Electronic Supplementary Material (ESI) for New Journal of Chemistry


# Supplementary Data

## Lewis acidity and sugar receptor activity of 3-aminosubstituted benzoxaboroles and their *ortho*-aminomethylphenylboronic acids analogues

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Table 1. p$K_a$ values of **1**, **2a-c** and **3a-c** determined in three independent experiments

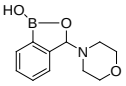
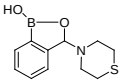
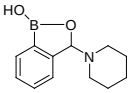
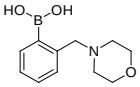
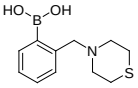
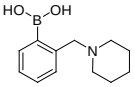
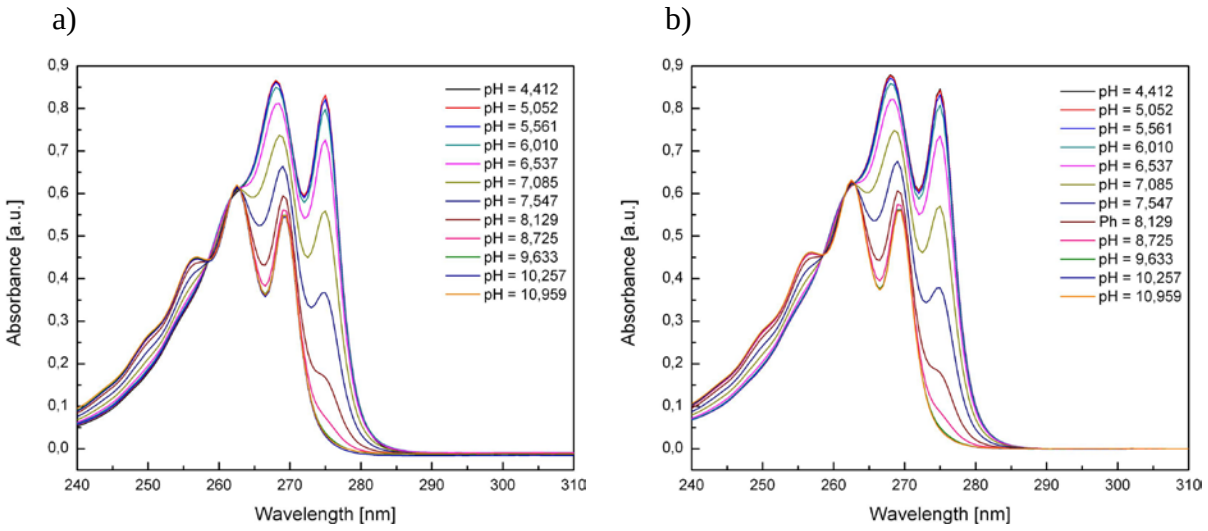
| |  **1** |  **2a** |  **2b** |  **2c** |  **3a** |  **3b** |  **3c** |
|---|---|---|---|---|---|---|---|
| **p$K_{a1}$** | **7,391** | **7,484** | **7,485** | **7,469** | **4,895** | **5,212** | **6,298** |
| **p$K_{a2}$** | **7,387** | **7,480** | **7,326** | **7,376** | **4,943** | **5,134** | **6,371** |
| **p$K_{a3}$** | **----** | **7,219** | **7,324** | **7,335** | **4,965** | **5,252** | **6,350** |
| **p$K_a$** | **7,389** | **7,394** | **7,378** | **7,393** | **4,934** | **5,199** | **6,340** |
| **+ / -** | **0,002** | **0,124** | **0,075** | **0,056** | **0,029** | **0,049** | **0,031** |

Figure 1. Spectral data and p$K_a$ determination; a) UV/vis spectral scans for compounds **1**, **3c** and phenylboronic acid (PBA) in solutions at various pH values; b) Normalized spectral scans (Aborbance$_{310nm}$ = 0); c) Spectral differences between solutions of the compounds under study; d) p$K_a$ plots

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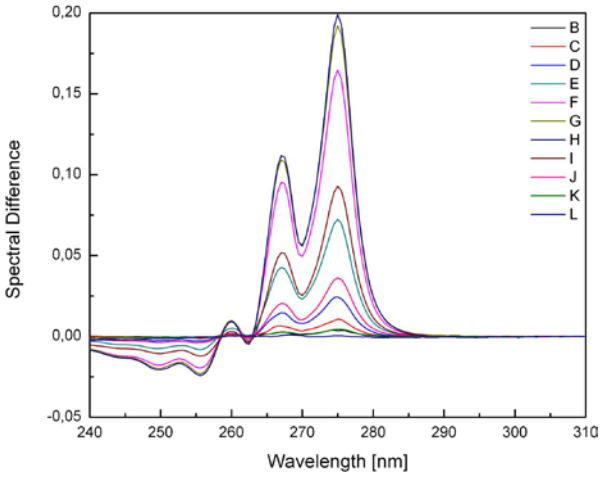
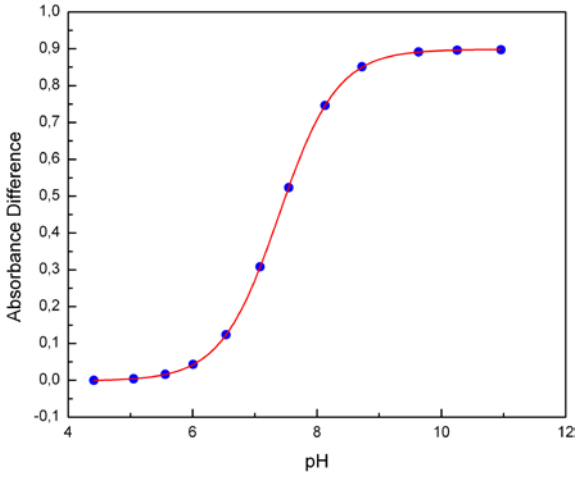
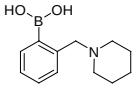
c)

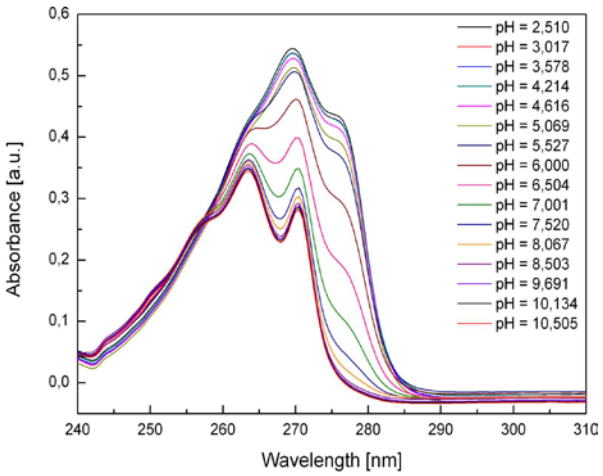



d)

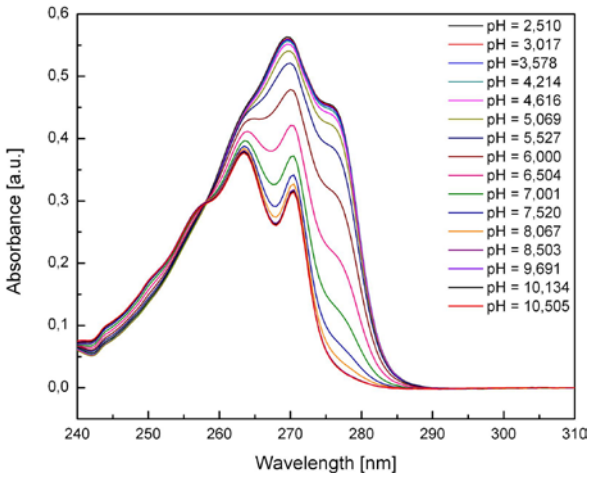


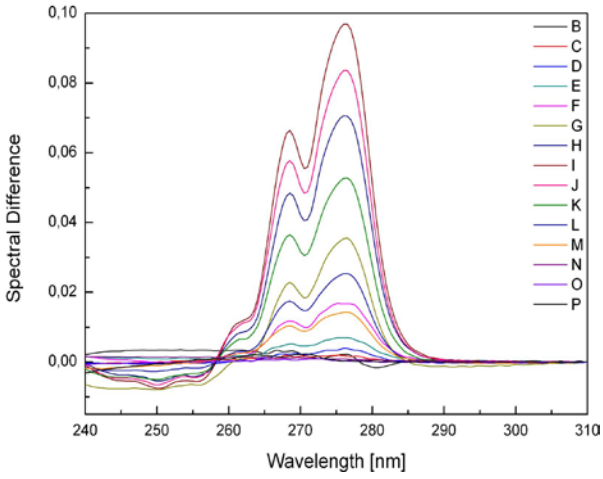

$a_1$)



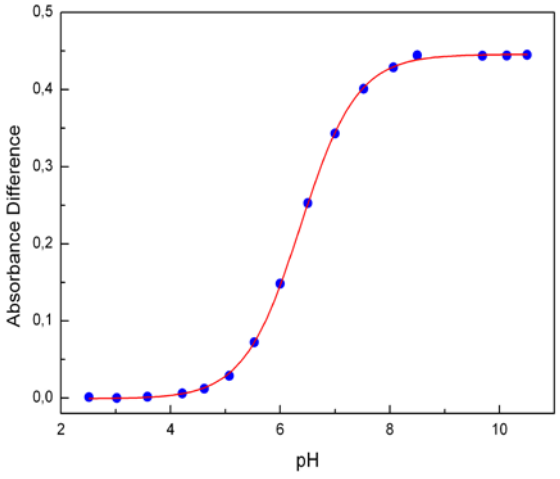

$b_1$)




$c_1$)




$d_1$)



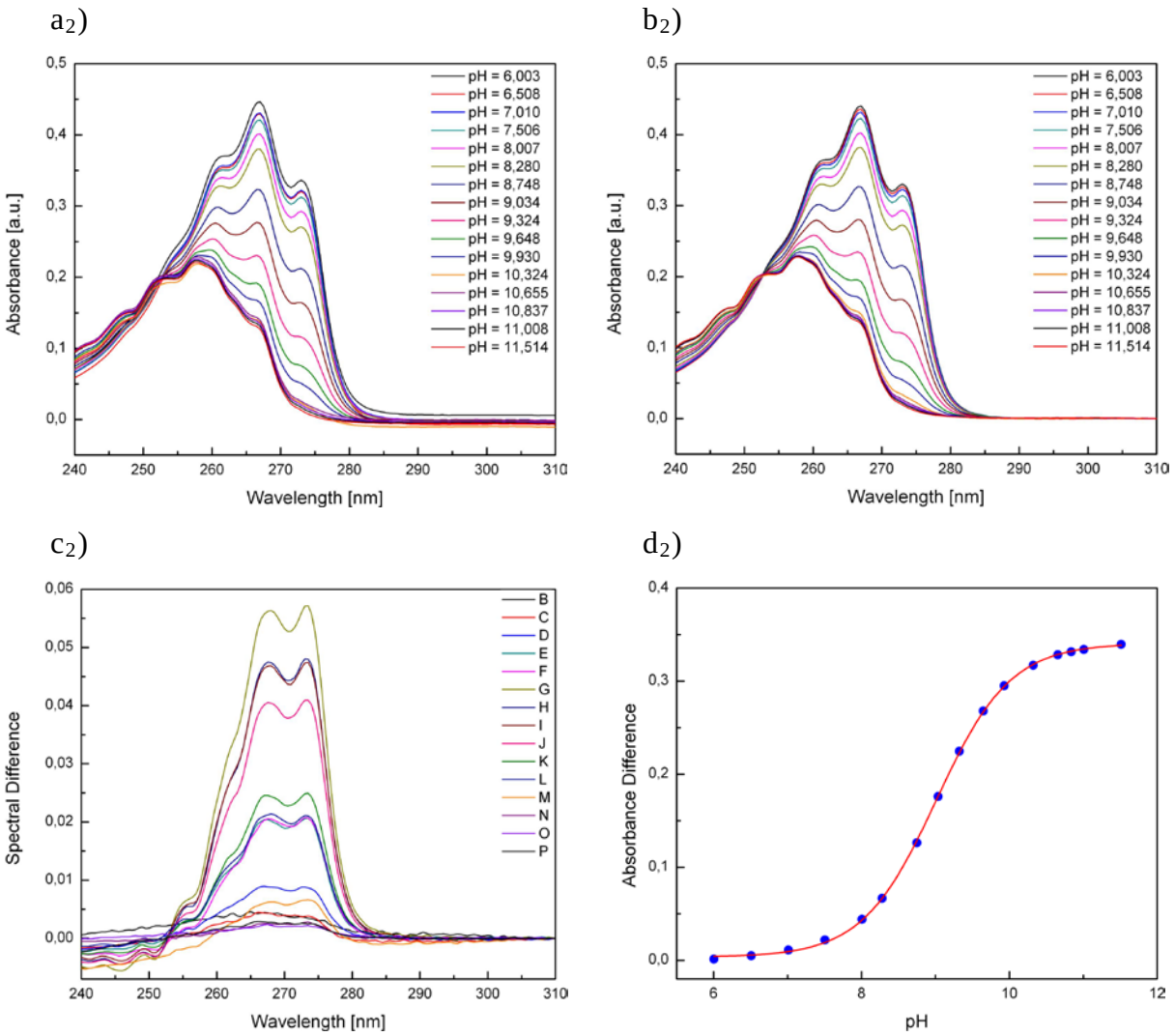



Table 2. The apparent binding constants ($K$ [$M^{-1}$]) of **1**, **2a-c**, **3a-c** with ARS, fructose, galactose and glucose.

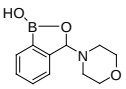
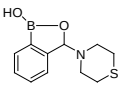
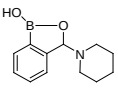
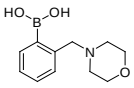
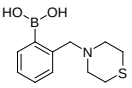
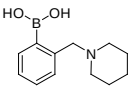
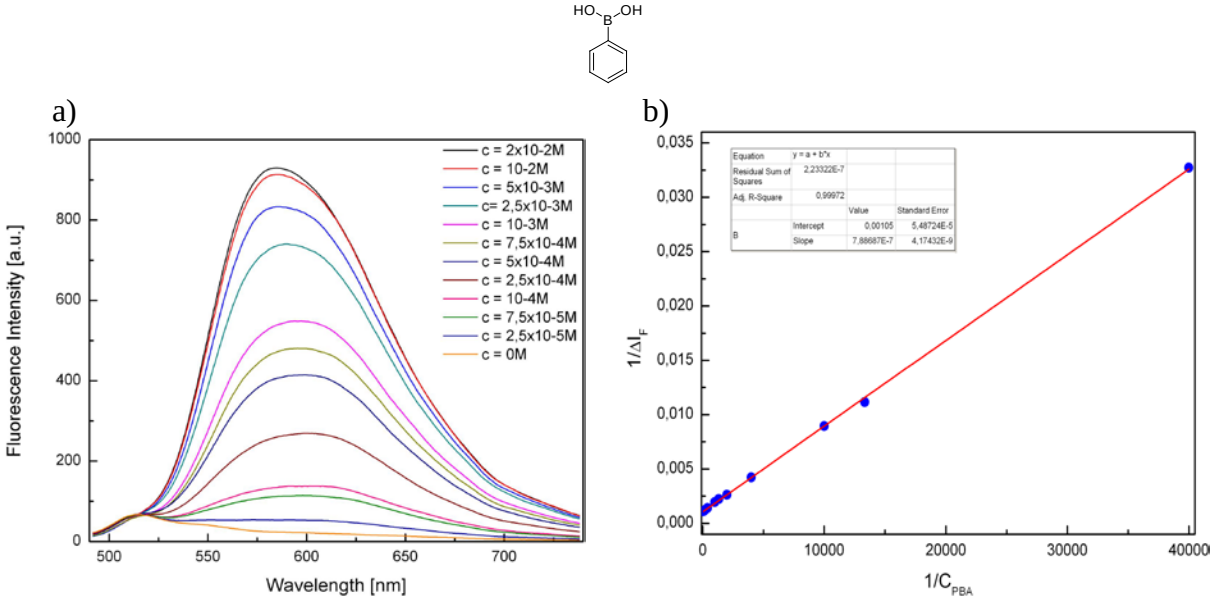
| |  **1** |  **2a** |  **2b** |  **2c** |  **3a**[1] |  **3b**[1] |  **3c** |
|---|---|---|---|---|---|---|---|
| $K_{ARS}$ | 659 | 1750±105 | 2556 | 2315 ± 124 | 2900 ± 120 | 720 ± 40 | 3209 ± 159 |
| $K_{Fru}$ | 50 | 395.8±31.7 | 263 | 930.1 ± 8.9 | 120 ± 30 | 55 ± 4 | 449 ± 12,7 |
| $K_{Gal}$ | 19.1 ± 0.6 | 78.4 ± 12.1 | 17.46 | 58.7 ± 0.2 | 100 ± 20 | 5.7 ± 0.8 | 48.5 ± 15.5 |
| $K_{Glu}$ | 3.9 | 10.05±0.17 | 14.22 | 33.05 ± 1.65 | 13 ±5 | 2.4 ± 0. 9 | 32.10 ± 9.02 |

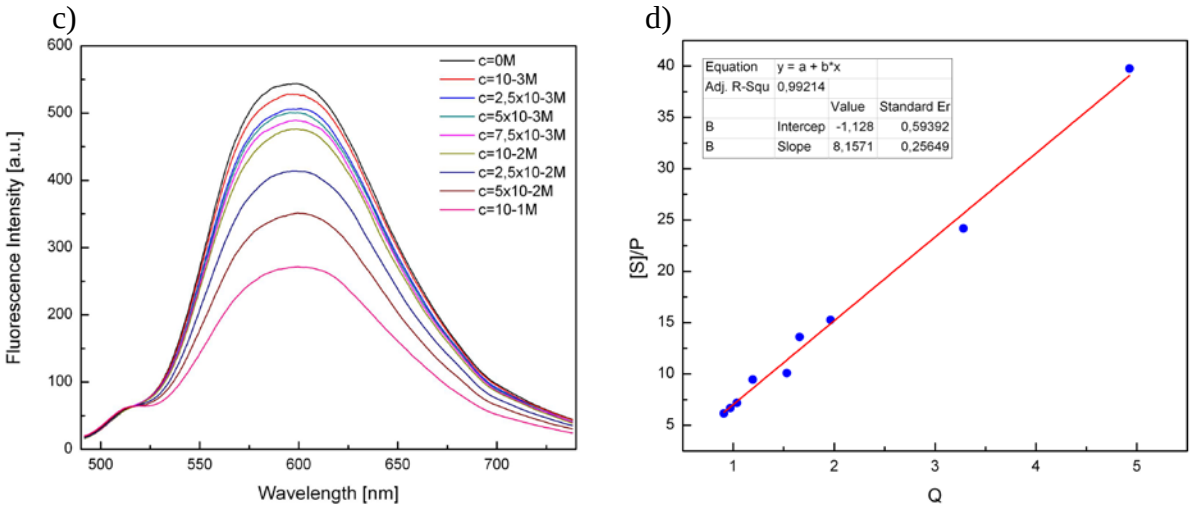
Figure 2) The apparent binding constants determination by ARS method; a) Fluorescence spectrum of ARS at different concentrations of boronic acid; b) $1/\Delta I_F$ versus $1/C_{\text{boronic acid}}$; c) Titration of fructose into a solution of ARS and boronic acid where 20% of ARS is in a free form; d) [S]/P versus Q




Equations for binding constant determination:

$$\frac{1}{\Delta I_F} = (\Delta k p_0 K_{eq1})^{-1} \frac{1}{[C_{boronicacid}]} + (\Delta k p_0 I_0)^{-1}$$

The binding constant of ARS-phenylboronic acid ($K_{ARS}$) is the quotient of the intercept and the slope in a plot of $1/\Delta I_F$ versus $1/C_{\text{phenylboronic acid}}$. We compared value of $K_{ARS}$ =1331$M^{-1}$ (obtained in our lab) to the previously reported[2,3] ($K_{ARS}$=1300$M^{-1}$) to validate our method.



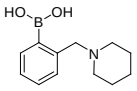

The binding constant of fructose-phenylboronic acid ($K_{FRU}$) is determined by plotting [S]/P versus Q where:

$$P = [L_0] - \frac{1}{QK_{ARS}} - \frac{[I_0]}{Q+1}$$

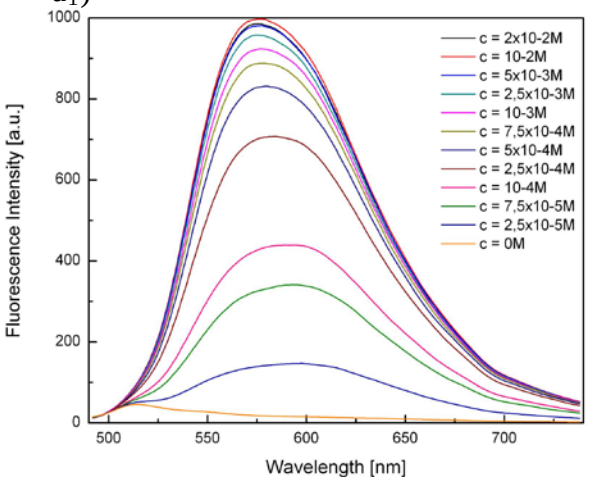
$L_0$ – Total concentration of phenylboronic acid
$I_0$ – Total concentration of ARS
$Q$ – ratio of concentration of free ARS to complexed ARS

The binding constant of fructose-phenylboronic acid ($K_{FRU}$) can be calculated by dividing $K_{ARS}$ by the slope of the plot equation:

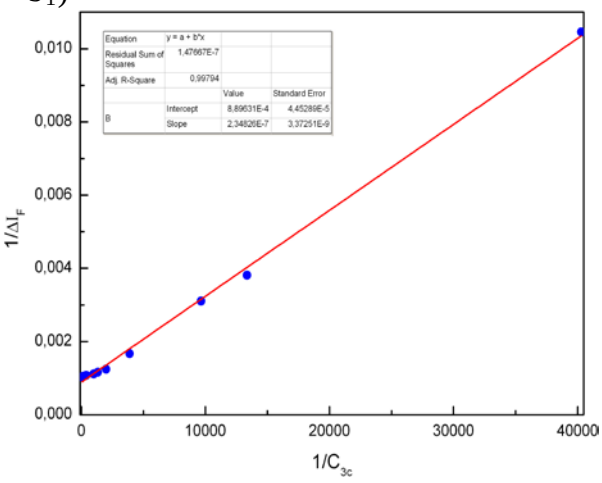
$$\frac{[S_0]}{P} = \frac{K_{ARS}}{K_{FRU}}Q + 1$$ where $[S_0]$ – Total concentration of fructose



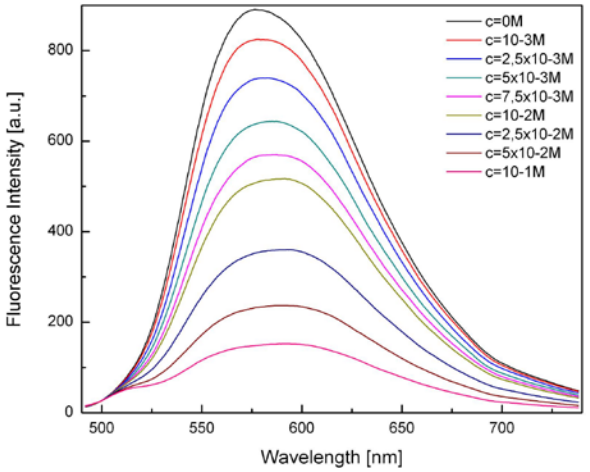

a$_1$)



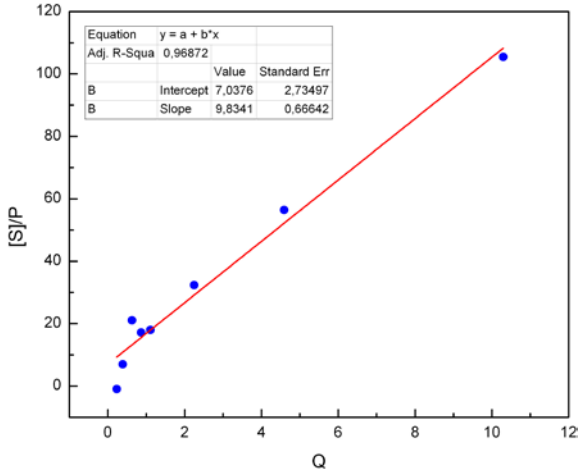

b$_1$)



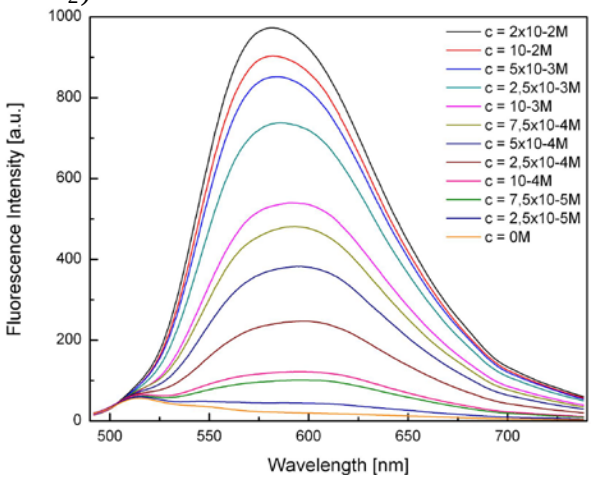

c$_1$)




d$_1$)




a$_2$)

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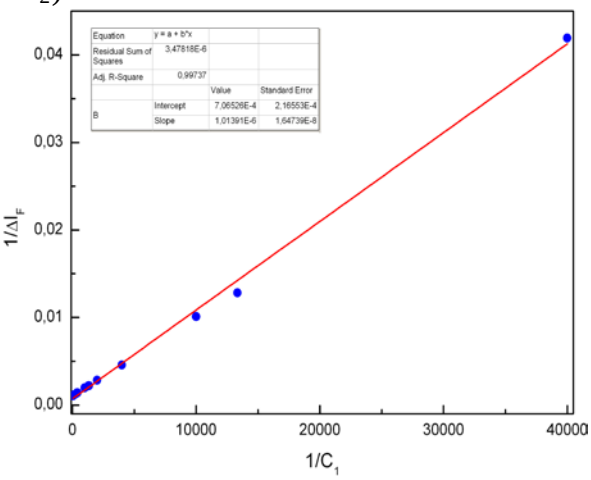


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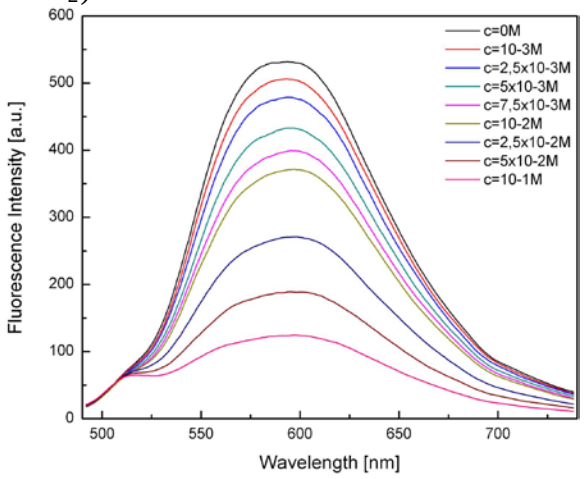
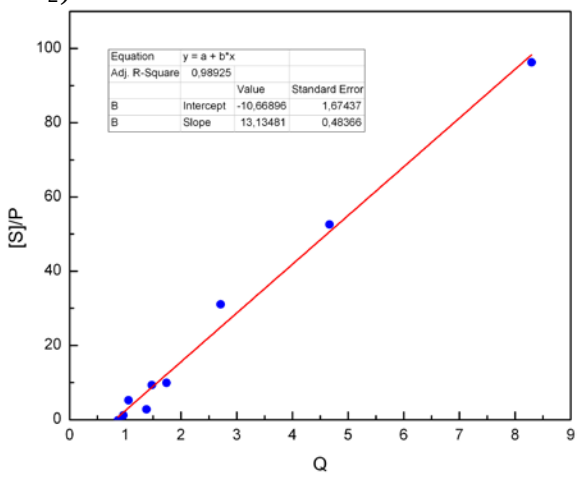
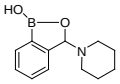
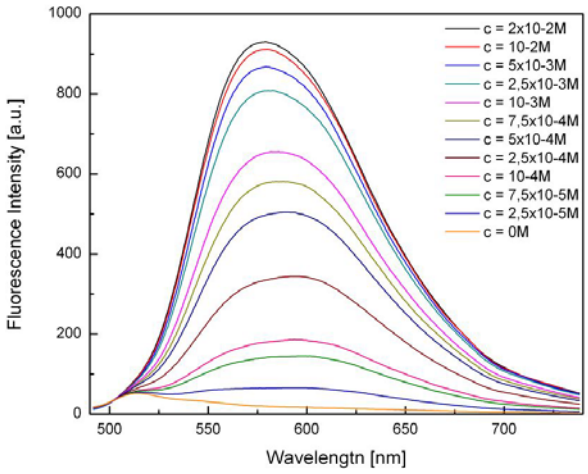



d$_2$)




a$_3$)

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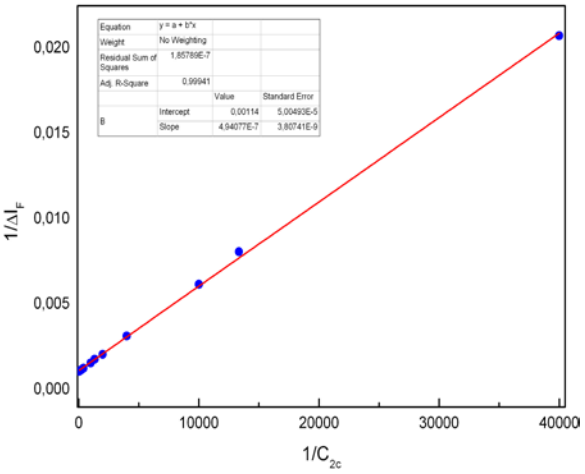
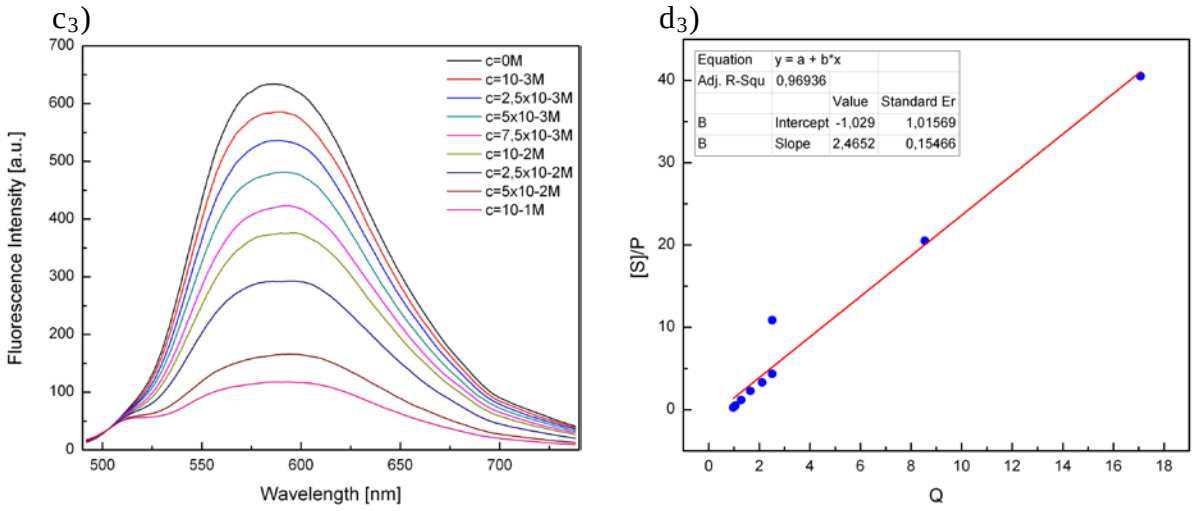
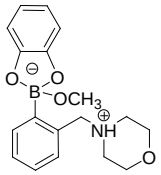





**5a**

Table 3. Selected geometrical parameters for **5a**.

| bond lengths, Å | | bond angles, º | |
|---|---|---|---|
| O1–C12 | 1.3541(15) | C11–N1–C7 | 112.16(9) |
| C1–B1 | 1.6230(17) | C11–N1–C8 | 109.83(9) |
| O1–B1 | 1.5152(15) | C8–N1–C7 | 112.16(9) |
| O3–C10 | 1.4259(15) | C6–C1–B1 | 120.08(10) |
| O3–C9 | 1.4243(15) | C2–C1–B1 | 122.68(10) |
| O4–B1 | 1.4580(15) | O1–B1–C1 | 109.74(9) |
| O4–C18 | 1.4306(15) | O4–B1–O1 | 111.77(10) |
| O2–C13 | 1.3572(15) | O4–B1–O2 | 110.21(9) |
| O2–B1 | 1.5102(15) | O4–B1–C1 | 109.55(9) |
| N1–C11 | 1.4940(15) | O2–B1–O1 | 103.20(9) |
| N1–C7 | 1.5094(15) | O2–B1–C1 | 112.27(9) |
| N1–C8 | 1.4969(15) | N1–C7–C2 | 110.97(9) |
| | | torsion angles, º | |
| C2–C1–B1–O4 | –59.21(14) | C2–C1–B1–O2 | 178.00(10) |
| C1–C2–C7–N1 | 70.77(13) | C11–N1–C7–C2 | 68.01(12) |
| C11–N1–C8–C9 | –55.25(13) | C7–N1–C8–C9 | 179.30(9) |

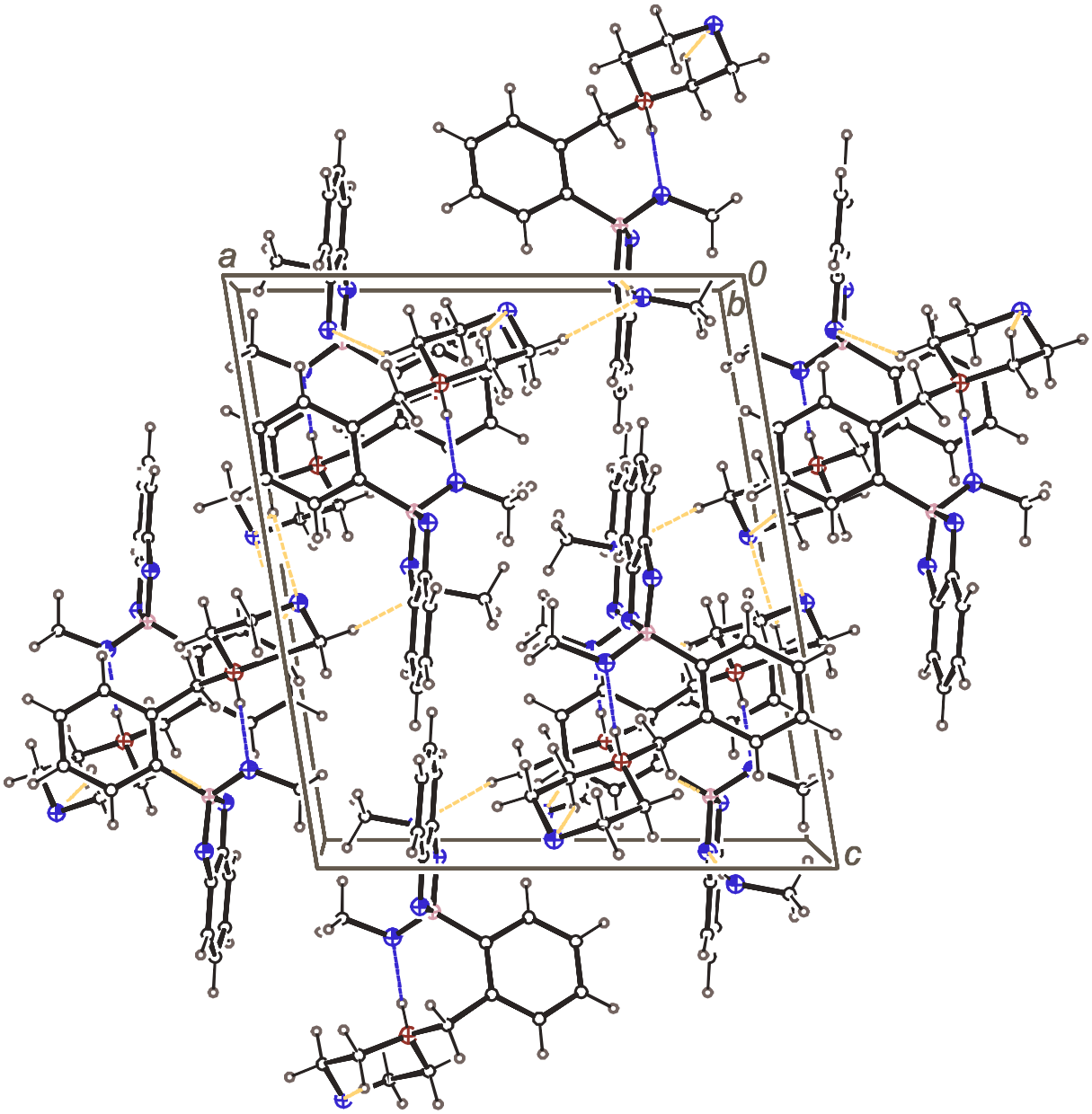
Table 4. Geometry of intra- and intermolecular interactions in **5a** (Å,°).

| | H…A | D…A | D–H…A |
|---|---|---|---|
| N1–H1…O4 | 1.75(2) | 2.6250(13) | 157(2) |
| O5–H5A…O2$^{i}$ | 1.97(2) | 2.7940(14) | 171(2) |
| C8–H8B…O3$^{ii}$ | 2.46 | 3.3787(15) | 154 |
| C11–H11B…O1$^{iii}$ | 2.53 | 3.3267(15) | 138 |
| C17–H17…O5 | 2.56 | 3.3863(17) | 145 |
| C9–H9A…O5$^{iv}$ | 2.57 | 3.2996(17) | 131 |
| C10–H10A…*Cg1*$^{iii\ a}$ | 2.55 | 3.3643(13) | 139 |
| C18–H18B…*Cg1* | 2.62 | 2.8736(14) | 95 |
| C18–H18A…*Cg2*$^{v}$ | 2.80 | 3.4091(14) | 121 |
| C5–H5…*Cg2*$^{vi}$ | 2.96 | 3.8364(13) | 154 |

Symmetry codes: (i) x,–1+y,z; (ii) 1–x,2–y,2–z; (iii) 1/2–x,1/2+y,3/2–z;(iv) 1/2+x,3/2–y,1/2+z; (v) 1–x,2–y,1–z; (vi) –x,2–y,1–z.

[a] *Cg*1 and *Cg*2 denote the gravity centers of the phenyl and catechol ring, respectively.

Figure 3. Packing diagram[4] of **5a** (view along [010] direction). The intermolecular hydrogen bonds are denoted with dashed lines.




1 A. Adamczyk-Woźniak *et al.*, *Appl. Organometal. Chem.*, 2008, **22**, 427.
2 G. Springsteen and B. Wang, *Chem. Commun.*, 2001, 1608.
3 G. Springsteen and B. Wang, Tetrahedron, 2002, **58**, 5291.
4 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.