Organic LETTERS

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Multifunctional Imidazobenzothiadiazole Probe Displaying Solvatofluorochromism and Ability To Form Ion-Pair Complexes in Solid State and in Solution

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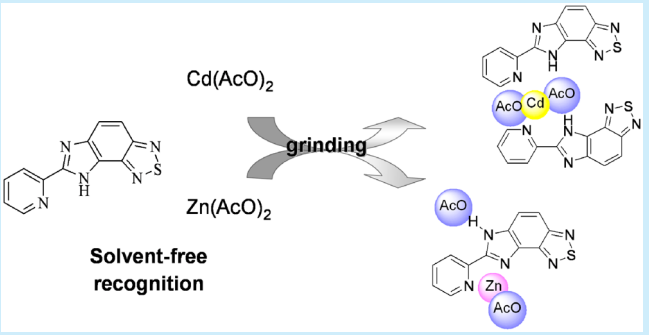
Supporting Information

ABSTRACT: Fluorescent solid 5-pyridylimidazobenzothiadiazole displays a remarkable solvatofluorochromism and with $Zn(AcO)_2$ and $Cd(AcO)_2$, either in solution or under solvent-free conditions, forms ion-pair complexes that in the solid state can be discriminated and separated by fluorescence measurements and selective extraction with diethyl ether or chloroform.



The development of synthetic strategies for the preparation of receptors able to bind concurrently a cation and an anion, i.e., ion-pair recognition receptors, as well as the isolation of the formed complexes are current research topics in the area of supramolecular chemistry.[1] In this context, it is worth noting that extraction and solubilization of salts have been developed due to the investigation of ion-pair recognition.

Despite the interesting photophysical properties of benzothiadiazole derivatives, both in solid state and in solution, this structural motif has not been incorporated so far into the framework of previously reported ion-pair receptors as either a binding site or fluorescent signaling unit.[2] Pyridylbenzimidazole exhibits both tunable coordination modes and supramolecular interactions because it is a multidentate ligand having an amphoteric nature[3] which includes a N−H hydrogen-bonding donor (imidazole ring) and a cation-binding site (aromatic N atoms). The development of solid-emissive fluorophores has received considerable attention due to their interesting applications.[4] However, organic compounds with intense fluorescence in both solution and solid state are rare. For this reason, the rational design of new families of this kind of fluorophore, in particular, those based on novel frameworks, remains quite challenging.[5]

Herein, we describe the synthesis and the binding properties of one rare ion-pair receptor **1**, which combines the fluorescent properties of the benzothiadiazole ring with the binding ability of the pyridylbenzimidazole fragment in a highly preorganized system. The resulting receptor **1** exhibits a remarkable perturbation of the fluorescence emission spectrum in the presence of $Cd(AcO)_2$ or $Zn(AcO)_2$ either in solution or in solid state. The Cd^{2+} cations causes toxicity in living cells disrupting the transport of the essential Zn^{2+} into and out of cells. Thus, molecular design strategies toward strict Zn^{2+}/Cd^{2+} discrimination are of significant interest.[6] Strikingly, receptor **1** is able to discriminate Cd^{2+} from Zn^{2+} not only in solution but also in the solid state.

The synthesis of the target receptor **1** was accomplished with 19% yield from reaction of 4,5-diamino-2,1,3-benzothiadiazole[7] and pyridine-2-carboxaldehyde as starting materials in nitrobenzene (Figure 1). Then the ion-pair recognition properties of receptor **1** were analyzed in solution and solid state by means of ^1H NMR experiments and absorption and emission spectroscopies.

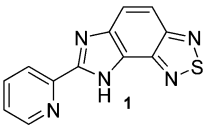


Figure 1. Imidazobenzothiadiazole receptor **1**.

Receptor **1** is a fluorescent yellow powder, and the solutions of this receptor in organic solvents display solvatofluorochromism under UV irradiation (λ = 365 nm) (Figure 2). Whereas the UV−vis absorption spectra did not show noticeable solvatochromism, the wavelength of the emission maximum bathochromically shifts when the solvent polarity is increased (Figure 2). These findings suggest an excited state of **1** with a stronger polarity than that in the ground state. Therefore, as the solvent

Received: March 27, 2015

DOI: 10.1021/acs.orglett.5b00895
Org. Lett. XXXX, XXX, XXX−XXX

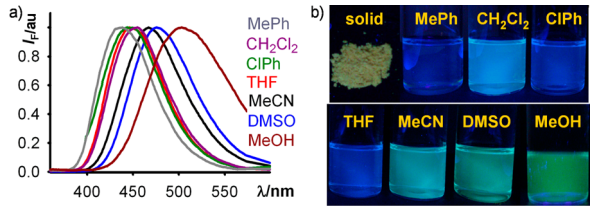


Figure 2. (a) Solvent-dependent emission spectra of **1** (λ_{exc} = 300 nm). (b) Visual changes observed in the fluorescence under UV lamp (λ = 365 nm) in the solid state and in solution in different solvent.

polarity increases a solvatofluorochromic red shift is observed as a consequence of the stronger dipole−dipole interaction between the polar solvent molecules and the excited state of **1**.[8]

The sensing properties of receptor **1** toward cations and anions[9] in acetonitrile solution were studied first. The UV−vis spectrum of receptor **1** exhibits two bands at λ = 301 and 360 nm. It is worth noting that the addition of Cd^{2+} and Zn^{2+} to **1** promoted the most significant changes in its absorption spectrum consisting of a progressive appearance of a new low energy (LE) band blue-shifted (λ = 325 nm). Titration studies toward anions revealed that only AcO^- anion induced detectable changes, ($\Delta\lambda$ = 10 nm), whereas CN^-, F^- and $HP_2O_7^{3-}$ anions clearly induced deprotonation ($\Delta\lambda$ = 57 nm) (see Figures S11 and S12, Supporting Information).

Receptor **1** showed a strong fluorescence in CH_3CN (2×10^{-6} M) displaying an intense band at λ = 466 nm (Φ = 0.262) when excited at λ_{exc} = 300 nm, which was also affected in the presence of the above-mentioned ions. Therefore, only after the addition of Cd^{2+} (I_0/I_F = 2.9; $\Delta\lambda$ = 34 nm; Φ = 0.146) and Zn^{2+} (I_0/I_F = 4.7; $\Delta\lambda$ = 29 nm; Φ = 0.106) cations was a significant decrease in the fluorescence intensity with concomitant red-shift of the wavelength of the emission band observed, whereas addition of AcO^- anions (I_0/I_F = 1.1; $\Delta\lambda$ = 7 nm) promoted just a slight decrease in intensity along with a negligible shift in the emission band (Figure S14).

Ion-pair complex formations in solution have been studied by using absorption and emission techniques. Stepwise addition of aqueous solutions of $Cd(AcO)_2$ or $Zn(AcO)_2$ ($c = 2.5 \times 10^{-2}$ M) to a solution of receptor **1** in CH_3CN (5×10^{-5} M) elicited the same optical response in the absorption spectrum; namely the progressive appearance of a new high energy band located at λ = 317 nm ($\Delta\lambda$ = 16 nm), together with a blue-shifted low energy band at λ = 350 nm ($\Delta\lambda$ = −10 nm). A well-defined isosbestic point at λ = 310 nm indicated the occurrence of a neat interconversion between the uncomplexed and complexed species. Binding assays using the method of continuous variations (Jobs plot) suggest a 2:1 (receptor/$Cd(AcO)_2$) and 1:1 (receptor/$Zn(AcO)_2$) binding model.

Next, titrations with these salts were studied by fluorescence spectroscopy. Addition of an aqueous solution (c = 1.2 × 10^{-3} M) of the corresponding acetate to a solution of receptor **1** in CH_3CN (c = 2 × 10^{-6} M) (λ_{exc} = 320 nm) resulted in the appearance of a red-shifted broad emission band at λ = 515 nm ($\Delta\lambda$ = 49 nm; (Φ = 0.349) for $Cd(AcO)_2$ and at λ = 500 nm ($\Delta\lambda$ = 34 nm; Φ = 0.317) for Zn(AcO). In addition, a well-defined isoemissive point appeared in the region of 490 nm. Nonlinear regression global analysis[10] on fluorogenic titrations gave apparent association constants of β = 9.53 × 10^{12} M^{-2} for $Cd(AcO)_2$ and K = 1.51 × 10^7 M^{-1} for $Zn(AcO)_2$ (Figure 3). The stoichiometries proposed from the above spectroscopic data have been further confirmed by ESI-MS experiments.

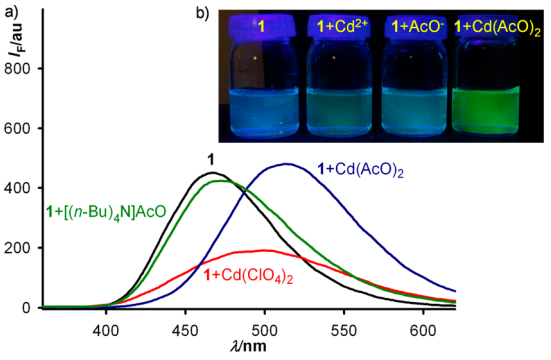


Figure 3. (a) Changes in the emission spectra of **1** in CH_3CN (2×10^{-6} M) in the presence of the indicated species, added in aqueous solution (1.2×10^{-3} M); (b) visual changes observed.

To seek more detailed information on the capability of receptor **1** to form ion-pair complexes, a ^1H NMR spectroscopic analysis was also performed in DMSO-d_6. While gradual addition of an aqueous solution of the Cd^{2+} or Zn^{2+} cations did not promote any change in the spectrum of the free receptor[11] (Figure 4b), addition of AcO^- anion in water induced an upfield

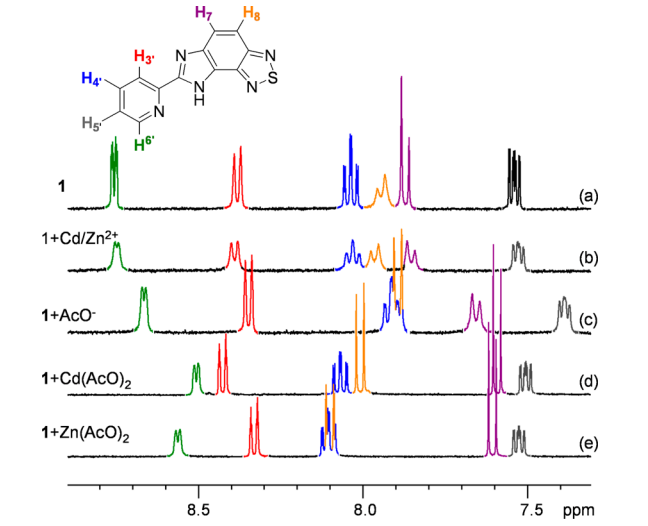


Figure 4. Evolution of ^1H NMR of **1** in DMSO-d_6 (2×10^{-3} M) in the presence of the indicated species.

shift of all signals (Figure 4c). The detection of the ion-pair formation was evidenced by addition of $Cd(AcO)_2$ or $Zn(AcO)_2$ either as an aqueous solution or in the solid state. In both cases, a strong perturbation in the spectrum of the free receptor was observed (Figures 4d,e).

The solvent-free synthesis of the solid ion-pair complexes was achieved by grinding the receptor **1** with $Cd(AcO)_2$ (2:1) or with $Zn(AcO)_2$ (1:1) in a mortar using a pestle for 30 min at constant temperature. No purification of the resulting powder was performed. Strikingly, no examples toward the formation of ion-pair complexes in the solid state have been reported so far.[12] The ion-pair complex formation through this viable alternative to conventional methods was investigated by X-ray powder diffraction (PXRD) and spectroscopic techniques.

The presence of several peaks in the XRPD of the resulting material, which are absent both in the acetate and in the receptor patterns, together with the fact that neither the fingerprint *d*-spacing-intensity pattern of the $Cd(AcO)_2$ nor the receptor **1** can

DOI: 10.1021/acs.orglett.5b00895
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be recognized in the XRPD, are indicative of the formation of a new compound. The resulting diffraction patterns are broadened which may be ascribed to the small size of the corresponding crystallites. The formation of the ion pair was assigned to be $[\mathbf{1}_2 \cdot Cd(AcO)_2]$ by comparing the IR, ^{1}HNMR, absorption, and emission spectra of the starting materials with those of the pure complexes. A similar result was achieved when $Zn(AcO)_2$ was used as the inorganic salt partner. IR spectra of the free receptor **1**, $Zn(AcO)_2$, and $Cd(AcO)_2$, as well as the corresponding ion-pair complexes, were obtained. The latter show the expected carbonyl band associated with the acetate anion present in these complexes together with a fingerprint which does not match with any of the other species (Figures S38 and S39).

Interestingly, the ^{1}H NMR spectra of the solid ion-pair complexes prepared, $[\mathbf{1}_2 \cdot Cd(AcO)_2]$ and $[\mathbf{1} \cdot Zn(AcO)_2]$, in DMSO-$d_6$, were found to be identical to those of the corresponding complexes formed in solution (Figures 4d,e). The UV–vis spectrum of the receptor **1** in the solid state displayed an absorption band at $\lambda = 313$ nm, appearing at nearly the same position as in the Zn^{2+} complex ($\lambda = 317$ nm), whereas the Cd^{2+} complex showed a red-shifted band at $\lambda = 323$ nm ($\Delta\lambda = 10$ nm) (Figures S40 and S41). Fluorescence studies revealed that both complexes are emissive in the solid state and also displayed solvatofluorochromism (Table S11). As shown in Figure 5 the emission spectra of the receptor **1** showed a broad

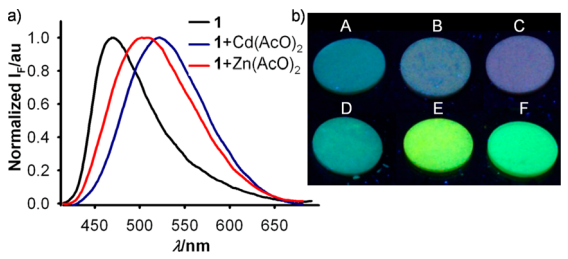

Figure 5. (a) Emission spectra in the solid state of receptor **1** (black line) ($\Phi < 0.01$), and ion pair complexes $[\mathbf{1} \cdot Zn(AcO)_2]$ ($\Phi < 0.01$) and $[\mathbf{1}_2 \cdot Cd(AcO)_2]$ ($\Phi < 0.01$). (b) Visual changes observed in the fluorescence (UV lamp, $\lambda = 365$ nm) of solid KBr pellets of the free receptor (A) and after grinding with $Cd(ClO)_4$ (B), $Zn(OTf)_2$ (C), $[(n\text{-}Bu)_4N]OAc$ (D), $Cd(AcO)_2$ (E), and $Zn(AcO)_2$ (F).

emission band centered at $\lambda = 470$ nm, while the $[\mathbf{1} \cdot Zn(AcO)_2]$ and $[\mathbf{1}_2 \cdot Cd(AcO)_2]$ complexes displayed a red-shifted emission band at $\lambda = 500$ ($\Delta\lambda = 30$ nm) and $\lambda = 522$ nm ($\Delta\lambda = 52$ nm), respectively.

One direct consequence of this behavior is that the receptor allows the otherwise insoluble $Cd(AcO)_2$ and $Zn(AcO)_2$ salts to dissolve in organic solvents. Extraction experiments demonstrated that the host is capable of solubilizing both acetates in acetonitrile and chloroform. Interestingly, a selective extraction of $Zn(AcO)_2$ in the presence of $Cd(AcO)_2$ was successfully achieved when an equimolecular mixture of these salts was extracted with a solution of receptor **1** ($c = 10^{-6}$ M) in diethyl ether: the Zn^{2+} salt was soluble in diethyl ether, whereas the Cd^{2+} salt remained insoluble in the form of the ion-pair complex (Figure S43). Likewise, a selective extraction of $Zn(AcO)_2$ in the presence of $Cd(AcO)_2$ was achieved when an equimolecular mixture of these salts was extracted with a solution of receptor **1** ($c = 10^{-6}$ M) in chloroform. After filtration, the resulting solution displayed an emission spectrum identical to that registered for the ion-pair $[\mathbf{1} \cdot Zn(AcO)_2]$ complex in this solvent (Figure 6). Further evidence that confirms the higher affinity of the receptor

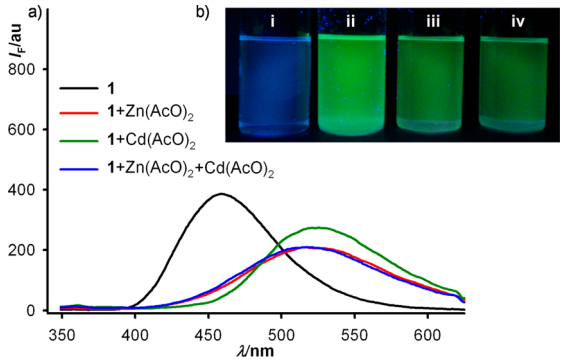

Figure 6. (a) Emission spectra of **1** (5×10^{-6} M) in $CHCl_3$ after stirring with the solid salts. (b) Visual changes observed in the fluorescence under the UV lamp ($\lambda = 365$ nm) of (i) **1**; (ii) **1** + $Cd(AcO)_2$; (iii) **1** + $Zn(AcO)_2$; (iv) **1** + $Cd(AcO)_2$ + $Zn(AcO)_2$.

1 for $Zn(AcO)_2$ arises from ^{1}H NMR studies. Indeed, simultaneous addition of both metal acetates to a solution of **1** in DMSO-d_6, resulted in the same spectrum as that obtained by adding only $Zn(AcO)_2$ (Figure S45).

Unfortunately, all attempts to obtain good quality crystals of the ion-pair complexes for their X-ray study were unsuccessful. Therefore, density functional theory (DFT) calculations were finally carried out at the RI-BP86-D3/def2-TZVPP//RI-BP86-D3/def2-SVP level to gain more insight into the nature of the ion-pair complexes formed upon addition of $Cd(AcO)_2$ or $Zn(AcO)_2$ to receptor **1**. According to the above experimental findings, 1:1 and 2:1 binding models were found for $Zn(AcO)_2$ and $Cd(AcO)_2$, respectively. Screening of the possible modes of interaction between these acetates and **1** (Figures S1 and S2) reveals that species $[\mathbf{1} \cdot Zn(AcO)_2]$ and $[\mathbf{1}_2 \cdot Cd(AcO)_2]$ are the more stable species for 1:1 and 2:1 stoichiometries, respectively (Figure 7).

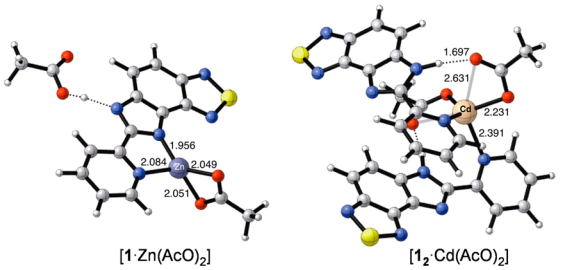

Figure 7. Computed most stable structures for complexes resulting upon complexation of **1** with $Zn(OAc)_2$ (left) or $Cd(OAc)_2$ (right). Bond distances are given angstroms. All data have been computed at the RI-BP86-D3/def2-SVP level.

As seen in Figure 7, the Zn^{2+} cation in $[\mathbf{1} \cdot Zn(AcO)_2]$ is coordinated by one bidentate AcO^- ligand and the nitrogen atoms lone-pairs of the pyridine and benzimidazole moieties of **1**. The other AcO^- is bound to **1** through a hydrogen bond via the NH group of the imidazole. Therefore, this species can be viewed as a ligand-separated AcO–**1**–Zn(OAc) ion-pair complex. Differently, the Cd^{2+} cation in $[\mathbf{1}_2 \cdot Cd(AcO)_2]$ is surrounded by both AcO^- ligands and the nitrogen atoms of the pyridine moieties of two different molecules of **1** in a highly distorted octahedral coordination. Moreover, two clear hydrogen bonds between the acetates and the NH of the benzimidazoles (computed NH···OAc bond lengths of 1.637 and 1.697 Å)

DOI: 10.1021/acs.orglett.5b00895
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contribute further to the stabilization of this species, which can be viewed as a contact **1**−Cd(OAc)$_2$−**1** ion-pair complex.

The nature of the interactions in [**1**·Zn(AcO)$_2$] and [**1**$_2$·Cd(AcO)$_2$] was analyzed in detail with the help of the atoms and molecules (AIM) method. As seen in Figure S3, the AcO$^-$ in [**1**·Zn(AcO)$_2$] is not only bound to the NH group but also interacts with the H7 and H3′ hydrogen atoms of the receptor, as revealed by the occurrence of bond critical points (BCPs) and bond paths (BPs) running between the oxygen atoms of the AcO$^-$ and these hydrogen atoms. These additional stabilizing interactions are likely responsible for the observed upfield shifts of the corresponding signals in the ^{1}H NMR spectrum (Figure 4).

Besides the above commented well-defined NH···OAc hydrogen bonds in [**1**$_2$·Cd(AcO)$_2$], this species is further stabilized by intramolecular $\pi-\pi$ interactions between the pyridine fragment of one molecule of **1** and the benzimidazole moiety of the adjacent receptor as confirmed again by the presence of BCPs and BCs (Figure S3) running between both aryl groups (computed C···C bond distances ranging from 3.172 to 3.264 Å).[13] Again, the observed shift of the signals of the involved aromatic hydrogen atoms in the corresponding ^{1}H NMR spectrum may be ascribed to these intramolecular interactions.

In conclusion, fluorescent solid 5-pyridylimidazobenzothiadiazole receptor **1**, which displays a noticeable solvatofluorochromism, behaves as an ion-pair receptor either in solution or in the solid state. The solvent-free prepared solid [**1**$_2$·Cd(AcO)$_2$] and [**1**·Zn(AcO)$_2$] complexes show a remarkable different fluorescent behavior both in solution and solid state, which allows the discrimination between them. In addition, formation of the ion-pair complexes in solution, which also displayed solvatofluorochromism, allows the selective extraction of the Zn^{2+} salt in the presence of the Cd^{2+}salt either by a chloroform or diethyl ether solution of the receptor. Whereas the Zn^{2+} complex can be viewed as a ligand-separated AcO−**1**−Zn(OAc) ion-pair complex, our calculations showed that the Cd^{2+} counterpart can be considered as a contact **1**−Cd(OAc)$_2$−**1** ion-pair complex. Moreover, within this structural motif, significant features such as strong fluorescence in solution and in solid state and unusually large Stoke shifts are observed. These properties qualify these ion-pair complexes as multifunctional fluorophores that can also be employed for the future development of luminescent displays and light sources.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section. Synthesis, NMR, and titration data. Cartesian coordinates for all computed structures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b00895.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by MINECO-Spain (Project CTQ 2011/27175, CTQ-2013-44303-P) and European FEDER. M.A. thanks MICINN for a predoctoral grant.

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(9) The cations tested were Li^+, K^+, Mg^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} (added as perchlorate salts) and Na^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, and Hg^{2+} (added as triflate salts). The anions tested were F^-, Cl^-, Br^-, AcO^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$, added as tetrabutylammonium salts.

(10) *Specfit/32 Global Analysis System*, version 3.0.36 for 32-bit Windows Systems, 1999−2004 Spectrum Software Associates (SpecSoft@compuserve.com) acquired from Bio-logic, SA (www.bio-logic.info) in January 2005.

(11) When the experiments were carried in CD_3CN, the addition of these cations promoted a remarkable downfield shift of all the signals, and the ion-pair complexes displayed a set of signals similar to those found in DMSO-d_6.

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DOI: 10.1021/acs.orglett.5b00895
Org. Lett. XXXX, XXX, XXX−XXX