. This improved fluorescence response upon binding at acidic pH is in stark contrast to the normal a-PET boronic acid chemosensors [24–27]. Furthermore, we found that the recognition of tartaric acids with the chemosensor **1** is enantioselective. For example, The *S,S*-**1** gives larger response to *L*-tartaric acid than the *D*-tartaric acid. With *R,R*-**1**, however, the profile is reversed. This mirror effect is typical enantioselective response for the chiral boronic acid chemosensors.

Previously we reported a boronic acid chemosensor based on anthracene/naphthalethylamine which shows improved fluorescence transduction at acidic pH, due to the intramolecular interaction between the chirogenic center (naphthalene subunit) and the fluorophore [27]. For the new chemosensor **1**, however, such an interaction is unlikely. Thus we propose that the sensing mechanism is a hybrid d-PET and a-PET. The a-PET effect will be suppressed upon binding with analytes, thus the emission was enhanced at acidic pH [30–32]. Furthermore, the restriction of the conformation upon binding with analytes may also enhance the fluorescence emission at acidic pH.

The binding titration of the chemosensor **1** with L- and D-tartaric acid was studied (Fig. 3). Enantioselectivity was observed and the result is in consistent with the pH titration (Fig. 2). With *S,S*-**1**, larger fluorescence enhancement was observed with the L-tartaric acid. With *R,R*-**1**, however, higher fluorescence response was observed with the D-tartaric acid. Moderate enantioselectivity was observed for the recognition of tartaric acid with chemosensor 1 at pH 4.0. For example, the binding constants of *S,S*-**1** toward D- and L-tartaric acids are $(4.64\pm0.70)\times10^5$ M^{-1} and $(5.60\pm0.47)\times10^5$ M^{-1}, respectively. The enantioselectivity is K_D/K_L=1.0 : 1.2. With *R,R*-**1**, the binding constants toward D- and L-tartaric acid are $(1.04\pm0.05)\times10^6$ M^{-1} and $(8.68\pm0.49)\times10^5$ M^{-1}, respectively. Thus the enantioselectivity is K_D/K_L=1.2 : 1.0. These reversed k_D/k_L ratios indicated the enantioselectivity of the binding constants. We noticed the binding constants are slightly smaller than the previous carbazole-based chiral boronic acid chemosensors [30], which is tentatively attributed to the larger binding pocket of chemosensor **1** than chemosensor **9**

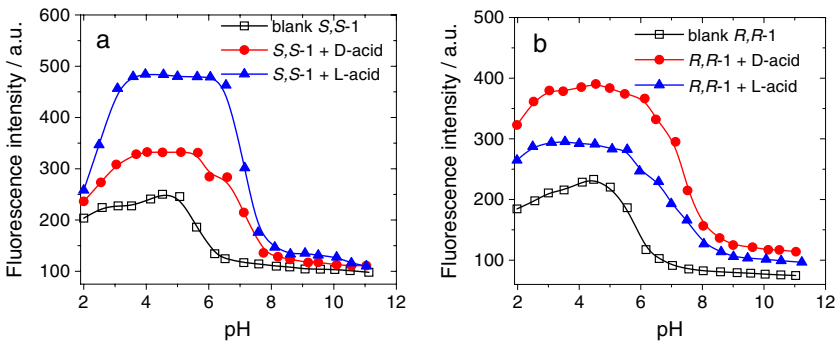


Fig. 2 Fluorescence intensity-pH profiles of (a) *S,S*-**1** and (b) *R,R*-**1** in the presence of D- and L-tartaric acid. λex=330 nm, λem=389 nm, 1.0×10^{-6} mol dm^{-3} of chemosensors in 0.05 mol dm^{-3} NaCl ionic buffer (52.0% methanol in water), *c*(D- and L-tartaric acid)=1.25×10^{-2} mol dm^{-3}. 20 °C

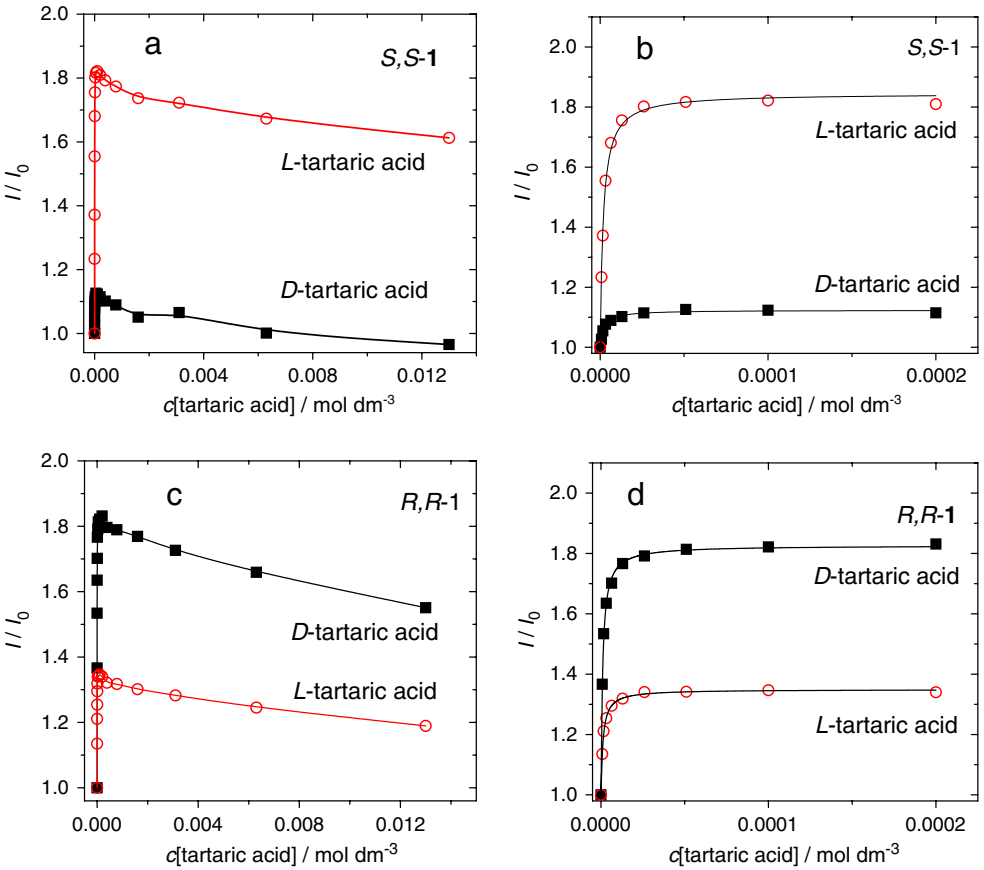


Fig. 3 Relative fluorescence intensity of *S,S*-**1** and *R,R*-**1** versus concentration of D- and L-tartaric acid. λex=330 nm, λem=389 nm, pH=4.0, 1.0×10^{-6} mol dm^{-3} of chemosensor in 0.05 mol dm^{-3} NaCl ionic buffer (52.0% methanol in water). 20 °C

(Scheme 1) [30]. The enantioselective fluorescence response with *R,R*-**1** is $[k_D F(D)]/[k_L F(L)]=1.0:2.0$. With *S,S*-**1**, the enantioselective fluorescence response with *R,R*-**1** is $[k_D F(D)]/[k_L F(L)]=1.6:1.0$, where k is binding constants with D- or L-tartaric acid, F is the fluorescence enhancement in the presence of D- or L-tartaric acid.

Furthermore, we observed a consecutive emission enhancement/diminishment with increasing the tartaric acid concentration. Similar result is found for the recognition of L- and D-tartaric acid with *S,S*-**1** and *R,R*-**1** at pH 6.0. The decrease of the fluorescence at higher tartaric acid concentration is not due to the quenching effect of tartaric acid. The fluorescence enhancement is due to the binding of tartaric acid with boronic acid, thus the suppressed PET effect via B-N interaction, either the direct or the intramolecular hydrogen bonding [36, 37]. Previously we observed such emission enhancement/diminishment for a BINOL based boronic acid chemosensor [24]. We propose the emission enhancement/diminishment is due to the transition of the binding stoichiometry from 1:1 binding to 1:2 binding. 1:1 cyclic binding shows extra emission enhancement than the 1:2 opened form binding. In order to elucidate the fluorescence enhancing mechanism, the binding complex of the enantiomers were optimized.

DFT Optimization of the Geometry of the Binding Complexes The binding complexes of *S,S*-**1**-L-tartaric acid and *S,S*-**1**-D-tartaric acid were optimized (the results of the complex *S,S*-**1**-L-tartaric acid was presented in Fig. 4). The binding complex was considered as a methanol-inserted

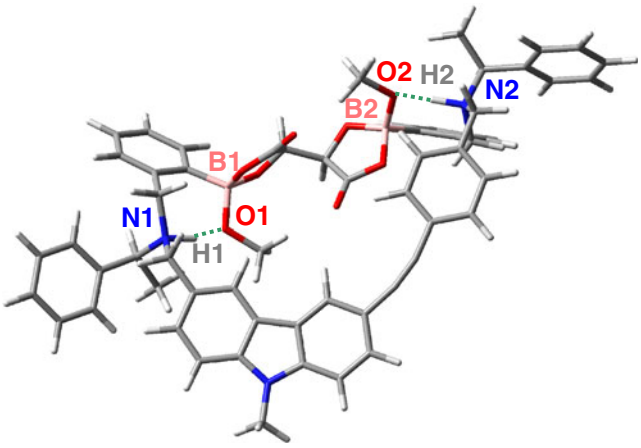


Fig. 4 Optimized structure of the binding complex of *S,S*-**1**-(*R*)-L-tartaric acid. Calculated by DFT at the B3LYP/6-31G(d) level using Gaussian 09W

zwitterionic structure [36, 37]. The optimized intramolecular hydrogen binding structures are in agreement with the experimental results [36, 37]. For example, the hydrogen bond N(1)-H(1)···O(1) shows bond length of N-O: 2.553 Å, H-O: 1.455 Å and the angle N-H···O is 163 °.

The optimized structure shows a deformed ethynylene linker (the C−C≡C angle is 168°), indicates that the 1:1 binding macrocycle induces a significant intramolecular conformation constrain, thus the 1:1 binding complex is unstable, which will change to 1:2 (opened form) binding stoichiometry at high analytes concentration. We found that the energy of the *S,S*-**1**-L-tartaric acid binding complex is stabilized by 10.5 kJ mol^{-1} compared to the *S,S*-**1**-D-tartaric acid binding complex. This observation is in line with the binding constants studies (Fig. 3). Currently aided by molecular modeling, we are actively working to design new chemosensors with smaller deformation of the molecular backbone, so that tight binding can be achieved.

Conclusions

In summary, we prepared chiral bisboronic acid chemosensors based on ethynylated carbazole fluorophore. The chiral chemosensors show red-shifted emission than the chemosensors with unsubstituted carbazole fluorophore. a-PET effect was found for the chemosensors. Enantioselective recognition of tartaric acids was observed with these chemosensors. Improved fluorescence response at acidic pH was observed, which is rare for a-PET chemosensors. We propose that the sensing at acidic pH is due to hybrid a-PET/d-PET and conformation restriction upon binding mechanism. Consecutive fluorescence emission enhancement/diminishment were observed with increasing the concentration of the tartaric acids. We propose a transition of the binding stoichiometry from 1:1 binding to 1:2 binding is responsible for the consecutive fluorescence emission enhancement/diminishment changes. Our results will be useful for design of chiral boronic acid chemosensors with improved fluorescence response at acidic pH, which are rarely reported.

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