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## A supramolecular H-bond driven light switch sensor for small anions†

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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**A cationic iridium complex with a 2, 2'-bibenzimidazole ligand can act as luminescent sensor for various anions. Strong H-bond supported ion pair bonding with an electron accepting dinitrobenzoate anion switches the luminescence "off". The luminescence of the sensor is switched back "on" when benzoate is replaced by competing H-bonded small anions, therefore leading to enhanced sensitivity of the sensor system.**

Due to their essential roles in biological, environmental and chemical processes, the development of specific phosphorescent sensors for the efficient detection of ions is an important subject in the field of supramolecular chemistry.<sup>1–7</sup> Among the numerous designs of anion receptors, the incorporation of luminescent chromophores into a receptor which are sensitive to interactions between the host and guest molecules, has gained increased attention due to their low detection limit and high sensitivity.<sup>8–14</sup> The advantage of luminescence-based sensors is the high sensitivity of luminescence detection compared to other spectroscopic methods.<sup>2</sup> For anion receptors based on hydrogen bonding interactions, various organic compounds with the polarized N-H functional group, such as pyrrole, imidazole, urea, sulfonamide, amide, and thiourea moieties, are capable of providing a hydrogen bonding function to certain anions.<sup>2</sup> For ruthenium complexes various imidazole type sensor systems are known that can be used as anion sensor systems.<sup>1,2,15–24</sup> Further, supramolecular architectures on bibenzimidazole basis are known.<sup>25</sup> Therefore, we reasoned that d<sup>6</sup> metal complexes of 2,2'-bibenzimidazole (BBI-H<sub>2</sub>) would also be particularly interesting candidates. Prior spectroscopic studies on iridium complexes with imidazole type ligands indicated that they provide numerous preferable properties: (a) the MLCT excited states of these molecules are emissive and long-lived (IrBBI-H<sub>2</sub>: 44 ns in air equilibrated chloroform; [Ir(Meppy)<sub>2</sub>Biim]<sup>+</sup> (Biim = biimidazole, ppy = phenylpyridine, R1): 1.2

μs in deoxygenated dichloromethane), (b) in the excited state the metal complexes become a potent electron donor, (c) the optical emission spectra of the complexes correspond to the protonation state of the 2,2'-bibenzimidazole ligand and Ir(BBI)-H<sub>x</sub> (X = 0, 1, 2) shows strong protonation state dependent luminescence in all three protonation states.<sup>26,27</sup>

We showed elsewhere that the photophysics of the complex IrBBI-H<sub>2</sub> can be influenced by hydrogen bonds in the ligand periphery. Systematic studies on this system revealed that IrBBI-H<sub>2</sub> is a convenient hydrogen bond donor for various anions under aerobic conditions like fluoride, bromide or iodide. Strong bonding interactions between the weakly basic anions and the complex, and a virtually stoichiometric reaction to their respective ion pair is generally observed. However, recognition of the H-bonded ion pair is possible merely through a luminescence increase from an already strongly

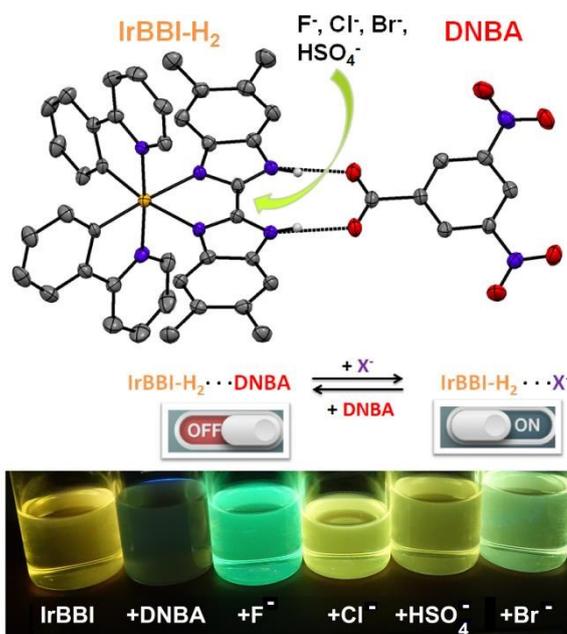
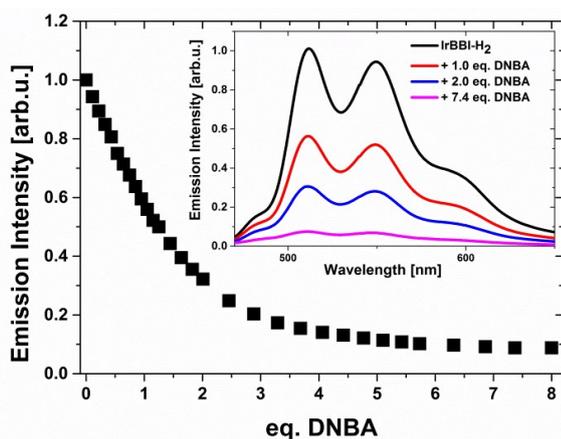


Fig. 1 Top: Scheme of the luminescent On/Off sensor for anions, bottom: picture of the different solutions of IrBBI in chloroform and excess anions.

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† Electronic Supplementary Information (ESI†) available: Experimental procedures, spectral and analytical data, determination of association constants, crystallographic data for IrBBI-H<sub>2</sub><sup>+</sup>-DNBA<sup>-</sup>. See DOI: 10.1039/x0xx00000x

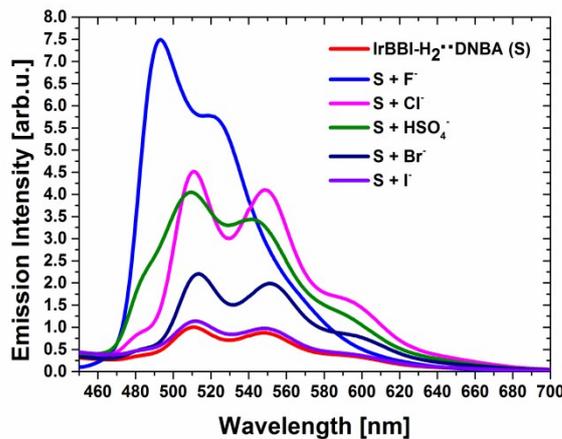
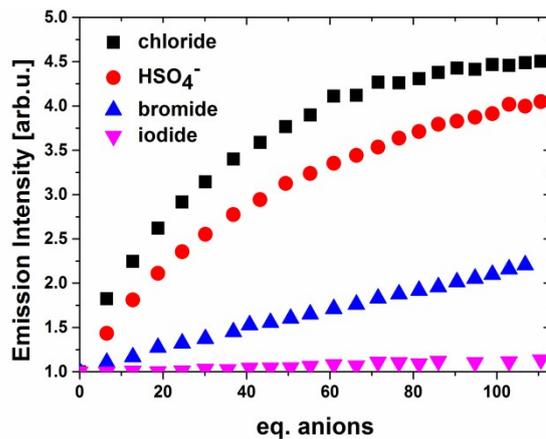


**Fig. 2** Main: plot of the normalized iridium luminescence intensity as a function of number of equivalents of DNBA added; Inset: luminescence of IrBBI-H<sub>2</sub> as a function of increasing amounts of DNBA (one measurement of three, average can be found in ESI<sup>†</sup>).

fluorescent pristine chromophore (i.e. its PF<sub>6</sub> salt).<sup>28</sup> Therefore, we have developed an off-switch strategy to enhance the sensitivity of the iridium (III) bibenzimidazole system, employing the proton coupled electron transfer (PCET) quenching mechanism described by Nocera et al. and Wenger et al. The 3,5-dinitro benzoate anion (DNBA) was employed accordingly, in order to efficiently quench the luminescent excited state of IrBBI-H<sub>2</sub> virtually switching its luminescence “off” in the first place.<sup>26,29,30</sup> The expected H-bond ion pairing of IrBBI-H<sub>2</sub><sup>+</sup>⋯DNBA<sup>-</sup> was observed in the crystal structure of the donor–acceptor couple (Fig. 1, top). The N⋯O distances of 2.690(3) and 2.616(3) Å are comparable to the values reported for **R1** (2.632(4) Å, 2.640(4) Å)<sup>26</sup> and sparsely shorter than those previously observed in ion pairs of similar complex salts.<sup>31–33</sup>

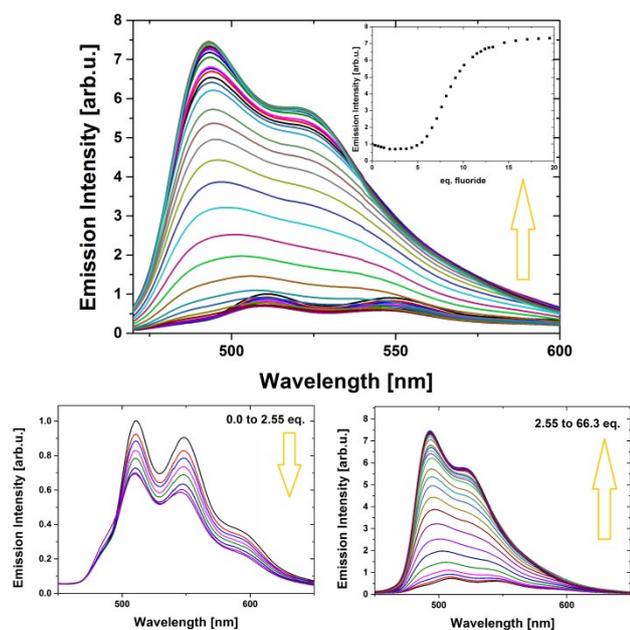
The formation of hydrogen-bonded IrBBI-H<sub>2</sub><sup>+</sup>⋯DNBA<sup>-</sup> pairs in solution can further be observed *via* <sup>1</sup>H NMR experiments. A shift of the N-H signals directly involved in the salt bridge as well as the shift of H-7'' and H4'' and weaker H3' (ESI<sup>†</sup>) can be observed in chloroform, or dichloromethane, when benzoate is added to a solution of the iridium complex (ESI<sup>†</sup>). Interestingly, the N-H signal in chloroform vanishes completely after addition of one equivalent of benzoate and in DCM it is virtually not visible, therefore no direct calculation of an association constant was possible.

As reported previously, the luminescence spectrum upon photoexcitation of IrBBI-H<sub>2</sub> at 378 nm in chloroform shows two characteristic band maxima.<sup>28</sup> In the PF<sub>6</sub> salt of IrBBI-H<sub>2</sub> this emission has a lifetime of 44 ns in air equilibrated chloroform solution<sup>27</sup>, which is indicative of an emissive excited state that has a mixed MLCT and π–π\* intraligand (IL) character as observed for many other cyclometalated Ir complexes.<sup>26,34–40</sup>



**Fig. 3** Top: plot of the normalized luminescence intensity of IrBBI-H<sub>2</sub>⋯DNBA (S) as a function of number of equivalents anions added; bottom: luminescence intensity of IrBBI-H<sub>2</sub>⋯DNBA with 110 eq. of each anion.

As seen from Fig. 2, addition of DNBA leads to a dramatic decrease of the iridium luminescence intensity (black squares) due to oxidative quenching of the MLCT/IL state by DNBA anion as reported for **R1**.<sup>26</sup> Approximately 50% of the luminescence intensity of the PF<sub>6</sub> salt of IrBBI-H<sub>2</sub> is quenched upon addition of the first equivalent of DNBA and after 7 eq. saturation of the quenching kinetics is observed at about 8% residual luminescence, which has been defined within this work as “off” state. In contrast, control experiments with [Ir(ppy)<sub>2</sub>(bipy)]<sup>+</sup> (bipy = bipyridine; **R2**) show only weak oxidative quenching of **R2** by DNBA down to 53 % upon addition of 7 eq., the respective kinetics indicating an ordinary bimolecular quenching mechanism due to the lack of H-bonds (see ESI<sup>†</sup>).<sup>26</sup> Accordingly, two effects must be taken into account for this, i.e. (i) the formation of tightly bound IrBBI-H<sub>2</sub><sup>+</sup>⋯DNBA<sup>-</sup> ion pairs as observed in the solid state, and (ii) efficient electron transfer from the excited iridium complex within the ion pair due to the spatial preorganization.<sup>26</sup>



**Fig. 4** Luminescence of IrBBI-H<sub>2</sub><sup>+</sup>...DNBA<sup>-</sup> (S) as a function of increasing amounts of fluoride (depicted is each only one of at least two distinct measurements); inset: plot of the normalized IrBBI-H<sub>2</sub><sup>+</sup>...DNBA<sup>-</sup> luminescence intensity as a function of number of equivalents of anions added.

Titration experiments of the IrBBI-H<sub>2</sub><sup>+</sup>...DNBA<sup>-</sup> (active sensor, S) system were carried out with five different anions which are, in principle, able to replace DNBA as H-bond acceptor from the IrBBI-H<sub>2</sub>-DNBA ion pair and therefore switch the luminescence of the chromophore back "on". (Fig. 3 and Fig. 4). As expected, all anions cause a significant change in the luminescence intensity of the IrBBI-H<sub>2</sub><sup>+</sup>...DNBA<sup>-</sup> system. That is an increase of 750 % (fluoride), 450 % (chloride), 405 % (hydrogen sulfate), 220 % (bromide) and the weakest effect of 118 % upon titration with iodide (Fig. 3 and Fig. 4). Two general mechanisms need to be distinguished here, that is on the one hand (i) deprotonation of the acidic secondary amine functions of the cationic iridium complex by the basic fluoride ions. This is characterized by the hypsochromic shift and change of the vibronic structure of the emission spectrum. This mechanism has the strongest effect, as it has been reported elsewhere that the fully deprotonated complex IrBBI<sup>-</sup> exhibits stronger luminescence as compared to the pristine protonated PF<sub>6</sub> salt.<sup>27</sup> Also, due to the negative charge of the latter complex, electrostatic repulsion additionally inhibits collision induced quenching by the DNBA anion in solution. On the other hand (ii) the weakly basic anions Cl<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> establish competing H-bonds, whereas the general capability to replace DNBA nicely corresponds with the basicity of the anions. Accordingly, strong effects were observed with Cl<sup>-</sup> and HSO<sub>4</sub><sup>-</sup>, whereas Br<sup>-</sup> and lastly I<sup>-</sup> only show a slightly minor effect. Remarkably, the intensity of hydrogen bonded complexes of chloride and hydrogen sulfate is comparable to the value of the R2...DNBA interaction, indicating that residual luminescence quenching corresponds predominantly with collision induced reaction between an anion stabilized IrBBIH<sub>2</sub><sup>+</sup>-X<sup>-</sup> ion pair and DNBA.

Generally, the final curve shape after the titration experiment correlated to fluoride interaction with IrBBI-H<sub>2</sub><sup>+</sup>...DNBA<sup>-</sup> resembles the twofold deprotonated species IrBBI<sup>-</sup>, whereas the structured emission of the other ions is characteristic for

**Table 1** Associations constants (K<sub>a</sub>) of IrBBI-H<sub>2</sub>-X interaction.

Anion	Fluoride	Chloride	Hydrogen sulfate	Bromide	Iodide
K <sub>a</sub> (M <sup>-1</sup> )	n. d.*	33195 (1232)	17804 (283)	1572 (328)	n. d.*

\* n. d. = not determined

the fully protonated species of IrBBI-H<sub>2</sub>. Association constants (K<sub>a</sub>) between IrBBI-H<sub>2</sub> in the presence of 6.86 eq. DNBA and the investigated anions were determined for a 1 : 1 complex model (chloride: K<sub>a</sub>(M<sup>-1</sup>) = 33195 (1232), hydrogen sulfate: K<sub>a</sub>(M<sup>-1</sup>) = 17804 (283), bromide: K<sub>a</sub>(M<sup>-1</sup>) = 1572 (328)). This quantitative affinity trend for IrBBI-H<sub>2</sub> follows that of a simple biimidazole type metal complex and corresponds to the decreasing basicity in a group of the PSE. For the HSO<sub>4</sub><sup>-</sup> ion, additional stabilization through the formation of a Y-shaped H-bond framework should be taken into account.

In order to check for selectivity between the different anions, a titration experiment with a mixture of the different anions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, reading an identical ionic strength as for the individual anions) was carried out. Fluoride anions were excluded, as they deprotonate the sensor system. The anion mixture also causes a significant change in the luminescence intensity of the quenched IrBBI-H<sub>2</sub><sup>+</sup>...DNBA<sup>-</sup> system and reaches a maximum of 214 % of the initial luminescence intensity (ESI<sup>+</sup>). As the diverse binding behavior is predominately dependent on the different basicity of the investigated anions, selectivity was not observed.

In order to gain selectivity, spatial confinement of the H-bond framework through introduction of substituents in the 7,7'-positions is suggested as target of ongoing research.<sup>41</sup>

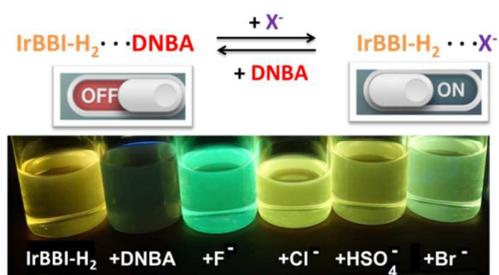
In conclusion, the present results demonstrate that an iridium complex with a 2,2'-bibenzimidazole ligand forms hydrogen-bonded 1 : 1 adducts with 3,5-dinitro-benzoate anions. Due to oxidative quenching, the latter anion acts as an off-switch of the otherwise strongly luminescent iridium complex, providing a significant sensitivity enhancement of IrBBI-H<sub>2</sub> towards selected anions.

Subsequently, the presented system exceeds to the best of our knowledge all ruthenium(II) biimidazole-type sensors known in literature so far, regarding an increase in luminescence intensity of e.g. 450 % for chloride and as the change in luminescence intensity can easily be followed with the naked eye.

Financial support by the Carl Zeiss Stiftung by means of a PhD scholarship (to D. S.) is thankfully acknowledged.

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A new, strongly luminescent iridium(III) bibenzimidazole anion sensor system based on an H-bond driven light switch is presented.