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3,6-Disubstituted Carbazole-Based Bisboronic Acids with Unusual Fluorescence Transduction as Enantioselective Fluorescent Chemosensors for Tartaric Acid

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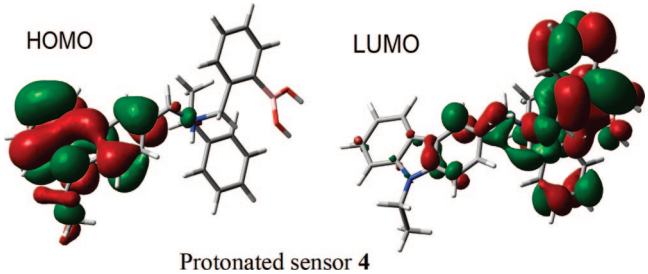

Protonated sensor **4**

Carbazole-based bisboronic acids were found to be enantioselective fluorescent sensors for tartaric acid. The fluorescence response toward the enantiomers of tartaric acid at neutral pH displayed enhancement/diminishment. The sensor displays an unusual fluorescence intensity−pH relationship with diminished emission at acidic pH but enhanced emission at basic pH. Photoinduced electron transfer (PET) from the fluorophore to the protonated amine/phenylboronic acid unit is proposed to be responsible for this effect, which is rationalized by density functional theory (DFT) calculations.

Synthetic receptors and fluorescent chemosensors for enantioselective recognition of chiral compounds, such as chiral α-hydroxyl carboxylic acids, are a subject of increasing interest.[1−8] The majority of these chiral fluorescent sensors are based on hydrogen bonding interactions.[2−6] These systems work well in noncompetitive solvents but fail in protic solvents due to the severe interference of protic media with the hydrogen bonding receptor. In order to develop chiral fluorescent chemosensors that are effective in aqueous media, especially toward α-hydroxyl acids, which are bioactive or versatile chiral building blocks, boronic acid based fluorescent sensors have been designed and some of these sensors display tight binding toward sugars or polyhydroxyl acids, such as glucose, tartaric acid, mandelic acid or glucarate, etc.[9−16]

We previously reported a BINOL-based boronic acid sensor with a unique signal transduction profile where the fluorescence intensity of the sensor is either enhanced or diminished with the two enantiomers of tartaric acid.[13] Anthracene-based sensors were also prepared and show very high binding constants and enantioselectivity toward tartaric acid (e.g., **6** in Scheme 1).[14,15] Recently, we designed a new BINOL boronic acid, which is enantioselective on sorbitol, but the sensor failed to show fluorescence enhancement/diminishment toward tartaric acids.[16]

Herein we report new chiral boronic acid sensor **3** (Scheme 1), based on 3,6-disubstituted carbazole, that shows high enantioselectivity toward tartaric acids and, surprisingly, a reverse fluorescence intensity−pH relationship[14,15] (i.e., diminished fluorescence intensity at acidic pH but stronger emission at basic pH).[9,10] Furthermore, fluorescence enhancement/

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(1) Stibor, I.; Zlatušková, P. *Top. Curr. Chem.* **2005**, *255*, 31.
(2) (a) Pu, L. *Chem. Rev.* **1998**, *98*, 2405. (b) Pu, L. *Chem. Rev.* **2004**, *104*, 1687. (c) Willener, Y.; Joly, K. M.; Moody, C. J.; Tucker, J. H. R. *J. Org. Chem.* **2008**, *73*, 1225. (d) Liu, S.; Pestano, J. P. C.; Wolf, C. *J. Org. Chem.* **2008**, *73*, 4267. (e) Mei, X.; Wolf, C. *Tetrahedron Lett.* **2006**, *47*, 7901. (f) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094. (g) Duke, R. M.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 8043. (h) dos Santos, C. M. G.; McCabe, T.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 3135.
(3) (a) Lin, J.; Rajaram, A. R.; Pu, L. *Tetrahedron* **2004**, *60*, 11277. (b) Li, Z.-B.; Lin, J.; Pu, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 1690. (c) Li, Z.-B.; Lin, J.; Sabat, M.; Hyacinth, M.; Pu, L. *J. Org. Chem.* **2007**, *72*, 4905.
(4) Alfonso, I.; Rebolledo, F.; Gotor, V. *Chem.—Eur. J.* **2000**, *6*, 3331.
(5) Alfonso, I.; Dietrich, B.; Rebolledo, F.; Gotor, V.; Lehn, J.-M. *Helv. Chim. Acta* **2001**, *84*, 280.
(6) (a) Xu, K.-X.; He, Y.-B.; Qin, H.-J.; Qing, G.-Y.; Liu, S.-Y. *Tetrahedron: Asymmetry* **2005**, *16*, 3042. (b) Qin, H.; He, Y. B.; Hu, C.; Chen, Z.; Hu, L. *Tetrahedron: Asymmetry* **2007**, *18*, 1769.
(7) Hernández, J. V.; Almaraz, M.; Raposo, C.; Martín, M.; Lithgow, A.; Crego, M.; Caballero, C.; Morán, J. R. *Tetrahedron* **2007**, *18*, 1769.
(8) (a) Li, C.; Wang, G.-T.; Yi, H.-P.; Jiang, X.-K.; Li, Z.-T.; Wang, R.-X. *Org. Lett.* **2007**, *9*, 1797. (b) Ghosh, K.; Adhikari, S. *Tetrahedron Lett.* **2006**, *47*, 3577.
(9) James, T. D.; Shinkai, S. *Top. Curr. Chem.* **2002**, *218*, 159.
(10) James, T. D. *Top. Curr. Chem.* **2007**, *277*, 107.
(11) Mohr, G. J. *Anal. Bioanal. Chem.* **2006**, *386*, 1201.
(12) (a) Wiskur, S. L.; Ait-Haddou, H.; Lavigne, J. J.; Anslyn, E. V. *Acc. Chem. Res.* **2001**, *34*, 963. (b) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3666. (c) Zhu, L.; Anslyn, E. V. *J. Am. Chem. Soc.* **2004**, *126*, 3676. (d) Cordes, D. B.; Gamsey, S.; Singaram, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3829. (e) He, M.; Johnson, R. J.; Escobedo, J. O.; Beck, P. A.; Kim, K. K.; St. Luce, N. N.; Davis, C. J.; Lewis, P. T.; Fronczek, F. R.; Melancon, B. J.; Mrse, A. A.; Treleaven, W. D.; Strongin, R. M. *J. Am. Chem. Soc.* **2002**, *124*, 5000. (f) Jiang, S.; Escobedo, J. O.; Kim, K. K.; Alptürk, O.; Samoei, G. K.; Fakayode, S. O.; Warner, I. M.; Rusin, O.; Strongin, R. M. *J. Am. Chem. Soc.* **2006**, *128*, 12221. (g) Ni, W.; Fang, H.; Springsteen, G.; Wang, B. *J. Org. Chem.* **2004**, *69*, 1999. (h) Gao, X.; Zhang, Y.; Wang, B. *Org. Lett.* **2003**, *5*, 4615. (i) DiCesare, N.; Lakowicz, J. R. *Tetrahedron Lett.* **2001**, *42*, 9105. (j) DiCesare, N.; Lakowicz, J. R. *J. Phys. Chem. A* **2001**, *105*, 6834.
(13) Zhao, J.; Fyles, T. M.; James, T. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 3461.
(14) (a) Zhao, J.; Davidson, M. G.; Mahon, M. F.; Kociok-Köhn, G.; James, T. D. *J. Am. Chem. Soc.* **2004**, *126*, 16179. (b) Zhao, J.; James, T. D. *Chem. Commun.* **2005**, 1889.
(15) Chi, L.; Zhao, J.; James, T. D. *J. Org. Chem.* **2008**, *73*, 4684.
(16) Liang, X.; James, T. D.; Zhao, J. *Tetrahedron* **2008**, *64*, 1309.

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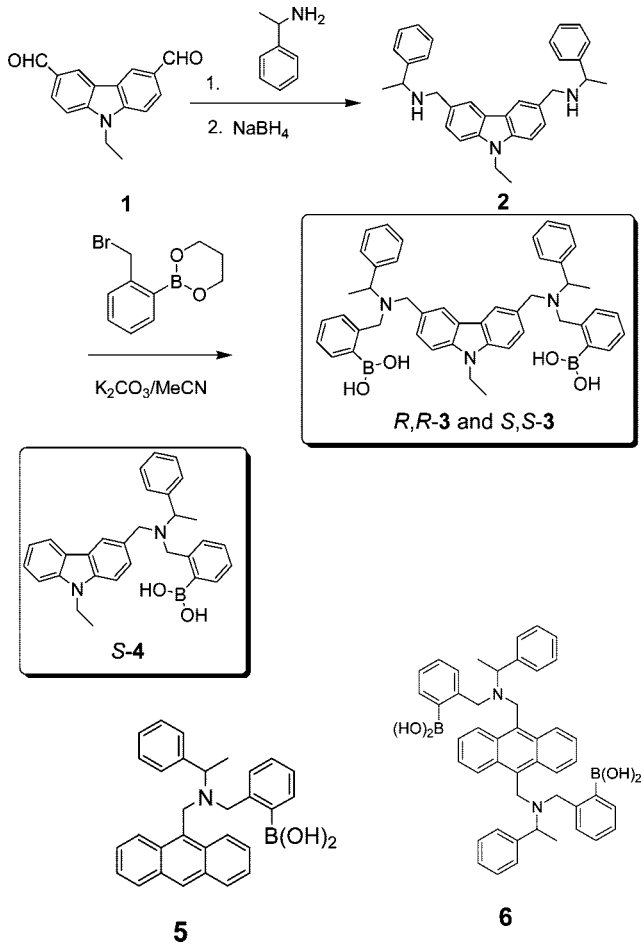
SCHEME 1. Enantioselective Fluorescent Sensors 3 and 4 for α-Hydroxyl Carboxylic Acids (Reported Sensors 5 and 6 Are Also Presented)



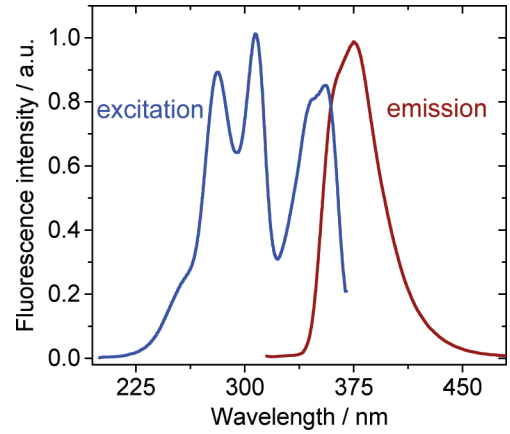


FIGURE 1. Normalized excitation and emission spectra of (*R*,*R*)-**3**: 3.0×10^{-6} mol dm^{-3} of sensor in 0.05 mol dm^{-3} NaCl ionic buffer (52.1% methanol in water); pH 7.5, $\lambda_{ex} = 307$ nm, $\lambda_{em} = 375$ nm, 22 °C.

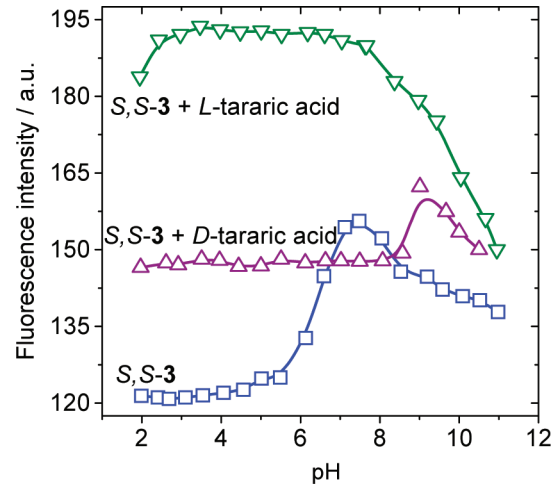


FIGURE 2. Fluorescence intensity−pH profile of (*S*,*S*)-**3** in the presence of D- and L-tartaric acid: $\lambda_{ex} = 307$ nm, $\lambda_{em} = 375$ nm, 3.0×10^{-6} mol dm^{-3} of sensor in 0.05 mol dm^{-3} NaCl ionic buffer (52.1% methanol in water), *c*(D- and L-tartaric acid) = 0.05 mol dm^{-3}, 22 °C.

diminishment toward D- and L-tartaric acid was observed at neutral pH. A reverse PET mechanism (i.e., electron transfer (ET) from the fluorophore to the protonated amine/phenylboronic acid unit) is proposed to be responsible for the unusual fluorescence−pH relationship and has been rationalized by density functional theory (DFT) calculations.

Synthesis of chiral sensors **3** and **4** is outlined in Scheme 1. Reductive amination of 3,6-diformyl-9-ethylcarbazole with (*R*)- and (*S*)-benzylmethylamine leads to chiral amine **2** then by reaction with 2-(2-bromobenzyl)-1,3,2-dioxaborinane to obtain (*R*,*R*)-**3** and (*S*,*S*)-**3**. The model monoboronic acid sensor (*S*)-**4** was synthesized with a similar approach. The previously reported sensor **5** is used as a model compound in DFT calculation/mechanistic studies.[14]

The emission and excitation fluorescence spectra of (*R*,*R*)-**3** are shown in Figure 1. The excitation and the emission wavelengths for the binding studies were selected as 307 and 375 nm, respectively.

The pH versus fluorescence intensity (I_F) profile of **3** with or without analytes is shown in Figure 2.[5,6,13−16] Surprisingly, this apparent PET chemosensor gave a reverse fluorescence response as a function of pH, compared to normal PET sensors.[9,10,13−15] Usually, a PET sensor containing a N atom gives an emission in acidic media stronger than that in basic media, due to protonation of the N atom in acidic media (thus suppression of the PET process leads to intensified fluorescence).[13−17] However, sensor **3** gives stronger emission at basic pH (pK_a of 6.55 ± 0.55). This reverse PET effect is beneficial to the recognition of tartaric acid, due to the reduced background fluorescence and the enhanced signal transduction.[13,14]

Enantioselectivity is found for **3** (Figure 2). For example, in the pH range of 2.0−6.0, (*S*,*S*)-**3** gives much higher fluorescence enhancement in the presence of L-tartaric acid, when compared with D-tartaric acid. With (*R*,*R*)-**3**, a mirror effect is observed (Figure S25). Furthermore, the fluorescence profile of enhancement/diminishment previously found for the axially chiral BINOL-based sensor (observed at acidic pH)[13] is also observed for **3**, but now at neutral pH (pH 6.5−8.0). For example, at pH 7.4, the fluorescence intensity of (*S*,*S*)-**3** is intensified in the presence of L-tartaric acid, while with D-tartaric acid, the fluorescence intensity is diminished. With (*R*,*R*)-**3**, a mirror effect is observed. To the best of our knowledge, this type of

(17) de Silva, A. P.; H.; Gunaratne, Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.

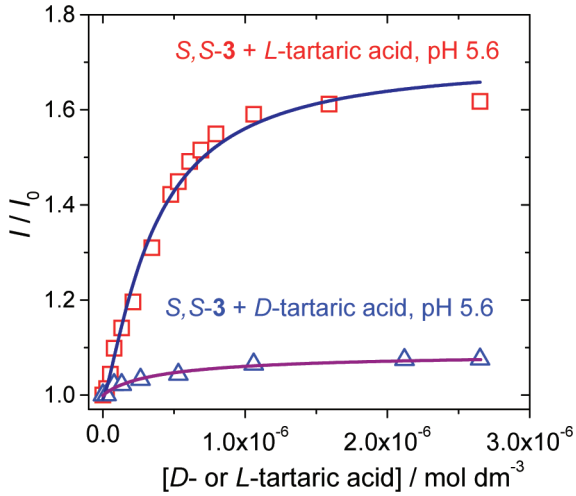


FIGURE 3. Relative fluorescence intensity of (*S*,*S*)-**3** versus concentration of L- and D-tartaric acid: λ_{ex} = 305 nm, λ_{em} = 375 nm, pH = 5.6, 1.0 × 10^{-6} mol dm^{-3} of sensor in 0.05 mol dm^{-3} NaCl ionic buffer (52.1% methanol in water), 25 °C.

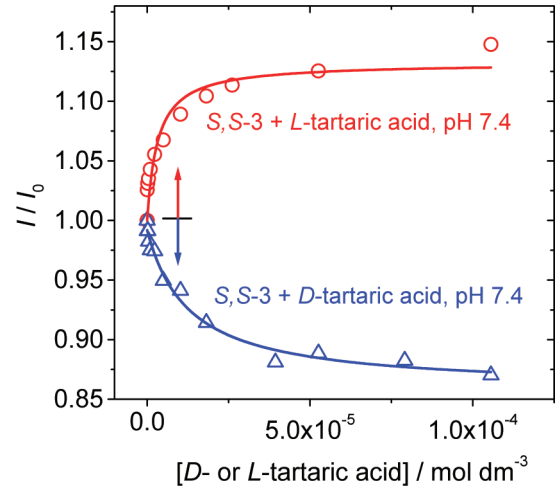


FIGURE 4. Relative fluorescence intensity of (*S*,*S*)-**3** versus concentration of L- and D-tartaric acid, at pH 7.4: λ_{ex} = 305 nm, λ_{em} = 375 nm, 1.0 × 10^{-6} mol dm^{-3} of sensor in 0.05 mol dm^{-3} NaCl ionic buffer (52.1% methanol in water), 25 °C.

signal transduction is rarely observed, and this is only the second example of such a unique enantioselective fluorescence signal response.[13]

On the basis of the I_F−pH studies (Figure 2), pH 5.6 and 7.4 were selected to further investigate the binding and enantioselectivity of these systems.

The titrations of (*S*,*S*)-**3** with D- and L-tartaric acid at pH 5.6 are shown in Figure 3. Higher fluorescence enhancement was observed in the presence of L-tartaric acid versus D-tartaric acid. The apparent binding constants for D- and L-tartaric acid are K_D^{app} = (2.31 ± 0.00) × 10^6 and K_L^{app} = (2.84 ± 0.00) × 10^6 M^{-1}, respectively, thus the enantioselective response $K_D^{app}F(D)/K_L^{app}F(L)$ = 1.0:1.8,[13] where *F* is fluorescence enhancement of the sensor in the presence of D- or L-tartaric acid. With (*R*,*R*)-**3**, a mirror effect is observed (Figure S30), for which K_D^{app} = (3.80 ± 0.02) × 10^6 and K_L^{app} = (2.67 ± 0.23) × 10^6 M^{-1}, respectively, with the enantioselective response $K_D^{app}F(D)/K_L^{app}F(L)$ = 1.7:1.0.[13]

The binding of sensor **3** with tartaric acid at pH 7.4 was also investigated (Figure 4). For (*S*,*S*)-**3**, fluorescence enhancement is observed with L-tartaric acid, and the apparent binding constant is K_L^{app} = (1.18 ± 0.35) × 10^5 M^{-1}. With D-tartaric acid, however, a fluorescence diminishment was observed with K_D^{app} = (7.78 ± 1.51) × 10^4 M^{-1}. Thus the enantioselective response $K_D^{app}F(D)/K_L^{app}F(L)$ is (−1.0):(+1.6). With (*R*,*R*)-**3**, a mirror effect in enantioselectivity is observed (Figure S31), for which K_D^{app} = (3.65 ± 1.07) × 10^4 and K_L^{app} = (2.11 ± 1.58) × 10^4 M^{-1}, with the enantioselective response $K_D^{app}F(D)/K_L^{app}F(L)$ is (+1.6):(−1.0). Herein we noticed the deviation of the enantioselectivity (K_D^{app} and K_L^{app}) from the perfect mirror effect;[12c,13,14] this may be due to some experimental uncertainties, which are difficult to eliminate completely.

Such fluorescence intensity enhancement/diminishment responses toward the enantiomers of analytes are rarely reported,[13] although quenching upon anion sensing is known for normal PET sensors.[2g] The exact mechanism for this unique fluorescence intensity enhancement/diminishment is unclear, but we believe this effect might be more common for chiral fluorescent sensors than we previously thought (i.e., not restricted to axially chiral BINOL moiety).[13] Our results will inspire design of new enantioselective fluorescent sensors since the effect enhances analytical performance.[10,13]

The unusual PET behavior of sensor **3** still puzzled us (Figure 2). The fluorescence intensity−pH profile of model sensor **4**, a monoboronic acid, is similar to that of sensor **3** (Figure S27); therefore, the reverse PET response is unlikely caused by formation of a cyclic 1:1 binding complex, instead, the reverse PET effect is probably due to the carbazole fluorophore. The reverse PET response is also unlikely due to the hybridization change of the boronic acid group[12g] because the boronic acid moiety is not directly appended to the fluorophore and the apparent pK_a does not support the boronic acid hybridization mechanism (Figure 2).[14] Since the carbazole moiety is a well-known strong electron donor,[18] we envision that PET from the carbazole moiety to the amine and boronic acid moiety is highly possible, especially when the amine is protonated. Such an ET from fluorophore to the positively charged N atom will quench the fluorescence.[19] Thus, at acidic pH, the fluorescence was diminished due to the reverse PET effect. The acidity of the boron atom of the boronic acid moiety also facilitated the potential reverse PET.[9,10]

To help confirm this reverse PET mechanism, theoretical calculations based on DFT and time-dependent DFT (TDDFT) were performed for **4** (Figure 5, see Supporting Information for more details).[20]

The frontier molecular orbitals for protonated **4** reveal that there is ET from the fluorophore to the protonated amine unit on excitation (see Supporting Information), which leads to fluorescence quenching of the carbazole fluorophore.[19] For neutral sensor **4**, the orbitals are localized on carbazole, for both HOMO and LUMO, so there is no charge transfer and the fluorescence is intensified when compared with the protonated **4**. The TDDFT calculations also predict, to some extent, ET from the amine unit to carbazole moiety for neutral **4**, which is in agreement with the normal PET effect, or a-PET (fluorophore as the electron *a*cceptor in PET).[21] Similar results were found

(18) (a) Galmiche, L.; Mentec, A.; Pondaven, A.; L'Her, M. *New J. Chem.* **2001**, *25*, 1148. (b) Velasco, D.; Castellanos, S.; López, M.; López-Calahorra, F.; Brillas, E.; Julia, L. *J. Org. Chem.* **2007**, *72*, 7523.
(19) De, A. K.; Ganguly, T. *J. Lumin.* **2001**, *92*, 255.
(20) Frisch M. J.; *Gaussian 03*, revision B.05; Gaussian Inc.: Pittsburgh PA, 2003.
(21) McCarroll, M. E.; Shi, Y.; Harris, S.; Puli, S.; Kimaru, I.; Xu, R.; Wang, L.; Dyer, D. J. *J. Phys. Chem. B* **2006**, *110*, 22991.

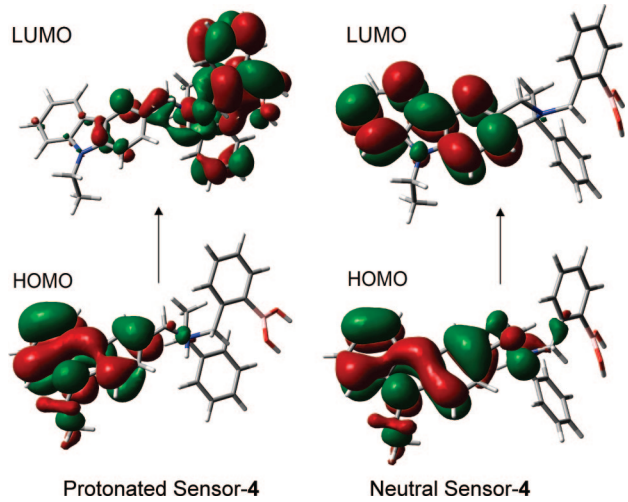


FIGURE 5. Mechanism of the reverse PET effect: HOMO and LUMO of protonated and neutral sensor **4**, calculated with DFT/TDDFT at the B3LYP/6-31G(d) level using Gaussian 03.

for **3** (see Supporting Information). At basic pH, the PET from carbazole to the amine unit is inhibited, but the normal PET (i.e., ET from the amine unit to fluorophore) occurs, thus on balance the fluorescence intensity will be intensified, but not significantly.[14] These calculations are consistent with experimental results and rationalize the concept of d-PET (fluorophore as electron *d*onor in the PET process).[21,22] On the basis of the calculated molecular orbitals, the free energy changes ($\Delta G°$) of the ET of protonated sensor **4** is estimated as −0.22 eV (−21.2 kJ mol^{-1}).[21,22]

To rationalize the putative d-PET effect, sensor **5**, which shows normal PET response,[14] was also studied for TDDFT calculations, and the results indicate that no ET from fluorophore to the charged amine unit occurs. Instead, there is ET from the N unit to the fluorophore for the neutral **5**, thus it belongs to the normal a-PET sensor. According to our putative mechanism, neutral **5** should give weak emission whereas protonated **5** gives intensified emission, which are in full agreement with experimental observations.[14]

These TDDFT calculations/experimental results might be suggesting a general role for the reverse PET effect, and it can potentially be used to design new sensors that give improved signal transduction at acidic pH, where the normal PET sensors give poor signal transduction.[9,10,13,14]

In summary, new 3,6-disubstituted carbazole-based bisboronic acid for enantioselective recognition of tartaric acid is reported. The unique fluorescence response of enhancement/diminishment toward the enantiomers of tartaric acid was found at neutral pH. The new sensors show an unusual PET effect of diminished fluorescence at acidic pH, by which improved signal transduction resulted. A mechanism of electron transfer from fluorophore to the protonated amine/phenylboronic acid unit (d-PET) was proposed and supported by DFT/TDDFT calculations. Our future aim is to study this reverse PET effect and to explore its potential applications in new fluorescent PET sensors.

(22) Ueno, T.; Urano, Y.; Setsukinai, K.; Takakusa, H.; Kojima, H.; Kikuchi, K.; Ohkubo, K.; Fukuzumi, S.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 14079.

Experimental Section

(***S,S*)-3:** (*S*,*S*)-**2** (0.92 g, 2 mmol), 2-(2-bromobenzyl)-1,3,2-dioxaborinane (0.50 g, 4 mmol), and K_2CO_3 (1.18 g, 8.56 mmol) were mixed in dry MeCN (30 mL) and refluxed for 10 h under N_2. The mixture was cooled and the solvent evaporated, and CH_2Cl_2 was added. The organic layer was washed with water and dried over $MgSO_4$. After evaporation, the residue was purified with column chromatography (Al_2O_3, CH_2Cl_2/MeOH, 100:1, v/v); 0.3 g of white powder was obtained: yield 20.4%; mp 216.4−217.8 °C; ^{1}H NMR (400 MHz, $CDC1_3$) δ (ppm) = 7.80 (s, 2H), 7.72 (s, 2H), 7.14−7.30 (m, 20H), 4.25 (q, 2H, J = 8.0 Hz), 4.05 (q, 2H, J = 8.0 Hz), 3.83 (dd, 4H, J = 12.0 Hz), 3.58 (d, 2H, J = 8.0 Hz), 3.30 (d, 2H, J = 8.0 Hz), 1.52 (d, 6H, J = 8.0 Hz), 1.32 (t, 3H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDC1_3$) δ (ppm) = 141.9, 139.6, 139.2, 136.2, 134.9, 131.4, 130.0, 129.3, 128.2, 127.6, 127.5, 127.2, 122.6, 121.8, 108.5, 57.5, 57.0, 53.8, 37.7, 15.7, 13.9; $[\alpha]^{25}_D$ = −33.4 ± 0.9 (c = 0.39 in MeOH); TOF MS ESI$^+$ calcd for $C_{46}H_{51}B_2N_3O_4$ ($[M + 2H]^{2+}$) 365.7033, found 365.7031. Anal. Calcd for $C_{46}H_{49}B_2N_3O_4 \cdot 2CH_3OH$: C, 72.64; H, 7.24; N, 5.29. Found: C, 72.98; H, 6.93; N, 5.36.

(*R*,*R*)-**3** was prepared with the same methods: mp 218.4−219.7 °C; ^{1}H NMR (400 MHz, $CDC1_3$) δ (ppm) = 7.88 (s, 2H), 7.80 (br, 2H), 7.23−7.43 (m, 20H), 4.33 (q, 2H, J = 8.0 Hz), 4.13 (q, 2H, J = 8.0 Hz), 3.90 (dd, 4H, J = 12 Hz), 3.63 (d, 2H, J = 8.0 Hz), 3.38 (d, 2H, J = 8.0 Hz), 1.60 (d, 6H, J = 8.0 Hz), 1.41 (t, 3H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDC1_3$) δ (ppm) = 141.9, 139.7, 139.2, 136.2, 134.9, 131.4, 130.0, 129.3, 128.3, 127.7, 127.5, 127.2, 122.6, 121.8, 108.6, 57.5, 56.9, 53.9, 37.8, 15.8, 13.9; $[\alpha]^{25}_D$ = +34.8 ± 2.0 (c = 0.39 in MeOH); TOF MS ES$^+$ calcd for $C_{46}H_{51}B_2N_3O_4$ ($[M + 2H]^{2+}$) 365.7033, found 365.7026; calcd for $C_{46}H_{50}B_2N_3O_4$ ($[M + H]^+$) 730.3982, found 730.4019. Anal. Calcd for $C_{46}H_{49}B_2N_3O_4 \cdot 0.5CH_3OH$: C, 74.91; H, 6.89; N, 5.64. Found: C, 74.58; H, 6.81; N, 5.53.

(*S*)-**4** was prepared with the same methods: mp 120.7−122.5 °C; ^{1}H NMR (400 MHz, $CDC1_3$) δ (ppm) = 8.07 (d, 2H, J = 8.0 Hz), 7.91 (s, 1H), 7.82 (d, 1H, J = 8.0 Hz), 7.19−7.84 (m, 12H), 4.35 (q, 2H, J = 8.0 Hz), 4.12 (q, 1H, J = 8.0 Hz), 3.97 (d, 1H, J = 12.0 Hz), 3.86 (d, 1H, J = 12.0 Hz), 3.60 (d, 1H, J = 12.0 Hz), 3.52 (d, 1H, J = 12.0 Hz), 1.59 (d, 3H, J = 8.0 Hz), 1.42 (t, 3H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDC1_3$) δ (ppm) = 141.9, 140.3, 139.4, 139.2, 136.2, 131.4, 130.0, 129.3, 128.2, 127.6, 127.5, 127.3, 127.2, 125.7, 122.8, 121.8, 120.4, 118.8, 108.6, 108.4, 57.5, 56.9, 53.8, 37.7, 15.8, 13.9; $[\alpha]^{25}_D$ = −31.6 ± 0.5 (c = 0.78 in MeOH); TOF MS ESI$^+$ calcd for $C_{30}H_{32}BN_2O_2$ ($[M + H]^+$) 463.2557, found 463.2563. Anal. Calcd for $C_{30}H_{31}BN_2O_2$: C, 77.93; H, 6.76; N, 6.06. Found: C, 77.50; H, 7.18; N, 5.44.

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Supporting Information Available: General experimental methods, compound characterization data (IR, etc.), fluorescence spectra, and DFT/TDDFT calculation details of sensors **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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