Fluorescent chemosensors (FCS), which can selectively recognize guest species, offer an essential strategy for real-space and real-time monitoring or imaging. Design of high-performance FCS for biologically or environmentally important species is a topic attracting considerable attention in supramolecular chemistry. During the past few decades, numerous FCS have been developed based on molecular recognition through noncovalent interactions (e.g., hydrogen bonding in anion recognition,[2] metal–ligand interaction in sensing, for example, metal cations[3] or gaseous species[4]). Halogen bonding (XB)—the interaction based on donation of electron density from a Lewis base to an electron-deficient halogen atom—is a frequently occurring noncovalent interaction parallel to hydrogen bonding in molecular self-assembly processes.[5] However, XB has so far mostly been studied in silico and in solid state,[5a] and solution-phase molecular sensing through XB remains largely unexplored. The first and only two examples of XB-based FCS were reported recently by Beer’s group, both of which used macrocyclic halo-imidazolium receptors to recognize halide anions through charge-assisted XB in solution.[6] Compared with anions, common neutral Lewis bases are more intriguing XB acceptors in the construction of XB receptors for halogenated organic compounds. Many important environmental pollutants including polychlorinated biphenyls, dioxins and some toxic organometallics are halogen-abundant compounds while efficient FCS for these species are still unavailable. Herein, we report a design of off/on fluorescent chemosensors for organotin halides based on XB in solution.

Organotin compounds (OTCs) are known for their wide distribution and strongly toxic effect on marine organisms.[7] OTCs are represented by the formula $\text{R}_n\text{SnX}_{(4-n)}$, where Sn is the tin atom, R is an alkyl or aryl group, X is usually a halide or hydroxide anion, and $n$ ranges from 1 to 4. The degradation products of OTCs usually exist as di- or mono-organotin complexes,[8] both with high biological activities.[9] For studying the toxicology of OTCs, we have reported the first FCS for hydroxylated organotins.[10] Further effort was made to develop FCS for organotin halides by taking advantage of the XB activities of these species. Many percyanometallates were reported to be efficient XB acceptors.[5b,11] This enlightened us to synthesize binuclear ruthenium complexes $2a$ and $2b$ (Scheme 1), which contain two percyanometallate-based binding sites bridged by a 1,4-phenylenediacyl fluorophore, as the fluorogenic receptors. Both $2a$ and $2b$ were characterized by means of NMR ($^1$H, $^{13}$C, and $^{31}$P) spectra and high-resolution mass spectra. The structure of $2b$ has been confirmed by X-ray diffraction (Figure 1).

The optical responses of the synthesized receptors to OTCs were tested first in dichloromethane. The solution of $2a$ turns red immediately after addition of PhSnCl$_3$. As shown in Figure 2A, addition of PhSnCl$_3$ results in a decrease of the low-energy absorption of $2a$ ($\lambda_{\text{m}} = 345 \text{ nm}$) characteristic of

![Scheme 1. Synthesis of the binuclear ruthenium complexes.](image1)

![Figure 1. Molecular structure for the cation of $2b$. The counter anions and some of the hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x + 2, -y + 2, -z + 2$.](image2)
In the absence of OTCs, the random vibration was interpreted in terms of "aggregation-induced emission" (AIE). In the presence of OTCs, the binding-induced aggregation of \(2a\) results in intense aggregate-dominated emission but not in enhanced monomer emission occurring in most of the reported AIE systems. This noteworthy characteristics of \(2a\) supports the high target-to-background ratio of the fluorescence responses shown in Figure 2B.

The OTC binding mechanism underlying the AIE responses was studied. The strong triple infrared (IR) absorption bands of PhSnCl\(_3\) observed at 728, 691, and 442 cm\(^{-1}\), characteristic of the Sn–Cl bond stretching, were greatly weakened upon reaction with \(2a\); meanwhile, the intense N≡C stretching absorption of \(2a\) at 2134 cm\(^{-1}\) was also reduced markedly with a slight blue shift (Figure S6). These observations suggest the formation of XB interactions between the N≡C groups and the metal-bound halogen atoms in the reaction product. To confirm the important role of the XB-active percyanometallate moieties in the guest binding process, receptor \(2b\) was tested for a comparison with \(2a\). \(2b\) displayed absorption and fluorescence behaviors similar to \(2a\) in the presence of OTCs (Figure S16). However, the binding affinity of \(2b\) for organotin trichlorides was lower than that of \(2a\) because of its larger steric hindrance. Since both percyanometallates and halometallates are able to form XB interactions with different organotin species, different solvents were also tested as the sensing media. The spectral behaviors of \(2a\) or \(2b\) in trichloromethane are similar to those observed in dichloromethane. No spectral response has been observed when \(2a\) or \(2b\) was titrated with OTCs in lowly XB-active solvents such as ethanol or dioxane. However, when the solvent was changed from dichloromethane (XB donors) to acetonitrile (XB acceptors), the resulting responses to OTCs (Figure 3) were greatly different from those shown in Figure 2. All the investigated organotin halides induced a \(\pi\rightarrow\pi^*\) transition of the 1,4-phenylenediacl chromophore and the onset of a new long-wavelength absorption band (\(\lambda_{\text{em}} = 518\) nm). The remarkable red shift of low-energy absorption band indicates that the double-headed receptor molecules may be linked to form "J"-type aggregates of the fluorophores. Consequently, the intramolecular vibration or rotation of the fluorophores is significantly suppressed to give a high \(q_F\) of the aggregate emission. It is believed that the bulky ligands of \(2a\) also play an important role in this process to sterically preclude the \(\pi-\pi\) stacking of the fluorophores and the as-resulted fluorescence quenching. Interestingly, the OTC-induced aggregation of \(2a\) results in intense aggregate-dominated emission but not in enhanced monomer emission occurring in most of the reported AIE systems.

Figure 2. A) Absorption and B) photoluminescence spectra of \(2a\) (10 \(\mu\)M) in dichloromethane in the presence of different organotin species (50 \(\mu\)M): a) blank or other compounds including Bu\(_3\)SnCl, Bu\(_2\)SnCl, Bu\(_2\)Sn, Me\(_2\)SnCl\(_2\), Me\(_3\)SnCl, Ph\(_2\)SnCl\(_2\), Ph\(_3\)SnCl, Me\(_3\)SnBr, Et\(_3\)SnBr, Bu\(_3\)SnBr and Me\(_2\)SnBr. b) BuSnCl\(_3\), and c) PhSnCl\(_3\). The emission spectra were recorded upon excitation at 510 nm.

Figure 3. Fluorescence responses of A) \(2a\) and B) \(2b\) in acetonitrile to different organotin species (50 \(\mu\)M): a) blank, b) Me\(_2\)SnCl\(_2\), c) Bu\(_3\)SnCl, d) Ph\(_2\)SnCl\(_2\), e) Ph\(_3\)SnCl, f) Bu\(_3\)SnCl, g) Bu\(_3\)Sn, h) PhSnCl\(_3\), i) BuSnCl\(_3\), and j) Me\(_2\)SnBr. Concentration of \(2a\) or \(2b\): 10 \(\mu\)M. Excitation wavelength: \(2a\): 527 nm; \(2b\): 563 nm.
obvious red emission from 2a or 2b while no response was observed upon addition of Bu₄Sn which is not XB-active. Apparently, solvent molecules participate in the XB-driven guest binding process. It was therefore proposed that the receptor molecules were linked through the solvent-assisted XB interaction between the percyanometallate moieties and the metal-bound halogen atoms to form luminescent aggregates in the sensing reaction. Dependence on the assistance of solvent molecules makes the binding process changeful. As a consequence, no stable binding stoichiometry has been found in the sensing reaction, representing a case different from most coordination reactions (Figure S13).

The designed receptors were applied to the fluorescent detection of organotin halides. Figure 4 shows the fluorescence evolution of 2a in dichloromethane upon titration with PhSnCl₃. Interestingly, a multi-gradient response was observed. When less than two equivalents of PhSnCl₃ were added, there was no obvious absorption or fluorescence change. Further increase in the OTC concentration led to the onset and gradual enhancement of the red fluorescence. After change. Further increase in the OTC concentration led to the emission onset and gradual enhancement of the red fluorescence. After addition, there was no obvious absorption or fluorescence enhancement. Variation of the initial concentration of OTCs by the organic solvent.

Figure 5. 31P{¹H} NMR spectral traces of 2a in reactions with PhSnCl₃ in CD₂Cl₂. Conditions: A) [PhSnCl₃] = 2.0 [2a], B) [PhSnCl₃] = 3.0 [2a], and C) reaction time = 10 minutes.

The proposed binding mode was supported by the NMR spectral traces of the PhSnCl₃ sensing reactions (Figure 5). The characteristic 31P{¹H} NMR signal of 2a was slightly shifted by two equivalents of PhSnCl₃. However, it was up-field shifted remarkably when the OTC concentration was further increased. Furthermore, the signal region was greatly broadened, indicating the involvement of 2a in multiple binding ensembles because of aggregation. Based on the special signalling mechanism of 2a described above, the receptors were pretreated with two equivalents of PhSnCl₃ in dichloromethane, resulting in the off/on fluorescence response selective for PhSnCl₃ and BuSnCl₃ over other investigated OTCs. The variations of the PhSnCl₃ sensing responses indicate that most of the organotin halides participates in the target binding process (Figure 6A). Obviously, all the investigated organotin halides are able to interact with percyanometallate receptors through XB. However, only the organotin trihalides are sterically able to link two percyanometallate receptors together in dichloromethane, resulting in the off/on fluorescence response selective for PhSnCl₃ and BuSnCl₃ over other investigated OTCs (Figure 2). The coexistence of other organotin chlorides causes minor interferences, indicating their remarkably lower binding affinity compared with that of PhSnCl₃. As a different case, coexistence of a high concentration of organotin bromides significantly reduces the fluorescence responses. The accompanying reduction of the aggregate-dominated absorption response (Figure S14) makes it clear that the involvement of organotin bromides in the XB binding...
ensemble greatly counters the formation of J-aggregates of 2a. Interestingly, the sensing responses are enhanced by Me₃SnCl or Bu₃SnCl but greatly reduced by their bromide analogs, indicating a great difference between the steric effect of the XBs formed by organotin chlorides and that by their bromide analogs. Nevertheless, the different influences of the coexisting OTCs on the fluorescence responses were leveled in the presence of excess PhSnCl₃ (Figure 6B). The above observations indicate the remarkably higher affinity of 2a for PhSnCl₃ over other OTCs in dichloromethane and thus validate the target recognition ability of the fluorogenic XB receptors.

In summary, XB-driven molecular recognition has been used to develop the first FCS for organotin halides. Chromophore-bridged binuclear ruthenium complexes containing multiple isocyanide ligands were synthesized as XB-active receptors with AIE characteristics. Interaction with organotin halides leads to aggregation of the receptor molecules in solution and the resulting off/on fluorescence responses in the near-infrared region. Visual detection of organotin halides at the micromolar concentration level can be easily carried out by the developed FCS. Our study confirms that cooperation of multiple XBs in solution is able to support high-affinity binding between small molecules. Furthermore, the monomer-to-aggregate conversion of chromophores, which usually results in high-contrast spectral changes, has proven to be a suitable signaling strategy for XB-motivated molecular sensing. Both the recognition and signalling mechanisms discussed herein are highly constructive for further designs of FCS targeting challenging species such as dioxins and dioxin-like polychlorinated biphenyls.

**Experimental Section**

2a: A solution of BuNC (0.40 mL, 3.50 mmol) was slowly added to a solution of complex 1 (391.6 mg, 0.26 mmol) in CH₂Cl₂ (15 mL).

The reaction mixture was stirred for 30 minutes to give an orange solution. The volume of the mixture was reduced to 1 mL under vacuum. Addition of diethyl ether (10 mL) to the residue produced a light pink solid, which was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 266.9 mg, about 1 mL under vacuum. Addition of diethyl ether (10 mL) to the residue produced a light pink solid, which was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 266.9 mg, 95%. 1H NMR (CD₂Cl₂, 500.2 MHz): δ = 7.5–7.3 (m, 60H, PPh₃), 6.8 (s, 4H, C₆H₄), 6.6 (d, J(HH) = 15.5 Hz, 2H, RuCOCH=), 6.7 (d, J(HH) = 15.5 Hz, 2H, RuCOCH=), 1.1 (s, 18H, sBu), 1.0 ppm (s, 36H, sBu).

31P{1H} NMR (CD₂Cl₂, 202.5 MHz): δ = 256.7 (br, RuCO), 149.4 (br, RuCN), 147.7 (br, Ru-CN), 139.6 (s, RuCOCH), 137.0 (s, ipso-C₆H₄), 134.7–128.8 (m, PPh₃), 127.9 (s, C₆H₄), 125.3 (s, RuCO=CH), 58.5 (s, sBu), 58.3 (s, sBu), 30.1 (s, sBu), 29.9 ppm (s, sBu). HRMS (ESI) m/z for [C₅H₆N₂O₂P₄Ru₂]⁺: calc. 967.3333 [M⁺/2]⁺; found 967.3365 [M⁺/2]⁺ with expected isotopic distribution.

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