# Synthesis, photophysical properties and electronic structure of symmetrical substituted curcumin analogues and their $BF_2$ complexes

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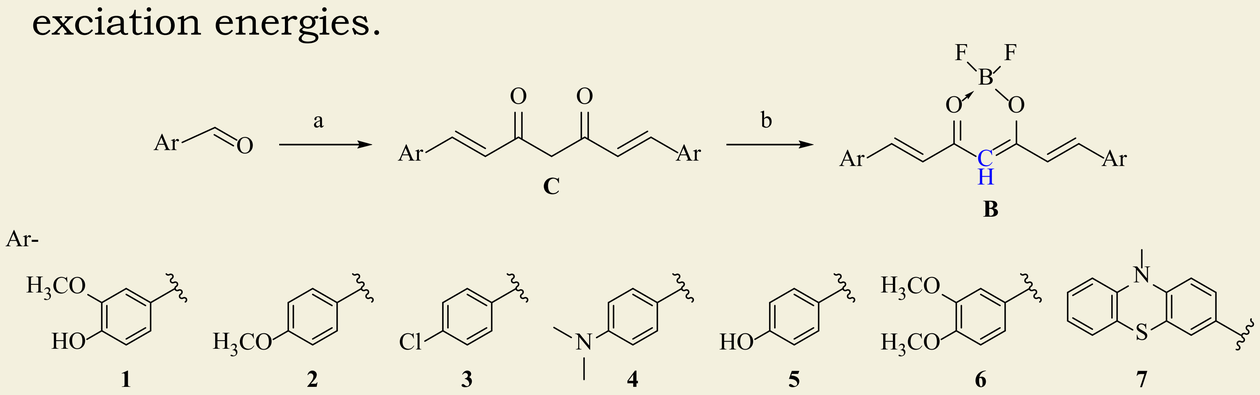
Symmetrically substituted curcumin analogues, compounds with electron donor moieties at both ends of the conjugated systems, and their difluoroboron complexes were synthesized, and their structures were fully characterized. Complexation with $BF_2$ resulted a bathochromic shift both in the absorption and emission spectra, indicating that the π-conjugation was more extended than the one in the initial compounds. The solvatochromic effect were studied, in case of phenothiazinyl-curcumin $BF_2$ complex was the most notably. A novel compound with enhanced photophysical properties, bearing phenothiazine moieties, is reported. Theoretical study of the investigated compounds was carried out using DFT and TD-DFT methods to evaluate the ground state geometry and vertical exciation energies.




**Scheme 1.** Synthesis of curcumin analogues: (a) 2 equiv. aromatic aldehyde, acetylacetone, $B_2O_3$, i-$PrNH_2$, $B(Oi\text{-}Pr)_3$, EtOAc, (**C1–C7**) (b) $BF_3{\cdot}Et_2O$, $CH_3COOH$, $Et_2O$, −5 °C, 24h (**B1–B7**).

Table 1. NMR data for compund C7, B1–B7.

| Comp. | δ (ppm) $^1$H NMR for CH | δ (ppm) $^{19}$F NMR | δ (ppm) $^{11}$B NMR |
|---|---|---|---|
| **B1** | 6.36[a] | -141.09 | -1.02 |
| **B2** | 6.34 [a] | -139.6 | -0.83 |
| **B3** | 6.59[b] | -139.2 | -0.93 |
| **B4** | 6.21[a] | -140.6 | -0.9 |
| **B5** | 6.40[a] | -141.2 | -1.05 |
| **B6** | 6.36[a] | -140.9 | -1.1 |
| **B7** | 6.47[c] | -150.8 | -0.96 |

*a.* *d6*-acetone, 600 MHz
b. $CDCl_3$, 400 MHz
*c.* *d6*-acetone, 400 MHz

Table 2. Maximum absorption wavelengths (λabs), molar absorption coefficients (ε), emission wavelengths (λem) and Stokes-shifts of compounds C7, B1–B7 in acetone.

| Comp. | $\lambda_{abs}$ (nm) | ε ($l{\cdot}mol^{-1}{\cdot}cm^{-1}$) | $\lambda_{em}$ (nm) | Stokes-shift ($cm^{-1}$) |
|---|---|---|---|---|
| **C7** | 350, 468 | 89712 | 522 | 2210 |
| **B1** | 418, 502 | 69500 | 524 | 4312 |
| **B2** | 405, 462, 482 | 68620 | 532 | 5593 |
| **B3** | 500 | 45324 | 534 | 1447 |
| **B4** | 343, 490 | 47790 | 575 | 3017 |
| **B5** | 465, 486 | 32081 | 538 | 2918 |
| **B6** | 474, 498 | 54810 | 570 | 3553 |
| **B7** | 399, 565 | 123700 | 528, 634 | 9289 |

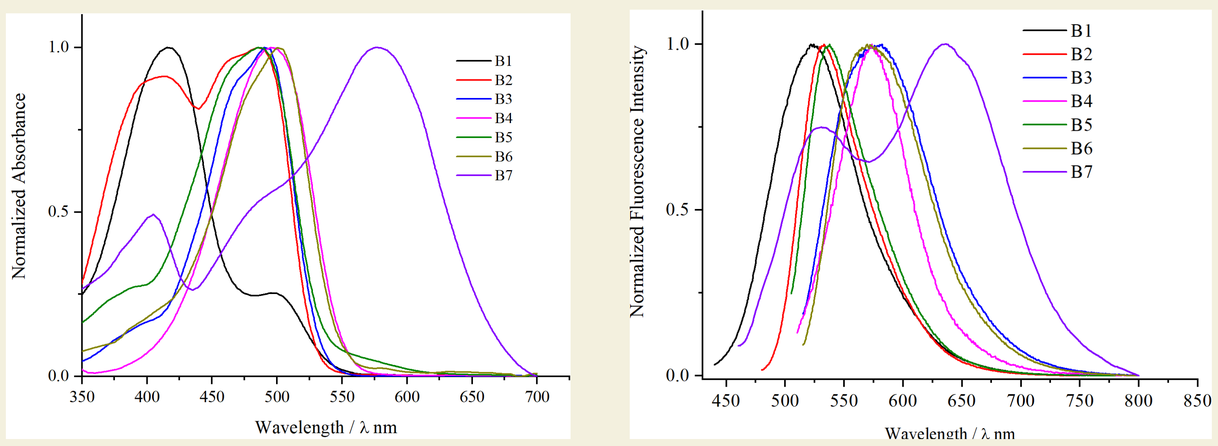



Fig.1. Normalized absorption (at ~$10^{-5}$ M) **(a)** and emission (**b**) spectra for compounds **B1–B7** in acetone.

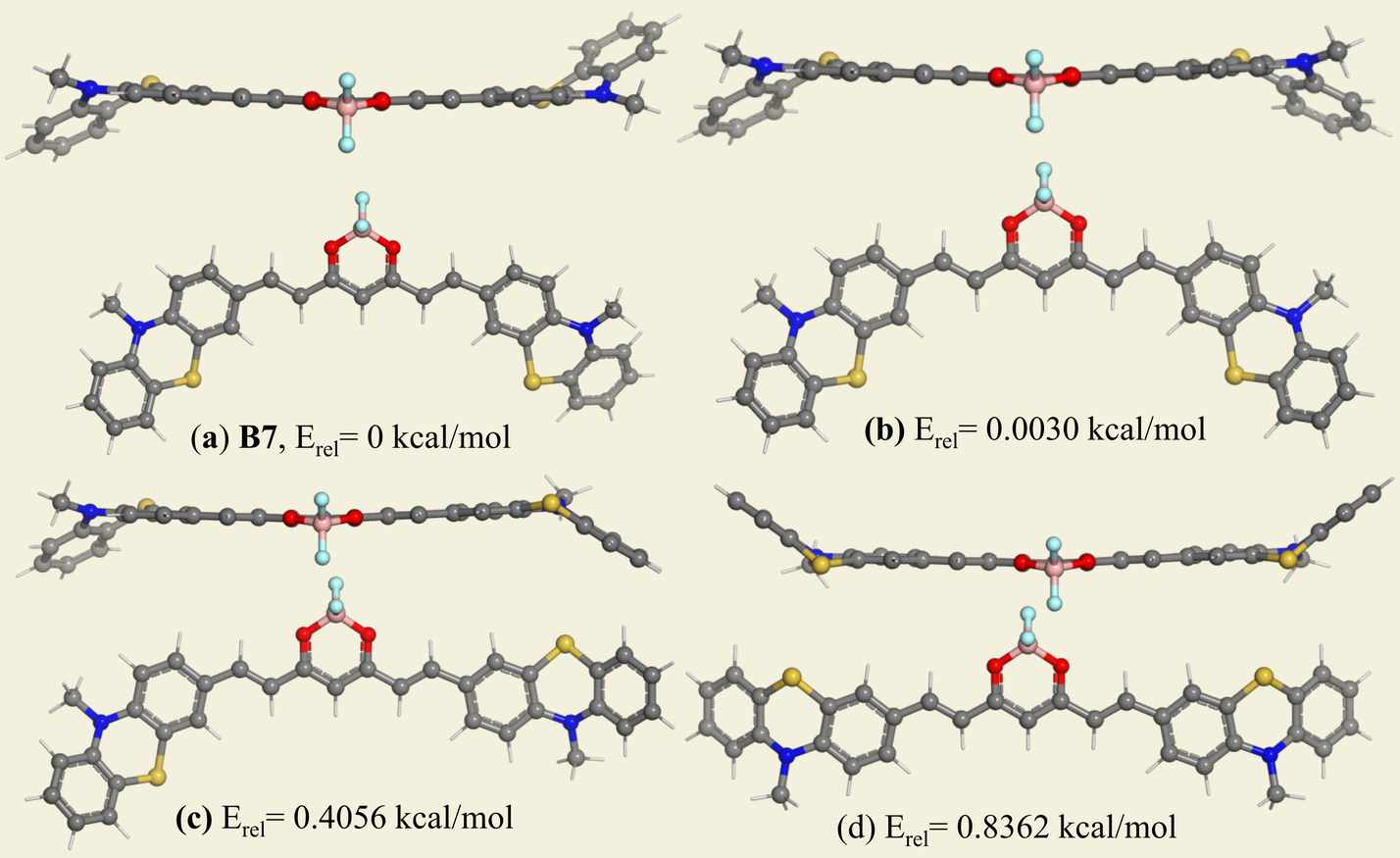



Fig.2. DFT optimized ground state conformations (top and side view) in gas phase of the phenothiazine derivative borondifluoride complex B7 calculated at the B3LYP/6-31G(d,p) level of theory. Values presented are calculated relative energies ($E_{rel}$) in kcal/mol.

***Equipments and program***

- Bruker Avance 400 and 600 MHz NMR,
- Thermo LTQ Orbitrap- HRMS
- Shimadzu GC-MS QP-2010 PLUS
- Perkin Elmer Lambda 35 UV-Vis
- Perkin Elmer FL-55 fluorescence
- Gaussian 09

## Conclusions

Symmetrical curcumin-analogues borondifluoride complexes **B1–B7** were synthesized, and their structures were fully characterized. Two novel compounds (**C7** and **B7**) with enhanced photophysical properties are presented. The ground state geometry of the structures, and the vertical excitation were investigated using the B3LYP functional with 6-311+G(d, p) basis set. The results from the theoretical calculation support the results from the measurements, the compound with phenothiazine unit has the most bathochromic shift in UV and fluorescence spectra.

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References
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