

Specific features of structures and fluorescence spectra of new methoxylated bis(pentafluorophenyl)boron β -diketonates: a quantum chemical study

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COMPUTATIONAL PROCEDURE

Structures and electronic spectra of compounds **1a–1d** were calculated at DFT and TDDFT levels of theory using the BHandHLYP functional^{S1}, def2-SVP^{S2} basis set for geometry optimizations and def2-TZVP basis set^{S3} for single-point calculations at optimized geometries, and the D3BJ dispersion correction^{S4,S5} for both ground and excited states. All calculations were carried out with the ORCA program, version 5.0.3.^{S6,S7} The BHandHLYP functional was selected because of the large fraction of Hartree–Fock exchange (50%), necessary for the adequate description of charge-transfer transitions. Note that whereas the values of λ are commonly underestimated with this functional, we did not use the double-hybrid B2PLYP functional to improve the calculated wavelengths as in the published work,^{S8} because the studied effect was evidently structure-dependent and single-point calculations at the BHandHLYP geometry, only possible in the current ORCA version, made a little sense in our case. We also could not calibrate the BHandHLYP functional to fit the experimental data as it was done before,^{S9} because experimental wavelengths for the whole set of structures **1a–1d** found in this work were not determined in the above mentioned work.^{S8} Dispersion corrections were included to take into account van der Waals interactions in the dkB(C₆F₅)₂ derivatives, bearing sterically interacting flexible fragments. Absorption (λ_{abs}) and emission (λ_{em}) wavelengths were calculated from S₀→S₁ and S₁→S₀ transition energies, respectively, at the geometries optimized for the ground and first excited state, respectively. Charges of particular fragments in the molecules (in fractions of electron charge) in the ground (S₀) and excited (S₁) states were calculated as sums of Mulliken atomic charges on the fragments and charge transfer between the fragments was estimated.

The fragments in Tables S2 and S3 were denoted as follows: (1) first pentafluorinated benzene ring, (2) second pentafluorinated benzene ring, (3) diketonate cycle, (4) non-methoxylated benzene ring (except for **1c**, in which both benzene rings are methoxylated), and (5) methoxylated benzene ring (except for **1a**, in which both benzene rings are non-methoxylated). In addition, since some structures of compound **1d** exhibit charge transfer within DBM phehyl fragments, charges on the halves of DBM (6) and (7) are also presented (charges on atoms B, C and H in the middle of the fragments are shared between the fragments).

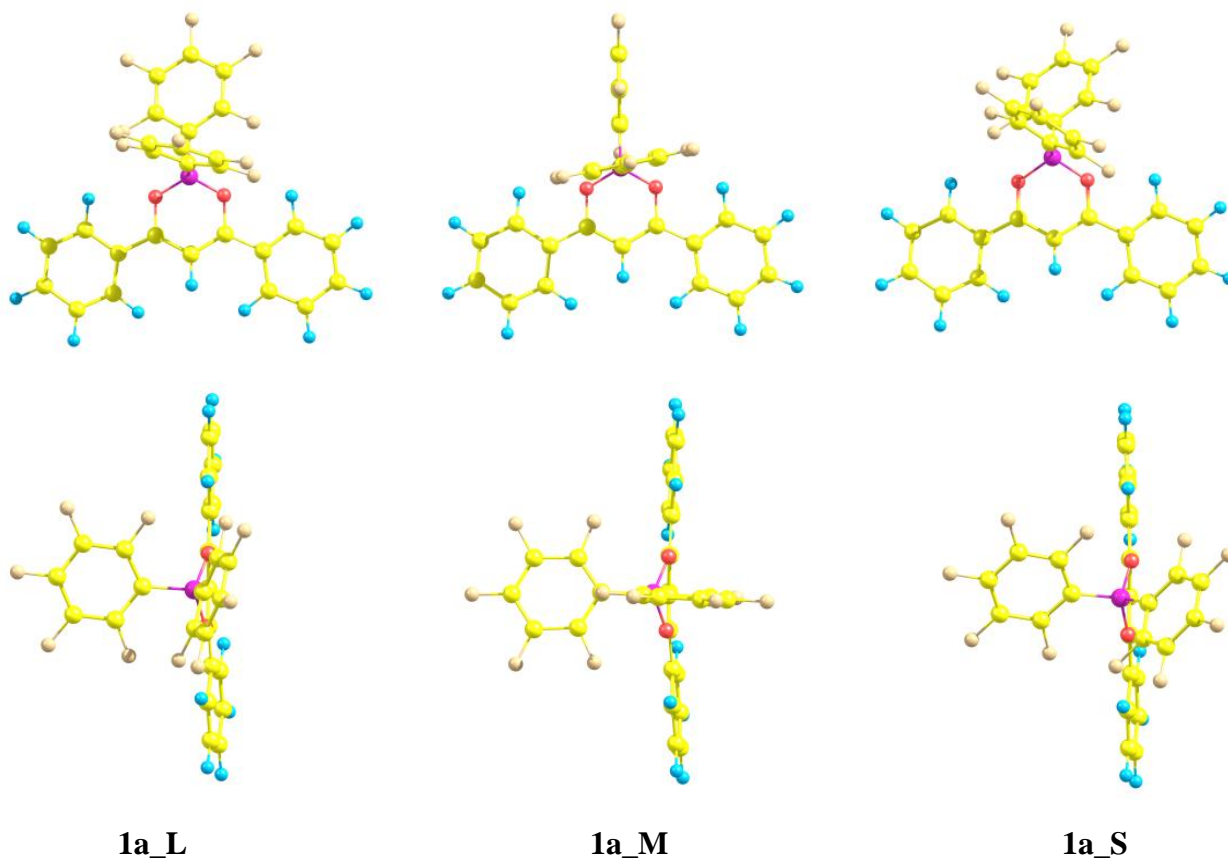


Figure S1 Optimized structures of diketonate **1a** in the S_1 excited state.

Table S1 Natural transition orbitals (donor and acceptor) of typical structures of diketonates **1a–1d**.

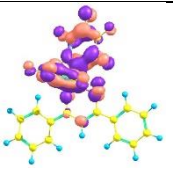
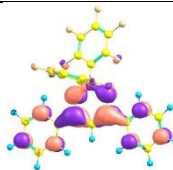
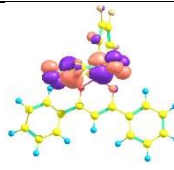
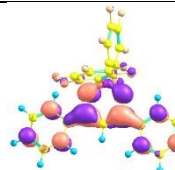
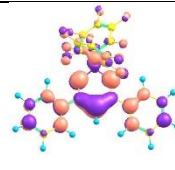
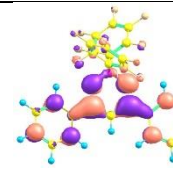
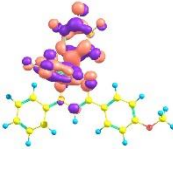
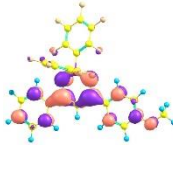
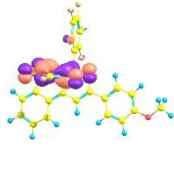
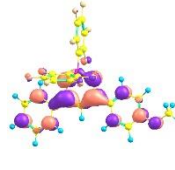
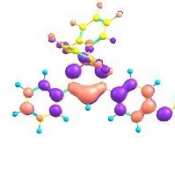
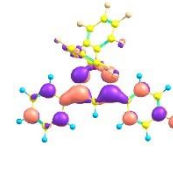
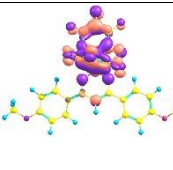
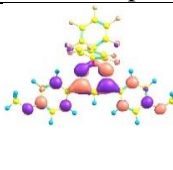
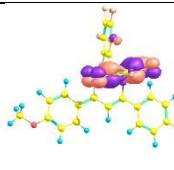
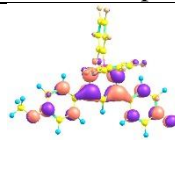
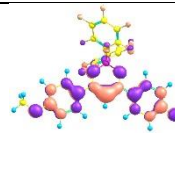
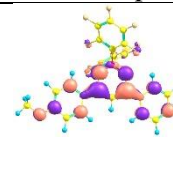
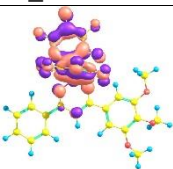
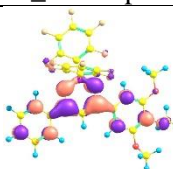
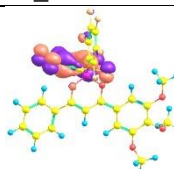
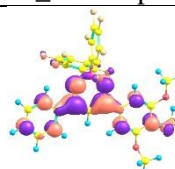
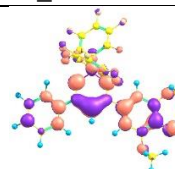
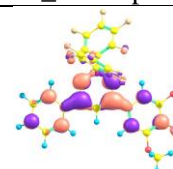
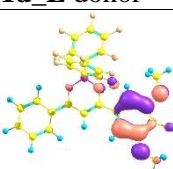
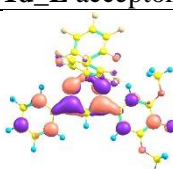
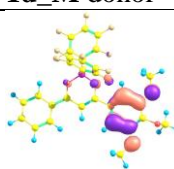
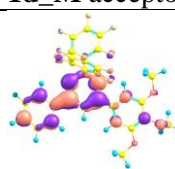
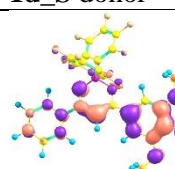
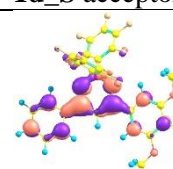
					
1a_L donor	1a_L acceptor	1a_M donor	1a_M acceptor	1a_S donor	1a_S acceptor
					
1b_L donor	1b_L acceptor	1b_M donor	1b_M acceptor	1b_S donor	1b_S acceptor
					
1c_L donor	1c_L acceptor	1c_M donor	1c_M acceptor	1c_S donor	1c_S acceptor
					
1d_L donor	1d_L acceptor	1d_M donor	1d_M acceptor	1d_S donor	1d_S acceptor
					
1d_SM1 donor	1d_SM1 acceptor	1d_SM2 donor	1d_SM2 acceptor	1d_SM3 donor	1d_SM3 acceptor

Table S2 Charges of fragments in the typical structures of diketonates **1a–1d** in the ground (S_0) and excited (S_1) states

S_0

Fragment	1a	1b	1c	1d
(1) C ₆ F ₅ 1	-0.23	-0.22	-0.23	-0.22
(2) C ₆ F ₅ 2	-0.25	-0.27	-0.27	-0.27
(3) diketonate cycle	0.34	0.34	0.32	0.32
(4) Ph 1	0.09	0.05	0.10	0.05
(5) Ph 2 methoxylated	0.05	0.10	0.09	0.11
(6) left half				0.21
(7) right half				0.28

Structures **1a**, **1b** and **1c**, S_1

Fragment	1a_L	1a_M	1a_S	1b_L	1b_M	1b_S	1c_L	1c_M	1c_S
(1) C ₆ F ₅ 1	0.07	-0.26	-0.24	0.06	-0.25	-0.24	0.05	-0.25	-0.25
(2) C ₆ F ₅ 2	0.03	0.46	-0.23	0.03	0.46	-0.26	0.02	0.46	-0.28
(3) diketonate cycle	0.07	-0.01	0.30	0.06	-0.04	0.25	0.04	-0.06	0.20
(4) Ph 1	-0.09	-0.10	0.07	-0.10	-0.12	0.04	-0.05	-0.07	0.16
(5) Ph 2 methoxylated	-0.09	-0.10	0.08	-0.04	-0.05	0.21	-0.06	-0.07	0.17

Structures **1d**, S_1

Fragment	1d_L	1d_M	1d_S	1d_SM1	1d_SM2	1d_SM3
(1) C ₆ F ₅ 1	0.06	-0.25	-0.26	-0.26	-0.26	-0.27
(2) C ₆ F ₅ 2	0.03	0.46	-0.23	-0.29	-0.31	-0.31
(3) diketonate cycle	0.05	-0.03	0.25	0.16	-0.02	-0.02
(4) Ph 1	-0.10	-0.11	0.06	-0.06	-0.10	-0.10
(5) Ph 2 methoxylated	-0.04	-0.07	0.18	0.46	0.69	0.69
(6) left half	-0.07	-0.11	0.17	-0.02	-0.16	-0.17
(7) right half	-0.02	-0.10	0.32	0.57	0.74	0.75

Table S3 Charge transfer (change of charge on the fragment) in structures of diketonates **1a–1d** upon excitation $S_0 \rightarrow S_1$.

Structures **1a–1c**

Fragment	1a_L	1a_M	1a_S	1b_L	1b_M	1b_S	1c_L	1c_M	1c_S
(1)C ₆ F ₅ 1	0.30	−0.01	0.01	0.28	−0.03	−0.02	0.28	−0.02	−0.02
(2)C ₆ F ₅ 2	0.28	0.71	0.02	0.30	0.73	0.01	0.30	0.73	−0.00
(3)diketonate cycle	−0.27	−0.36	−0.04	−0.28	−0.37	−0.09	−0.28	−0.38	−0.12
(4)Ph 1	−0.18	−0.19	−0.02	−0.16	−0.17	−0.01	−0.15	−0.17	0.06
(5)Ph 2 methoxylated	−0.14	−0.15	0.03	−0.14	−0.15	0.11	−0.14	−0.16	0.08

Structures **1d**

Fragment	1d_L	1d_M	1d_S	1d_SM1	1d_SM2	1d_SM3
(1) C ₆ F ₅ 1	0.28	−0.02	−0.03	−0.03	−0.04	−0.04
(2) C ₆ F ₅ 2	0.31	0.73	0.04	−0.02	−0.03	−0.04
(3) diketonate cycle	−0.27	−0.35	−0.07	−0.16	−0.34	−0.34
(4) Ph 1	−0.19	−0.20	−0.04	−0.15	−0.19	−0.19
(5) Ph 2 methoxylated	−0.13	−0.16	0.09	0.37	0.60	0.61
(6) left half	−0.28	−0.32	−0.04	−0.23	−0.37	−0.38
(7) right half	−0.31	−0.38	0.04	0.29	0.45	0.46

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