Selective interaction of N,N-bis(aminobenzyl)naphthalenediimides with fluoride anion


Abstract

In this work, the optical properties of N,N-bis(aminobenzyl)naphthalenediimides 2a–2d (BzNDIs) and their interaction with fluoride were studied. The results demonstrated that the amino group position in the benzyl substituent exerts an effect in the absorption and emission properties. Particularly, the N,N-bis(2-aminobenzyl)NDI 2b presented non-typical absorption and emission bands which indicate an intramolecular charge transfer from the amino phenyl group to the NDI core. As the concentration of 2b increases, the solution turns from colourless to a pale orange colour. The interaction of BzNDIs 2a–2d with anions was selective towards fluoride and the affinity was in the order para > ortho > meta with respect to the position of the amino group in the aminophenyl ring. Interestingly, the colour change in the solution of 2b upon addition of fluoride makes it a good candidate for a fluoride colorimetric detection. The voltammetry analysis indicates the ability of these molecules to accept two electrons, in consequence the interaction of two fluoride anions with the BzNDIs was observed.

Introduction

The interest of the scientific community in the supramolecular chemistry has been exponentially growing since the 1990s. For this reason, new aromatic molecules with standing spectroscopic, electronic and redox properties have been investigated. 1,4,5,8-Naphthalenediimides (NDIs) have been extensively studied because of their planar structure, high melting points, thermic resistance, neutrality, electron withdrawing character, redox properties and their capability of auto-organisation (1). Their versatile functionalisation in the imide group as well as the naphthalene core allows the preparation of a variety of NDI analogues with different physicochemical properties and applications (2).

NDIs represent an important class of organic compounds due to their unique physicochemical properties, and their use in materials research as n o p type semiconductors in electron transfer systems (3–6), and as dyes (7) or photosensitisers in solar cells (8). In the supramolecular chemistry field, several pH chemosensors (9), DNA intercalators (10, 11) and anion receptors (12) have been designed based in a NDI core structure.

The anion–π interactions are very important in the anion recognition because of many of the complexes are based in weak interactions which do not disturb the electronic and optical properties of the π-acceptors (13). NDIs are capable of interact with anions as fluoride and several chemosensors with detection purposes have been studied.

The strength of the anion–π interaction of NDIs depends of several factors, such the anion's ability to donate electrons (Lewis basicity) and the ability of NDI to accept the electrons (π acidity). The mechanisms of this interaction...
may be a charge transfer (CT), an electron transfer (ET) with strong anions and a photoinduced electron transfer (PET) with weak anions (12, 14–16).

Also, there are reports of the interaction between NDI units under specific conditions, where 'sandwich' type species are formed. These species are recognised because they have particular photophysical properties as an emission band shifted to higher wavelengths similar to an intermolecular excimer and/or exciplex (16–18).

Fluoride is present in drinking water and it may positively affect the human health at low concentrations (<1.0 ppm). This anion improves the tooth enamel chemical structure and prevents dental cavities reducing the micro-organism’s population and also it helps in the osteoporosis prevention. However, high concentration of fluoride (>1.5–2 ppm) may cause dental fluorosis and osteoporosis. The control of fluoride concentration in water still being an important health issue and more sensitive and selective fluoride chemosensors are desire for this purpose (19).

In this work, were synthesised a series of new N,N-dibenzylamino-1,4,5,8-naphthalenediimides (BzNDI) and their interaction with different anions was studied. A selective response was found with fluoride anion under reduction pressure and the solid was washed with petroleum ether, ethyl ether and ethyl acetate to obtain the corresponding N,N-dibenzynaphthalenediimide.

**Synthesis**

For the synthesis of N,N-dibenzyl-1,4,5,8-naphthalenediimides (2a–2d) in a round bottom flask was charged 1,4,5,8-naphthalenetetracarboxylic dianhydride (1) (0.37 mmol) in 40 mL of THF, after this time the benzylamine (0.74 mmol) was added and left to react for 3 h at 80 °C in constant stirring. Finally, the solvent was removed under reduce pressure and the solid was washed with petroleum ether, ethyl ether and ethyl acetate to obtain the corresponding N,N-dibenzylnaphthalenediimide.

N,N-dibenzyl-1,4,5,8-naphthalenediimide (2a). Brown solid (0.18 g, 0.40 mmol, >99.9%). Mp 241–243 °C. FTIR: 3032, 2835, 1701, 1660, 1243 cm⁻¹. 1H NMR (400 MHz, DMSO-d6): δ 8.23 (s, 4H), 7.41 (d, J = 7.1 Hz, 4H), 7.32 (m, 4H), 7.26 (m, 2H), 5.23 (s, 4H). MS(EI) m/z: 446.1 (M⁺, 100), 91.0 (25), 312.1 (20), 340.0 (30). HRMS (FAB⁺): Calculated for C28H21N4O4: 477.1563. Found: 477.1582. TGA: T_d = 255 °C.

N,N-bis(2-aminobenzyl)-1,4,5,8-naphthalenediimide (2b). Red solid (0.158 g, 0.33 mmol, 89% yield). Mp 140–142 °C. FTIR: 3413, 3344, 3002, 1692, 1651, 1323, 1242 cm⁻¹. 1H NMR (400 MHz, DMSO-d6): δ 8.87 (s, 4H), 6.96 (t, J = 7.4 Hz, 4H), 6.69 (d, J = 7.7 Hz, 2H), 6.45 (dd, J = 7.0 Hz, 2H), 5.19 (s, 4H), 5.12 (s, 4H). MS(EI) m/z: 476.1 (M⁺, 100), 106.0 (30), 249.0 (10). HRMS (FAB⁺): Calculated for C28H21N4O4: 477.1563. Found: 477.1535. TGA: T_d = 305 °C.

N,N-bis(3-aminobenzyl)-1,4,5,8-naphthalenediimide (2c). Purple solid (0.076 g, 0.16 mmol, 43%). Mp 270–272 °C. FTIR: 3453, 3367, 3088, 3002, 1699, 1653, 1243 cm⁻¹. 1H NMR (400 MHz, DMSO-d6): δ 8.87 (s, 4H), 6.94 (t, J = 7.7 Hz, 2H), 6.54 (m, 4H), 6.43 (d, J = 8.0 Hz, 2H), 5.75 (s, 4H), 5.15 (s, 4H). MS(EI) m/z: 476.1 (M⁺, 15), 171.0 (100), 352.0 (45). HRMS (FAB⁺): Calculated for C28H19N2O4: 447.1345. Found: 447.1320. TGA: T_d = 255 °C.

N,N-bis(4-aminobenzyl)-1,4,5,8-naphthalenediimide (2d). Purple solid (0.18 g, 0.34 mmol, 90%). Mp 305–306 °C. FTIR: 3416, 3332, 3040, 1698, 1662, 1242 cm⁻¹. 1H NMR (400 MHz, DMSO-d6): δ 8.64 (s, 4H), 7.11 (d, J = 8.0 Hz, 4H), 6.49 (d, J = 8.0 Hz, 4H), 5.75 (s, 4H), 5.08 (s, 4H). MS(EI) m/z: 476.2 (M⁺, 80), 106.1 (100), 249.1 (10), 371.2 (35). HRMS (FAB⁺): Calculated for C28H19N2O4: 447.1563. Found: 447.1482. TGA: T_d = 205 °C.

**Experimental section**

**Reagents**

Chemicals were purchased from Aldrich and used as received without further purification. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (C₁₄H₄O₄), Benzylamine, 2-Aminobenzylamine (C₇H₇N₂), 3-Aminobenzylamine (C₇H₈N₂), 4-Aminobenzylamine (C₇H₈N₂), Tetrahydrofuran (C₄H₈O), Dimethylsulphoxide (C₆H₅SO), Ethyl ether (C₄H₆O), Petroleum ether, Ethyl acetate (C₄H₆O₂).

**Instruments**

1H NMR spectra were measured in DMSO-d₆ with TMS as internal standard, on a Bruker Avance 400 MHz spectrometer. Electron impact mass spectrometry (EIMS) was recorder on an Agilent 5975C mass spectrometer and high resolution mass spectra were recorder on a JEOL MStation JM-700 mass spectrometer. FTIR spectra were collected on a Perkin Elmer Spectrum 400 FTIR spectrometer. Melting point was obtained with an Electrothermal apparatus. TGA analysis was performed on a TA Q50 Thermogravimetric analyzer with a heating rate 20 °C/min, on air atmosphere at 60 mL/min from 20 to 700 °C. Absorption spectra were measured on a Cary UV–vis Varian spectrometer, and a UV-2700 spectrophotometer SHIMADZU. Fluorescence emission and excitation spectra were recorded on a Nanolog fluorimeter in solution.

**Procedure for spectroscopic titrations**

The effect of anions upon the absorbance was examined by adding 5 μL of a 0.5 M anion stock solution to a known volume (3 mL) of a 5 × 10⁻⁵ M BzNDI solution. The addition
was limited to 0.045 mL, so that the dilution remained insignificant.

The effect of fluoride upon the fluorescence intensity was examined by adding 5 μL of a 0.5 M fluoride stock solution to a known volume (3 mL) of a 5 × 10⁻⁵ or 1 × 10⁻³ M BzNDI solution, respectively. The addition was limited to 0.045 mL, so that the dilution remained insignificant.

**Voltamperometric analysis**

Voltamograms were obtained in a potentiostat–galvanostat station using Ag/AgCl as reference electrode, Pt as counter electrode and vitreous carbon as working electrode. The solutions of 2a–2d (5 × 10⁻⁵ M, H₂O-DMSO 95:5) were prepared in an electrolytic solution of NaCl (0.1 M).

**Procedure for NMR titrations**

The effect of fluoride over the NMR signals of NDI 2a–2d was examined adding 5 μL of a 0.1 M Bu₄F stock solution to a known volume (0.5 mL) of a 5 × 10⁻³ M solution contained in an NMR tube. The addition was limited to 0.050 mL, so that the dilution remained insignificant.

**Results and discussion**

**Synthesis and characterisation**

The synthesis of BzNDIs 2a–2d from 1,4,5,8-naphthalentetraacrylic acid (1) and benzylamine (a), 2-aminobenzylamine (b), 3-aminobenzylamine (c) and 4-aminobenzyl amine (d) is depicted in Scheme 1. The yields were >99, 89, 43 and 90%, respectively, and all products are colored solids (see Figure S1) with high melting points. Also the products were analysed by TGA in order to evaluate their thermal stability. The T_d were 255 °C for 2a, 154 °C for 2b, 280 °C for 2c and 305 °C for 2d.

The ¹H NMR spectra were obtained in DMSO-d_6 (Figures S2–S5). There are two characteristic signals for these compounds, around 8.6–8.8 ppm appears one singlet corresponding to the naphthalene core hydrogens and around 5.0–5.3 ppm a singlet corresponding to the methylene hydrogens. The rest of signal belongs to the aromatic benzylic hydrogens. The IR spectra showed the symmetric and asymmetric vibrations for imide carbonyls at 1700 and 1660 cm⁻¹. The MS showed molecular ions at 446 amu for 2a and 476 amu for 2b, 2c and 2d. The HRMS confirmed the BzNDIs molecular composition.

**Spectroscopic characterisation**

The optical properties of the BzNDIs were evaluated by UV–vis and fluorescence spectroscopies. The spectra were obtained in different solvents as acetonitrile (ACN), o-dichlorobenzene (ODCB) and dimethylsulphoxide (DMSO) (20). In general, the absorbance of the BzNDIs was grater in DMSO (Figures S6–S8). The UV–vis spectra obtained in DMSO at 5 × 10⁻⁵ M for BzNDIs 2b, 2c and 2d are shown in Figure 1. The BzNDI 2c and 2d present a typical structured band with relative maximum peaks at 347, 365 and 384 nm. This result indicates that the substituents in the imide group does not affect the electric transitions in the NDI core. Interestingly, the spectrum of 2b presents an additional broad band in the visible region with a maximum at 460 nm. This absorption band is interesting because it is non-typical for this NDIs type. The broad band is present even at low solution concentrations (Figure S9). The latter indicates a non-concentration dependence and may be attributed to an intramolecular CT from the ortho amino groups presumably because of their proximity to the NDI core, which is evident from the broad CT band. In addition, the solutions become from colourless to pale orange as the concentration increases (Figure S10).

**Scheme 1.**

![Scheme 1](image-url)
respectively, in a concentration $\geq 5 \times 10^{-4}$ M. These excimer type bands increase their intensity as the concentration and they become predominant at higher concentrations.

Remarkably, the maximum excitation wavelength observed at high concentration is similar to the maximum wavelength for the broad absorption band in UV–vis (Figure 4). The observed concentration dependence of this emission band indicates the possible supramolecular stacking or assembly in the excited state at high concentration due to the planarity of NDI core \((16–18)\).

The geometries of BzNDIs were optimised with the PM6 semiempirical method and then by DFT using a non-local

Moreover, the magnitude of the absorbance ratio $\text{Abs}_{460}/\text{Abs}_{385}$ was in the order ODCB $>$ ACN $>$ DMSO indicating that the polarity of the solvent affect the CT process (Figure 2). This ratio is constant at different concentration and there is a linear dependence of $\text{Abs}_{460}$ respect the concentration in the same solvent (Figure S9).

The emission spectra were obtained at different concentrations in DMSO \((5 \times 10^{-5}, 1 \times 10^{-4}, 5 \times 10^{-4}, 1 \times 10^{-3} \text{ M})\). The BzNDIs presented the typical structured emission bands with a maximum at 440 nm at low concentration (Figure 3). However, the BzNDI 2b showed additional excitation and emission bands at 468 and 605 nm, respectively, in a concentration $\geq 5 \times 10^{-4}$ M. These excimer type bands increase their intensity as the concentration and they become predominant at higher concentrations.

Remarkably, the maximum excitation wavelength observed at high concentration is similar to the maximum wavelength for the broad absorption band in UV–vis (Figure 4). The observed concentration dependence of this emission band indicates the possible supramolecular stacking or assembly in the excited state at high concentration due to the planarity of NDI core \((16–18)\).

The geometries of BzNDIs were optimised with the PM6 semiempirical method and then by DFT using a non-local

Figure 2. (Colour online) Normalised absorption spectra of 2b in ODCB, ACN and DMSO at $5 \times 10^{-5}$ M.

Figure 4. (Colour online) Normalised absorption and excitation bands for 2b in DMSO.

Figure 3. (Colour online) (a) Emission spectra of 2b \((\lambda_{\text{exc}} = 401 \text{ nm})\), 2c \((\lambda_{\text{exc}} = 411 \text{ nm})\) and 2d \((\lambda_{\text{exc}} = 410 \text{ nm})\) at $5 \times 10^{-5} \text{ M}$ in DMSO. (b) Excitation and emission spectra of 2b in DMSO at different concentrations.
correlation B3LYP and a 6-31G+(d,p) basis set in the gas phase with Gaussian 09 computational package (21, 22). First, the structure of BzNDIs 2a–2d was optimised at semi empirical level, and then, a scan calculation was performed by rotation of the nitrogen–carbon bond in the imide and benzylidene from these geometries. The relative minimum energy geometries found for each BzNDI were fully optimised using DFT and then their frequencies were calculated. The molecules presented different spatial arrangements because of the different position of the amino group (Figure 5). In the BzNDIs 2b and 2d benzylidene groups are located in the same side of the NDI plane. Nevertheless, the benzylidene groups are located in opposite position in 2c. Interestingly, in 2b an intramolecular hydrogen bond between the amino and imide carbonyl groups is present. The distance of the hydrogen bond is 1.978 Å.

The intramolecular hydrogen bond is favoured in the less competitive solvents as ODCB and ACN. On the contrary, DMSO strongly competes for the hydrogen bond. These results may indicate that the CT process is assisted by the intramolecular hydrogen bond and therefore also it depends on the solvent.

Study of the interaction with anions

The interaction of BzNDIs 2a–2d with anions was studied by UV–vis spectroscopy under oxygen free experimental conditions (Figure 6). First, the titrations were done with tetrabutylammonium fluoride (TBAF) (0–150 M equivalents) which is known to be the most basic anion. The absorbance of BzNDIs bands (347, 365 and 384 nm)

Figure 5. (Colour online) Optimised geometries of BzNDIs 2a, 2b and 2c by DFT.

Figure 6. (Colour online) UV–vis spectra obtained by titration of BzNDIs 2a (a), 2b (b), 2c (c) and 2d (d) at $5 \times 10^{-5}$ M with TBAF (0–150 equiv) in DMSO.
The formation constants $K$ were calculated from the absorbance profiles at 478 nm (the BzNDI$^-$ radical maximum absorbance peak) using the HypSpec Version 1.1.33 program (see Table 1 and Figures S14–S17). The experimental data of $2a$ fits to a 1:1 and 1:2 complexes model, the values of $K_1 = 40 \pm 1$ M$^{-1}$ and $K_2 = 520 \pm 30$ M$^{-1}$ ($\beta_2 = K_1K_2 = 2.1 \pm 0.2 \times 10^4$ M$^{-2}$) indicate a positive cooperativity of CT from two fluoride anions. It is not possible to estimate the $K_1$ value in $2b$, $2c$ and $2d$ because of the higher cooperativity in the 1:2 complex formation as unique association product. In other words, the BzNDI$^-$ radicals are formed through a BzNDI-2F$^-$ association complexes, but BzNDI$^{2-}$ dianions are not present, the latter is evidenced by the absence of a broad absorption band with a maximum absorption peak at 545 nm ($^{14, 16}$).

The $\beta_2$ values are in agreement with absorbance profiles and show a complex stability order of $2d > 2b > 2c > 2a$.

The interaction of $2b$ was analysed following the emission at 440 nm ($5 \times 10^{-5}$ M) and at 605 nm ($1 \times 10^{-3}$ M). The fluorescence intensity increased in the titration at low concentration of $2b$ with fluoride (0–200 equiv). In the titration at high concentration, the fluorescence intensity decreased and the emission was slightly blue shifted as the fluoride was added (Figure 10). These results visually indicate a selective interaction of $2b$ with fluoride in DMSO (Figure 9).

The absorbance profiles showed that the BzNDIs $2b$–$2d$ strongly interact with fluoride compared with the benzyl NDI $2a$, the amino group in the benzyl moiety has a positive influence in the interaction with the anion. The BzNDI $2b$, $2c$ and $2d$ presented a linear response until 83 M equivalents of fluoride added and there is no change after this point (Figure 7). The sensibility was in the order $2d > 2b > 2c > 2a$.

The UV–vis spectra obtained upon the addition of tetrabutylammonium salts (F$^-$, Cl$^-$, Br$^-$, I$^-$, AcO$^-$ and BzO$^-$) showed that BzNDIs $2a$–$2d$ only interact with fluoride. It means there is selectivity in the response with this anion (Figure 8 and Figures S11–S13).

Table 1. $\beta_2$ values calculated for the association of BzNDIs with F$^-$.  

<table>
<thead>
<tr>
<th>BzNDI</th>
<th>Complex</th>
<th>$\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2a$</td>
<td>$2a$–$2F$</td>
<td>$2.1 \pm 0.2 \times 10^4$ M$^{-2}$</td>
</tr>
<tr>
<td>$2b$</td>
<td>$2b$–$2F$</td>
<td>$2.6 \pm 0.2 \times 10^4$ M$^{-2}$</td>
</tr>
<tr>
<td>$2c$</td>
<td>$2c$–$2F$</td>
<td>$2.1 \pm 0.2 \times 10^4$ M$^{-2}$</td>
</tr>
<tr>
<td>$2d$</td>
<td>$2d$–$2F$</td>
<td>$3.1 \pm 0.4 \times 10^4$ M$^{-2}$</td>
</tr>
</tbody>
</table>

The formation constants $K$ were calculated from the absorbance profiles at 478 nm (the BzNDI$^-$ radical maximum absorbance peak) using the HypSpec Version 1.1.33 program (see Table 1 and Figures S14–S17). The experimental data of $2a$ fits to a 1:1 and 1:2 complexes model, the values of $K_1 = 40 \pm 1$ M$^{-1}$ and $K_2 = 520 \pm 30$ M$^{-1}$ ($\beta_2 = K_1K_2 = 2.1 \pm 0.2 \times 10^4$ M$^{-2}$) indicate a positive cooperativity of CT from two fluoride anions. It is not possible to estimate the $K_1$ value in $2b$, $2c$ and $2d$ because of the higher cooperativity in the 1:2 complex formation as unique association product. In other words, the BzNDI$^-$ radicals are formed through a BzNDI-2F$^-$ association complexes, but BzNDI$^{2-}$ dianions are not present, the latter is evidenced by the absence of a broad absorption band with a maximum absorption peak at 545 nm ($^{14, 16}$).

The $\beta_2$ values are in agreement with absorbance profiles and show a complex stability order of $2d > 2b > 2c > 2a$.

The interaction of $2b$ was analysed following the emission at 440 nm ($5 \times 10^{-5}$ M) and at 605 nm ($1 \times 10^{-3}$ M). The fluorescence intensity increased in the titration at low concentration of $2b$ with fluoride (0–200 equiv). In the titration at high concentration, the fluorescence intensity decreased and the emission was slightly blue shifted as the fluoride was added (Figure 10). These results indicate that the interaction with fluoride disrupts the CT process
and the excimer type emission of the self-assembly species formed at high concentration in the excited state.

The fluorescence data obtained in the titration of 2b with fluoride at $5 \times 10^{-5}$ M fitted to a 1:1 and 1:2 complexes model, but with very low precision. The approximate values of association constants values are $K_1 = 40 \text{ M}^{-1}$ and $K_2 = 7000 \text{ M}^{-1}$ and the value of $\beta_2 = 3 \pm 2 \times 10^5 \text{ M}^{-2}$ is comparable with that obtained by UV–vis under the same experimental conditions. The data obtained by the titration at $1 \times 10^{-3}$ M fitted only with a 1:2 complex model and $\beta_2$ value were $1590 \pm 30 \text{ M}^{-2}$ (Figures S18 and S19). The difference in the $\beta_2$ values also may indicate that two different species are present in the excited state at the different concentrations. The monomeric BzNDI predominates at low concentration and the 'excimer type' supramolecular structures generated by the self-assembly of BzNDIs are predominant at high concentration (18).

In the cyclic voltamperometry analysis of BzNDIs one quasireversible reduction peak was found for 2a and two quasireversible reduction peaks for 2b, 2c and 2d (Figures S20–S23). The CV data indicate the ability of aminobenzyl NDIs to accept two electrons, which favours the association with two fluorides in the complex. Noteworthy, the $\pi$-acidity of the NDI core related with the energy of first reduction peak, which is affected by the position of the amino group in the benzylic group (Table 2). Typically, the aryl napthalenediimides (ArNDIs) present high $\pi$-acidity inducing to a non-selective interaction towards different anions. However, the $\pi$-acidity of BzNDIs is lower and induces to a selective interaction with the most basic anions. The $\pi$-acidity follows the order $2d > 2b > 2a > 2c$.

The interaction of the BzNDIs with fluoride was studied by $^1$H NMR in DMSO-$d_6$ (Figure 11). In the titration spectra,

![Figure 10](image1.png)

**Figure 10.** (Colour online) Emission spectra obtained by titration of 2b with TBAF in DMSO. (a) $[2b] = 5 \times 10^{-5}$ M, $\lambda_{\text{exc}} = 401 \text{ nm}$. (b) $[2b] = 1 \times 10^{-3}$ M, $\lambda_{\text{exc}} = 468 \text{ nm}$.

<table>
<thead>
<tr>
<th>BzNDI</th>
<th>$E_{1\text{red}}$ (mV)</th>
<th>$E_{2\text{red}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>$-531$</td>
<td>$-699$</td>
</tr>
<tr>
<td>2b</td>
<td>$-526$</td>
<td>$-679$</td>
</tr>
<tr>
<td>2c</td>
<td>$-542$</td>
<td>$-679$</td>
</tr>
<tr>
<td>2d</td>
<td>$-491$</td>
<td>$-724$</td>
</tr>
</tbody>
</table>

![Table 2](image2.png)

**Table 2.** BzNDIs redox potentials (vs Ag/AgCl in H$_2$O/DMSO 95:5).

![Figure 11](image3.png)

**Figure 11.** $^1$H NMR spectra obtained in the titration of BzNDI 2b with TBAF. $[2b] = 5 \text{ mM}$. 
it was observed that when the first aliquot was added two singlets at 8.73 and 5.18 ppm disappeared corresponding to the naphthalene \( \alpha \) and methylene \( \gamma \) hydrogens, respectively. The absence of these signal indicates the conversion of naphthalene core into a BzNDI\(^+\) paramagnetic species. The rest of the signals belongs to the aminophenyl group and are broadening as the fluoride is added to the solution. All the signals almost disappear with the addition of two molar equivalents of fluoride. The BzNDI 2a, 2c and 2d have the same behaviour in the titration with fluoride (Figures S24–S26).

**Theoretical calculations**

The HOMO and LUMO molecular orbital were calculated by DFT. In all BzNDIs the HOMO is mainly located in the aminophenyl group and the LUMO is in the NDI core (Figure 12). Normally, the distribution of the HOMO in NDIs where the imide is directly connected to aromatic groups is along the whole molecule and the LUMO is located in the NDI core (12,14). The results obtained by NMR studies respect the interaction with the fluoride are in agreement with the distribution of the HOMO and LUMO in these molecules, where only the signals of the NDI core and methylene group are affected.

**Gap band determination**

The gap band for BzNDIs 2b–2d was determined theoretically with the HOMO and LUMO energies obtained by DFT and experimentally by solid state UV–vis diffuse reflectance using the Kubelka–Munk model for semiconductor materials (23).

\[
E_g = \frac{(1239.84)(m)}{b} - b
\]

where: \( E_g \) = eV, \( m \) = line slope, \( b \) = intersection with the axis.

The gap band values are reported in Table 3 (Figure S27). If the gap band is correlated with the \( \pi \)-acidity of the NDI core, the experimental values are in accordance with the observed affinity to fluoride. The shortest gap band was for 2d and this BzNDI has more affinity to fluoride.

**Conclusions**

The series of BzNDIs were prepared in good yields and high purity in this work. The spectroscopic characterisation showed that the position of the amino group in the benzylic substituent has an influence in their photophysical properties and BzNDI 2b presented a red shifted emission band which depends on the solvent and the solution concentration due to a CT process from the aminobenzyl group to the NDI core. Noteworthy, the \( \pi \)-acidity of the BzNDIs is lower than typical ArNDIs inducing to a selective interaction with the most basic anion fluoride. Also the \( \pi \)-acidity is modulated by the position of the amino group in the benzylic substituent. The interaction with anions resulted in selectivity towards fluoride and the affinity was in the order para > orto > meta according with the UV–vis response profiles and the association constants. Noteworthy, the absorption properties for 2b make it a good candidate for colorimetric determination of fluoride. The \(^1\)H NMR studies demonstrated an electron transfer process from fluoride towards the NDI by detection of paramagnetic species.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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