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Chemical-Stimuli-Controllable Circularly Polarized Luminescence from Anion-Responsive π-Conjugated Molecules

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Supporting Information

ABSTRACT: Introduction of a BINOL−boron moiety to dipyrrolyldiketones as precursors of anion-responsive π-conjugated molecules results in the formation of a chiral environment in the form of anion-free receptors and anion-binding complexes. Conformation changes by inversion (flipping) of two pyrrole rings as a result of anion binding can control the chiroptical properties of the anion receptors. In particular, appropriate pyrrole β-substituents induce distorted receptor π-planes and, as a result, give larger circularly polarized luminescence (CPL), which can be tuned by chemical stimuli (anions). This is the first example of chemical-stimuli-responsive CPL properties.

Breaking of symmetry in molecules provides chiral environments, which exhibit chiral electronic and electrooptical properties. Among them, circularly polarized luminescence (CPL),[1,2] as observed in emissive chiral molecules[2c] and assemblies[2g] such as one-handed helicenes,[2b,h] lanthanide complexes with chiral ligands,[2d] polymers,[2e,f] and liquid crystals of helicenes,[2a] becomes an essential property for biological probing and display technologies. Such CPL-active materials have a tremendous amount of potential for highly sophisticated optical devices in comparison with conventional circular dichroism (CD)-active materials. However, there are few examples of the control and switching of CPL properties by external stimuli. As emissive π-conjugated molecules that are responsive to anions as chemical stimuli,[3] boron complexes of 1,3-dipyrrolyl-1,3-propanediones (e.g., **1a** and **2a** in Figure 1a), which show pyrrole inversion by anion binding (Figure 1b), afford various derivatives by substitution at the pyrrole α- and β-positions and the boron moiety of the central six-membered ring.[4−6] In particular, substitution of diol moieties on the core boron has been found to provide various receptor molecules with useful functionalities.[6] As one of the strategies to achieve chiroptical properties, the introduction of chiral diols would induce a chiral conformation of the core receptor π-planes. In this communication, we report the synthesis and anion-responsive chiroptical properties of diol−boron-substituted π-conjugated anion receptors, especially supported by bulky pyrrole β-substituents. The inversion of the pyrrole rings by anion binding enables the induction of conformational changes of the receptor π-planes followed by changes in the electronic and electrooptical properties.

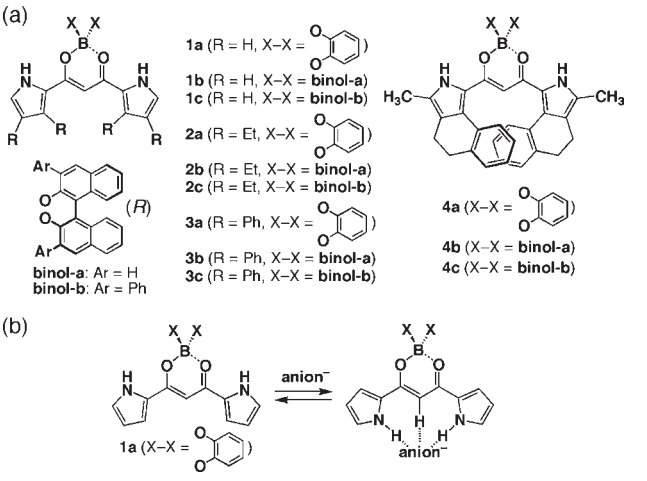

Figure 1. (a) π-Conjugated acyclic anion receptors **1a**−**c**, **2a**−**c**, **3a**−**c**, and **4a**−**c**. (b) Anion-binding mode of **1a**.

According to literature procedures,[6] β-phenyl-substituted and β-dihydronaphtho-fused catecholboron complexes **3a** and **4a** were prepared by treatment of the corresponding pyrroles[7,8] with malonyl chloride and the subsequent reaction with BCl_3 and catechol. As chiral substituents, we focused on 1,1′-bi-2-naphthol (BINOL) moieties. As in the case of **1a**, **2a**, **3a**, and **4a**, (*R*)-(+)-1,1′-bi-2-naphtholboron compounds **1b**, **2b**, **3b**, and **4b** and (*R*)-(+)-3,3′-diphenyl-1,1′-bi-2-naphtholboron compounds **1c**, **2c**, **3c**, and **4c** were obtained via the precursory diketone derivatives. The single-crystal X-ray structure of **2c** showed that the tilted dihedral angle between the two pyrrole rings is 21.61° as a result of steric hindrance between the ethyl moieties at the pyrrole β-positions, whereas that of **4a** with the totally pyrrole-inverted conformation is 22.37° (Figure 2).[9] It is essential to point out that **2c** forms intramolecular $\pi-\pi$ stacking between a pyrrole ring and a phenyl ring attached to the BINOL unit. In the packing diagram, even though **2c** shows no significant assembled structures, **4a** forms self-complementary dimers based on hydrogen bonding between NH and the catechol oxygen. Furthermore, the X-ray structure of **4a**·Cl^- as the tetrabutylammonium (TBA) salt showed a [1 + 1]-type receptor−anion complex wherein the dihedral angle between two pyrrole rings is 6.58°,

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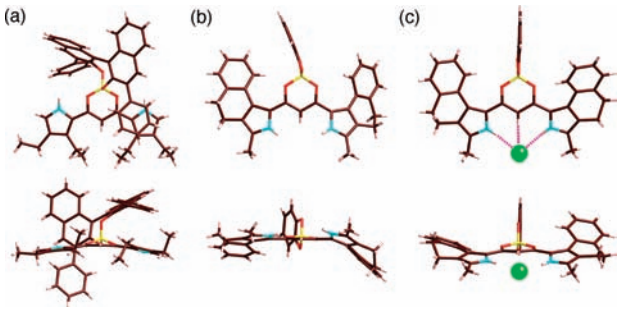

Figure 2. Single-crystal X-ray structures (top and side views) of (a) **2c**, (b) **4a**, and (c) **4a**·TBACl. Atom color code: brown, carbon; pink, hydrogen; yellow, boron; blue, nitrogen; red, oxygen; yellow-green (sphere), chlorine. Solvent molecules [hexane and CH_2Cl_2 for (a) and (b), respectively] and the TBA cation [in (c)] have been omitted for clarity. The solid-state structure of **4a** shown in (b) is quite different from that in solution ($CDCl_3$), wherein the two pyrrole rings are not inverted.

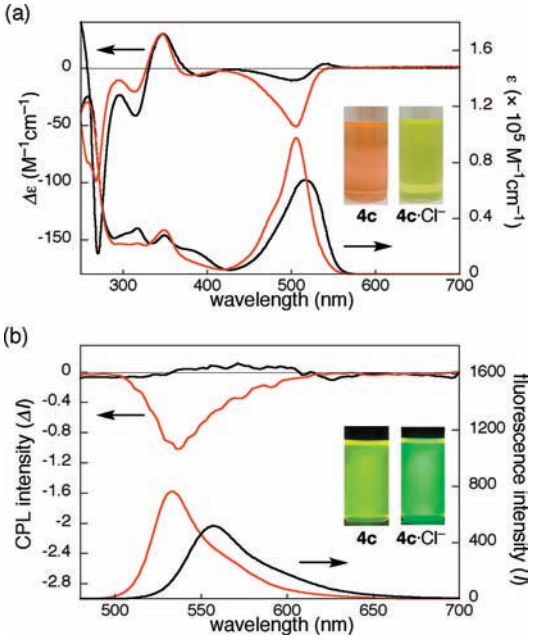

Figure 3. Spectral changes for **4c** (1.0×10^{-5} M in CH_2Cl_2) in (a) UV−vis absorption (bottom) and CD (top) and (b) fluorescence (bottom) and CPL (top) excited at the isosbestic point of UV−vis absorption spectrum, upon the addition of Cl^- as the TBA salt (50 equiv for UV−vis and 200 equiv for the other measurements as amounts sufficient for almost complete complexation; **4c**, black line; **4c**·Cl^-, red line), and corresponding solution photographs (insets).

which is smaller than that of anion-free receptor **4a**. On the other hand, conformational changes such as pyrrole inversion by anion binding in solution were suggested by ^{1}H NMR analysis, including nuclear Overhauser effect spectroscopy (NOESY).

The UV−vis absorption maxima (λ_{max}) and corresponding fluorescence emission maxima (λ_{em}) and emission quantum yields (Φ_F) of **1b**, **1c**, **2b**, **2c**, **3b**, **3c**, **4b**, and **4c** in CH_2Cl_2 (see Figure 3 for the spectra of **4c**) are summarized in Table 1[10] The λ_{max} and λ_{em} of **4b** and **4c** are red-shifted relative to those of the other receptors as a result of the introduction of fairly coplanar π-units at the β-positions. Even though most diol-substituted boron complexes show significantly weak fluorescence,

Table 1. Summary of UV−Vis Absorption Maxima (λ_{max}), Fluorescence Emission Maxima (λ_{em}) and Emission Quantum Yields (Φ_F) Excited at These λ_{max}, and Negative CD Maxima (λ_{CD}) in CH_2Cl_2

	λ_{max} (nm)	λ_{em} (nm)	Φ_F	λ_{CD} (nm)
1b	432	438	0.005	432
1c	437	441	0.005	433
2b	452	467	0.006	451
2c	456	472	0.009	452
3b	470	505	0.005	467
3c	473	499	0.004	470
4b	513	555	0.28	517
4c	518	554	0.51	500

π-extended **4b** and **4c** bearing a BINOL−boron moiety exhibit fairly strong emissions, presumably because of tuning of the molecular orbitals (MOs) suitable for preventing intramolecular electron transfer. Calculations at B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p) level showed that the orders and energy gaps of the MOs localized at the core dipyrrolyldiketone moieties and the aryldiol moieties are correlated with the fairly high Φ_F values of **4b** and **4c** relative to other diol−boron derivatives. Furthermore, Cotton effects in the CD spectra were observed for the chiral molecules **1b**, **1c**, **2b**, **2c**, **3b**, **3c**, **4b**, and **4c** (Table 1; see Figure 3a for **4c**); these molecules exhibit negative Cotton effects derived from core π-planes in CH_2Cl_2, suggesting that enantiomerically distorted *M*-like conformations are induced by the substituents on boron.

The conformations of π-conjugated anion receptors and their electronic and electrooptical properties can be controlled by anion binding. From the UV−vis absorption spectral changes upon the addition of anions such as TBA salts in CH_2Cl_2 (Figure 3a), the binding constants (K_a) of, for example, **1c**, **2c**, **3c**, and **4c** for Cl^- and $CH_3CO_2^-$ were estimated as 2500 and 86 000 M^{-1} for **1c**, 95 and 4400 M^{-1} for **2c**, 3700 and 55 000 M^{-1} for **3c**, and 8200 and 51 000 M^{-1} for **4c**, respectively, suggesting efficient anion binding by all of these except for **2c**.[11] There seemed to be no significant correlation between the K_a values and the stabilities of the molecular conformations estimated by DFT calculations.[12] Some of the receptors showed anion-modulated emission properties, as observed in the increasing Φ_F values of 0.40 (**4b**) and 0.72 (**4c**) upon the addition of excess TBACl (Figure 3b).[13] The increased emission quantum yields were correlated with the factors observed in the HOMO and LUMO localized at the dipyrrolyldiketone moieties of the receptor−anion complexes (also see the Supporting Information). Upon the addition of Cl^- as a TBA salt, the CD signals of, for example, **1c**, **2c**, **3c**, and **4c** in CH_2Cl_2 (1×10^{-5} M) exhibited changes in the intensities and λ_{CD} at 437, 452, 469, and 506 nm as negative signals, respectively (Figure 3a). The CD anisotropy factors g_{abs} (defined as $\Delta\varepsilon/\varepsilon$ at the wavelengths of the first Cotton effects) for **1c**, **2c**, **3c**, and **4c** were found to be $10^4 g_{abs}$ = 7.7, 6.8, 5.0, and 2.0, respectively, which were moderately changed to 7.1, 6.2, 4.2, and 4.9, respectively.[14] The g_{abs} values were correlated with multiple factors such as the distortion of the π-conjugated units in the core receptor π-planes.

On the basis of the chemical-stimuli-responsive behaviors in the steady state, induction of chirality of π-conjugated molecules in the excited state by anion binding was examined by CPL measurements.[1,2] In fact, the anion-responsive CPL property was

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observed in **4c** by complexation with Cl^- and $CH_3CO_2^-$ (Figure 3b), both of which exhibited a CPL anisotropy factor g_{lum} (defined as $\Delta I/I$, where ΔI and I are the CPL and fluorescence intensities, respectively) of 2×10^{-3}, whereas **4c** showed negligibly small CPL. To the best of our knowledge, this is the first example of chemical-stimuli-responsive CPL. The (*S*)-(−) isomer of **4c** showed the mirror images of these anion-responsive CD and CPL spectral changes. The enhancement of the g_{lum} value of **4c** by anion binding is greater than that of g_{abs} by Cl^- binding, suggesting that the anion-driven chiral induction, which is mainly due to conformation changes of the π-conjugated system, is more pronounced in the excited state than in the steady state. Such a distinct on/off switching of g_{lum} was not observed for the other receptors **1b**, **1c**, **2b**, **2c**, **3b**, **3c**, and **4b**, some of which could not provide exact g_{lum} values because of the smaller CPL intensities. In any case, our research suggests that the anion triggers CPL and that CPL measurements can be used for ion sensing.

In summary, we have demonstrated chemical-stimuli-responsive chiroptical properties using anion-responsive π-conjugated molecules. In regard to the structures of fluorescent molecules, it is essential to develop π-conjugated molecules possessing fairly planar but chirally distorted geometries, which are present in the BINOL−boron complexes of β-substituted dipyrrolyldiketones. At present, the combination of 3,3′-diphenyl-1,1′-bi-2-naphthol and β-dihydronaphthopyrrole has been found to be the most efficient for achieving anion-driven CPL enhancement. Thus, the property reported in this communication seems to result from the pyrrole modifications; a series of the related anion receptors have been reported to date,[4−6] and a myriad of unexplored properties are likely to be revealed. Further investigations to elucidate the fascinating properties of these pyrrole-based π-conjugated molecules are currently underway.

■ ASSOCIATED CONTENT

Supporting Information. Synthetic procedures, anion-binding properties, crystallographic data (CIF), and complete ref 12b. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) See the crystallographic data in the Supporting Information.

(10) (a) The corresponding BF_2 complexes **1d**, **2d**, **3d**, and **4d** exhibited high Φ_F values of 0.96,[5d] 0.98,[5b] 0.83, and 0.80, respectively. (b) Data for **1a**, **1d**, **2a**, **2d**, **3a**, **3d**, **4a**, and **4d** are summarized in the Supporting Information.

(11) (a) K_a values for anions are summarized in the Supporting Information. (b) Chiral receptors **2c**, **3c**, and **4c** showed almost no selectivity for recognizing asymmetric guest species such as L- and D-Phe anions as TBA salts.

(12) (a) The relative energies between the stable and preorganized pyrrole-inverted geometries of **2a**−**c** and **4a**−**c** are 5.32,[6a] 5.85, 6.06, 5.65, 6.50, and 4.83 kcal/mol, respectively, which are small compared to the values 9.05,[6a] 9.32, 9.55, 9.89, 11.10, and 9.81 kcal/mol for **1a**−**c** and **3a**−**c**, respectively. (b) Frisch, M. J.; et al. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

(13) Anion-modulated emission properties were also observed in the increases in Φ_F values of 0.008 (**1b**), 0.008 (**1c**), 0.062 (**2b**), 0.047 (**2c**), 0.010 (**3b**), and 0.024 (**3c**) upon the addition of excess TBACl.

(14) Upon the addition of Cl^- as a TBA salt, negative Cotton effects were observed for **1b**, **2b**, **3b**, and **4b** in CH_2Cl_2 with λ_{CD} at 435, 452, 460, and 506 nm, respectively, along with changes in $10^4 g_{abs}$ from 4.2, 3.9, 3.5, and 4.7 to 3.5, 4.2, 4.0, and 3.6, respectively.

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