Effect of the iodine atom position on the phosphorescence of BODIPY derivatives: a combined computational and experimental study

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Received: 4 October 2021 / Accepted: 1 December 2021 / Published online: 13 January 2022

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Abstract

A new BODIPY derivative (*o*-I-BDP) containing an iodine atom in the *ortho* position of the *meso*-linked phenyl group was prepared. Photophysical and electrochemical properties of the molecule were compared to previously reported iodo BODIPY derivatives, as well as to the non-iodinated analog. While in the case of derivatives featuring iodine substituents in the BODIPY core, efficient population of the triplet state is accompanied by a substantial positive shift of the reduction potential compared to pristine BODIPY, *o*-I-BDP displays phosphorescence and simultaneously maintains the electrochemical properties of unsubstituted BODIPYs. A theoretical investigation was settled to analyze results and rationalize the influence of iodine position on electronic and photophysical properties, with the purpose of preparing a fully organic phosphorescent BODIPY derivative. TD-DFT and spin–orbit coupling calculations shed light on the subtle effects played by the introduction of iodine atom in different positions of BODIPY.

Graphical abstract

Keywords Phosphorescence · Triplet state · DFT calculations · Spin–orbit coupling calculations · Singlet oxygen

Elena Bassan and Yasi Dai contributed equally to this work.

Dedicated to Angelo Albini on the occasion of his 75th birthday.

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1 Introduction

BODIPYs (*boron-dipyrromethenes*) are a class of organo-boron compounds that has long received much attention for their high molar absorption coefficients, high fluorescence

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quantum yields and photostability. These properties have consequently led to a variety of applications, such as sensors for metal ions [1], fluorescent probes or labels targeted toward biological components [2].

The ease of their chemical modification has brought forth the development of derivatives that possess novel photophysical features. In particular, BODIPYs that efficiently populate their lowest triplet excited state [3] have been recently designed by three main strategies: (i) introduction of heavy atoms, either by halogenation or insertion of heavy metals [4]; (ii) coupling of BODIPY to electron donating chromophores in donor–acceptor dyads [5]; (iii) BODIPY dimers [6]. In the last two classes, the population of the T_1 excited state is usually mediated by a photoinduced charge-transfer process and requires the synthesis of quite complex systems, while halogenation is an easier approach and affects the rate of spin-forbidden radiative and non-radiative processes. For instance, when iodine atoms are introduced at the 2 and 6 positions (Fig. 1), intersystem crossing (ISC) becomes efficient and the lowest triplet state can be populated, as demonstrated by Nagano et al. in 2005 [7]. This non-radiative deactivation becomes faster thanks to the internal heavy atom effect, as commonly observed for metal complexes containing heavy metal ion, e.g., Ru(II) or Ir(III) complexes [8]. Halogenation of the BODIPY core has therefore been extensively investigated for the development of drugs in photodynamic therapy [9], as it enables

the production of cytotoxic singlet oxygen without the use of heavy metals. More recently, these derivatives have been used as photosensitizers in photocatalytic reactions [10], which has required taking into consideration the effect of halogenation on their electrochemical redox potentials as well.

This work focuses on a series of iodinated BODIPY derivatives (Fig. 1) and the rationalization of the effect that the position of the iodine atom has on the photophysical and electrochemical properties of such compounds. I_2 -BDP is characterized by the presence of two iodine atoms directly linked to the chromophoric unit, while p -I-BDP possesses one iodine atom in the *para* position of the *meso*-linked phenyl group. The new BODIPY derivative, o -I-BDP, was designed by placing one iodine atom in the *ortho* position of the phenyl group so that the halogen is placed close to the BODIPY core, but is not directly attached to it. The effect of this substitution was studied photophysically, electrochemically and computationally.

2 Experimental and computational details

2.1 Synthesis of compounds

2-iodobenzaldehyde [11], p -I-BDP [12] and I_2 -BDP [13] were prepared according to literature procedures.

Synthesis of o -I-BDP. Dipyrromethane was synthesized according to a modified literature procedure [14]. Deionized water (17 mL) was degassed in a Schlenk tube and 2-iodobenzaldehyde (0.42 mmol, 97 mg, 1 eq.) was subsequently added. Distilled 2,4-dimethylpyrrole (10.5 mmol, 1.00 g, 25 eq.) was introduced, and the mixture was shielded from light and vigorously stirred at 80 °C for 24 h. After cooling at room temperature, AcOEt (20 mL) was added and the organic phase was separated. Aqueous phase was extracted with AcOEt (3 × 20 mL), and the collected organic phases were evaporated under reduced pressure to obtain a brown oil. The residue was filtrated on a silica plug (cyHex:DCM:AcOEt, 7:2:1), and the solvent was removed under reduced pressure to obtain dipyrromethane that was employed in the next step without further purification. Dipyrromethane was dissolved in anhydrous DCM (25 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.5 mmol, 114 mg, 1.2 eq.) was added. After stirring at r.t. for 12 h, anhydrous Et_3N (25.2 mmol, 2.55 g, 60 eq.) was added, followed, after 30 min, by the addition of $BF_3 \cdot Et_2O$ (16.8 mmol, 2.38 g, 40 eq.). The solution was stirred for 1 h and then filtered through a pad of Celite washing with DCM. Deionized water (20 mL) was added to the filtrate and the organic phase was separated. Aqueous phase was extracted with DCM (3 × 20 mL), and the collected organic phases were evaporated under reduced pressure. o -I-BDP

Fig. 1 Structure of the studied compounds and IUPAC numeration

was purified by flash chromatography (cyHex:AcOEt, 4:1) to obtain an orange solid (37% yield). ^1H NMR (CDCl₃, 400 MHz) δ 1.38 (s, 6H), 2.55 (s, 6H), 5.98 (s, 2H), 7.94 (d, 1H, J = 8.0 Hz), 7.48 (t, 1H, J = 7.6 Hz), 7.29 (d, 1H, J = 7.5 Hz), 7.15 (t, 1H, J = 7.7 Hz); ^{13}C NMR (CDCl₃, 100 MHz) δ 156.0, 142.4, 139.9, 139.6, 130.4, 129.0, 128.9, 121.2, 98.2, 14.7, 14.0; ^{19}F NMR (CDCl₃, 376.5 MHz) δ 145.93 (ddd, 1F, J = 32.9, 66.4, 109.4 Hz), 146.66 (ddd, 1F, J = 31.6, 64.4, 109.4 Hz).

2.2 Computational details

Ground-state equilibrium structures of each molecule shown in Fig. 1 were determined with density functional theory (DFT) calculations. Two functionals were considered in this case, the B3LYP and the M06-2X. The 6-31G* basis set was used for all atoms except iodine for which the LANL2DZ basis set and pseudopotential [15] were employed. Solvent effects were included by means of the polarizable continuum model (PCM) [16]. According to the experimental measurements, MeCN (ϵ = 35.688) was considered as solvent. The corresponding calculations are labeled as PCM-B3LYP/6-31G*/LANL2DZ and PCM-M06-2X/6-31G*/LANL2DZ. The nature of the stationary points determined by geometry optimization were verified by vibrational frequency calculations carried out at the same level of theory. All the reported geometries correspond to minima.

Excited state wavefunctions and excitation energies were calculated with time-dependent (TD)-DFT, using the M06-2X functional and the 6-311G* basis set, while iodine atoms were described as indicated above. In addition, selected TD-DFT calculations were carried out with the 6-311 + G* and def2-TZVP basis sets. Ten triplet and ten singlet excited states were included in the calculations. Due to the constrained cyanine nature of BODIPY and the insufficient electron correlation at TD-DFT level, excitation energies are systematically overestimated by ca. 0.4–0.5 eV [17–19] at this level of theory. Nevertheless, it has been shown in several benchmark works that the M06-2X functional is suitable to describe excitation energies in BODIPY derivatives and the variations induced by side groups, modifications of the skeleton, stiffening or extension of the conjugated path [19–22]. Excited state calculations are indicated as PCM-TD-M06-2X/6-311G*/LANL2DZ. Excitation energies in solution were initially determined with the use of the standard linear response (LR). Solute–solvent polarization effects in excited states were additionally determined with the state specific (SS) corrected linear response (cLR) [23, 24] approach. Only the fast solvent component was equilibrated (hereafter indicated as NEQ) in calculations of excited state energies used to model absorption spectra, while a fully equilibrated solvent was assumed (hereafter labeled EQ) for excited state energies employed in the

discussion of photo-deactivation processes. Accordingly, the solvent correction included in excited state calculations is indicated by the label LR, cLR(NEQ) or cLR(EQ). All calculations were performed with the Gaussian 16 package [25].

For spin–orbit coupling (SOC) calculations, we considered both PCM-B3LYP (Figure S1 and Table S1) and PCM-M06-2X (Figure S2 and Table S2) geometries. The SOC integrals were calculated with the spin–orbit mean-field (SOMF) method, with one-center approximation applied to the exchange term, (SOMF(1X)) [27, 28]. Relativistic corrections were included with the zeroth order regular approximation (ZORA) [29] using the basis sets specifically designed for these all-electrons calculations: SARC-ZORA-TZVP for iodine and ZORA-def2-TZVP for the remaining atoms. The calculations were carried out with ORCA 5.0.1 package [26] with the Tamm–Dancoff approximation (TDA) [30].

3 Results and discussion

3.1 Synthesis

The preparation of *o*-I-BDP was carried out with a slight modification of a synthetic procedure previously reported by one of us [14]. The synthesis takes advantage of the standard approach employed for BODIPY dyes. A dipyrromethane, obtained in a convenient green “on water” procedure starting from *o*-iodobenzaldehyde, is oxidized with DDQ, and, without purification, the derivative is treated with BF₃ ether complex in the presence of an excess of base (Et₃N). Compared to other procedures published in the literature, the “on water” procedure reduces the excess of 2,5-dimethylpyrrole and avoids Lewis or Brønsted acids, limiting decomposition or polypyrrolic products. The final BODIPY is conveniently purified by chromatography, in moderate isolated yields.

3.2 Photophysical characterization

The photophysical properties of *o*-I-BDP were studied in air-equilibrated acetonitrile solution and compared to those of I₂-BDP, *p*-I-BDP and BDP so as to rationalize the effects brought about by iodination at different sites of the BODIPY core. The absorption spectrum of *o*-I-BDP (Fig. 2B, solid line) presents a narrow band that corresponds to the S₀→S₁ electronic transition (λ_{max} = 503 nm, ϵ = 63,600 M^{−1} cm^{−1}). This band is blue-shifted compared to that of I₂-BDP and slightly red-shifted compared to that of *p*-I-BDP and BDP [31] (Table 1). The emission spectrum recorded at room temperature (Fig. 2B, dashed line) peaks at 521 nm and is attributable to *o*-I-BDP's fluorescence, given its small Stokes shift and its lifetime of 5.0 ns. The same trend

Fig. 2 Absorption (solid line), fluorescence (dashed line), and phosphorescence (dotted line) spectra of I_2 -BDP (**A**), o -I-BDP (**B**) and p -I-BDP (**C**)

observed for the absorption maxima is maintained for the fluorescence maxima as well (Table 1).

Interestingly, o -I-BDP presents a new emission band ($\lambda_{\text{max}} = 765$ nm) at 77 K in an EtOH/MeOH (1:1 v/v) glassy matrix with a lifetime of 520 μ s (Fig. 2B, dotted line). This band is assigned to o -I-BDP's phosphorescence due to its larger Stokes shift, its absence in aerated solutions at room temperature and its decay lifetime. I_2 -BDP also presents a similar band in the same spectral region, whereas p -I-BDP does not (Fig. 2A, C, and Table 1). These results are ascribable to the different positions occupied by iodine atoms, which strongly influence the efficiency of ISC between the lowest singlet (S_1) and triplet states, as well as the efficiency of phosphorescence. In fact, given the distance of the iodine atom from the chromophoric core, the ability of p -I-BDP to populate its lowest triplet state and thus display phosphorescence is strongly reduced and its photophysical properties resemble those of non-iodinated BDP [31, 32]. Conversely, ISC is favored in I_2 -BDP since the two iodine atoms are directly attached to the BODIPY skeleton. In the case of the o -I-BDP derivative, the presence of one iodine atom in the vicinity of the BODIPY core allows it to populate the lowest triplet excited state, even though it is not directly appended to it.

To understand the extent of this deactivation pathway, fluorescence quantum yields (Φ_{FLUO}) and singlet oxygen quantum yields (Φ_{Δ}) were measured for the three compounds (Table 1) and compared to those of BDP. Fluorescence quantum yield is expected to decrease upon increasing the rate of ISC and, consequently, Φ_{Δ} is expected to increase because singlet oxygen is generated by energy transfer from the lowest triplet excited state (T_1) of the BODIPY (Fig. 3).

In accordance with literature data [33], I_2 -BDP is characterized by the lowest value of Φ_{FLUO} and the highest value of Φ_{Δ} because the two iodine atoms are positioned in such a way that they are highly effective at inducing ISC and obtaining an efficient T_1 population. In addition to the efficient ISC process, a more stable S_1/S_0 conical intersection could also contribute to the reduced Φ_{FLUO} of I_2 -BDP [34]. o -I-BDP's Φ_{FLUO} (56%) is similar to that of p -I-BDP but, remarkably, Φ_{Δ} is 35% for o -I-BDP and

Table 1 Photophysical properties of studied compounds in air-equilibrated MeCN solution

Molecule	$\lambda_{\text{max ABS}}$ (nm)	$\lambda_{\text{max FLUO}}$ (nm)	τ_{FLUO} (ns)	Φ_{FLUO}	$\lambda_{\text{max PHOS}}$ (nm) ^a	τ_{PHOS} (ms) ^a	Φ_{Δ}
o -I-BDP	503	521	5.0	56%	765	0.52	35%
p -I-BDP	498	514	3.3	45%	^b	/	^b
I_2 -BDP	530	548	^c	1.8%	757	1.20	70%
BDP [31–33]	497	507	3.18	48%	n.r.	n.r.	1% ^d

n.r. not reported

^aAt 77 K in MeOH/EtOH (1:1 v/v)

^bNot detected

^cLifetime not determined due to low value of Φ_{FLUO}

^dIn DCM

Fig. 3 Jablonski diagram illustrating the main energy levels and deactivation pathways for BODIPY derivatives in the presence of molecular oxygen; η_{T_1} is the efficiency of T_1 population and η_{ET} is the efficiency of the bimolecular energy transfer process between BODIPY and ground-state molecular oxygen. The role of the T_2 state will be discussed in the computational section

Fig. 4 Cyclic voltammetry of I_2 -BDP (yellow line), o -I-BDP (blue line) and p -I-BDP (red line) (0.5 mM) in degassed MeCN solution containing tetraethylammonium hexafluorophosphate 0.05 M, as the supporting electrolyte and ferrocene as the internal standard. Working electrode: glassy carbon; counter electrode: Pt wire; quasi-reference electrode: Ag wire; scan rate = 0.3 V/s. Ferrocene's peaks have been removed for clarity

not detectable for p -I-BDP. These results indicate that the location of the iodine atom is crucial for the population of the triplet state: o -I-BDP exhibits a quite efficient T_1 population, although not as efficient as in I_2 -BDP. On the contrary, p -I-BDP is unable to undergo efficient ISC, similarly to what is reported for BDP [33]. Lastly, the higher Φ_{FLUO} of o -I-BDP compared to p -I-BDP can be imputed to the increased steric hindrance of its *meso* substituent. In

fact, a substituent in the *ortho* position decreases its rotational freedom and, in turn, its non-radiative deactivation.

3.3 Electrochemical characterization

The ground-state electrochemical potentials of the three BODIPY derivatives were studied by means of cyclic voltammetry (Fig. 4). o -I-BDP shows chemically and electrochemically reversible electron transfer processes, both in the anodic (+1.20 V vs. SCE) and cathodic region (−1.10 V vs. SCE) (Fig. 4, blue line).

Both these redox potentials are negatively shifted compared to those of I_2 -BDP, and are comparable to those measured for p -I-BDP and BDP [13], as presented in Fig. 4. Indeed, the presence of halogen atoms directly connected to the BODIPY core reduces its electron density, while derivatizations present on the *meso*-linked phenyl group have little influence on the electrochemical properties thanks to its orthogonality with respect to the chromophoric unit. Therefore, iodination in the *ortho* position of the phenyl group allows to maintain the redox potentials typical of fluorescent BODIPYs meanwhile allowing the population of their lowest triplet excited state.

3.4 Modeling photophysical properties of BDP and iodinated derivatives

To assist the interpretation of experimental results and rationalize the influence of iodine position, a computational investigation on the electronic structure and photophysical properties was carried out on BODIPY derivatives shown in Fig. 1.

3.4.1 Ground-state structures and frontier molecular orbitals

The computed equilibrium structures and bond lengths of the four BODIPY derivatives are collected in Figures S1, S2. We note that while PCM-B3LYP/6-31G*/LANL2DZ predicts an almost planar BODIPY core (the only exception is I_2 -BDP) and an almost orthogonal phenyl moiety for all molecules (see Figure S1 and Table S1), PCM-M06-2X/6-31G*/LANL2DZ geometries display deviations from orthogonality for the phenyl substituent, except for o -I-BDP, and are characterized by a more markedly out of plane tilted BF_2 group, as indicated by the dihedral angles in Table S2. In Fig. 5 and Figure S4, we see that the HOMO (H) and LUMO (L), calculated at both levels of theory, are localized on the BODIPY core. Focusing on the set of PCM-B3LYP molecular orbitals (MOs, Fig. 5), we note that the shape of the H is the same for all molecules except for I_2 -BDP. In the latter case significant electron density is computed also on the two iodine atoms. The electron density of L is

Fig. 5 Shapes and energies of H and L of BDP and iodinated derivatives calculated at PCM-B3LYP/6-31G*/LANL2DZ level

almost the same across the four molecules but due to the electron withdrawing character of iodine and its substitution on the BODIPY core, the LUMO energy of I_2 -BDP is significantly lowered. The substituent effect can be qualitatively explained via orbital interaction between fragments, or more quantitatively rationalized via absolutely localized molecular orbitals as demonstrated in recent work [35]. Due to the deviation from orthogonality, the MOs computed at PCM-M06-2X/6-31G*/LANL2DZ geometries (Figure S4), display some minor density contribution to phenyl substituents, especially for I_2 -BDP.

Accurate computational predictions of redox potentials require comparison of energies for both the starting molecule and its reduced/oxidized forms. However, we can qualitatively use Koopmans' theorem [36] to correlate the redox potentials of BODIPY derivatives with H/L computed

Fig. 6 Relationship between the $B/B^{\bullet-}$ redox potentials (see Table 2) and L energies of BODIPY derivatives calculated at PCM-B3LYP/6-31G*/LANL2DZ level (see Table S3)

Table 2 Redox potentials of the studied compounds in MeCN in V vs. SCE

Molecule	$E(B/B^{\bullet-})$ (V)	$E(B^{\bullet+}/B)$ (V)
<i>o</i> -I-BDP	− 1.10	+ 1.20
<i>p</i> -I-BDP	− 1.12	+ 1.18
I_2 -BDP	− 0.90	+ 1.29
BDP [13]	− 1.19	+ 1.21

energies. The result of such correlations is shown in Fig. 6 and S5, where a plot of the computed L/H energies versus experimental redox potentials shows good linearity especially for L energies. The fitting of H energies versus $B^{\bullet+}/B$ redox potentials shows some deviations: BDP's oxidation potential is slightly higher than those of *o*-I-BDP and *p*-I-BDP. It should be noted however that these differences are small and are within experimental uncertainties. Interestingly, both markedly different redox potentials of I_2 -BDP are correctly captured by computations.

3.4.2 Low-lying excited states

To identify the deactivation pathways of the four BODIPY derivatives, we determined the most relevant excitation energies and excited state wavefunctions with PCM-TD-M06-2X calculations, using the LANL2DZ basis set for iodine and three different basis sets for the remaining atoms: 6-311G*, 6-311 + G* and def2-TZVP (including the standard LR description of solvent effects) at the PCM-B3LYP/6-31G*/LANL2DZ optimized ground-state geometries (see Table S4). The corresponding molecular orbitals are depicted in Figure S6. As expected, the S_1 and T_1 states are dominated by the $H \rightarrow L$ excitation, localized on the BODIPY core. In addition to the lowest triplet state, in Table S4 we also report the excitation energy of the second lowest triplet T_2 , which is computed to be very close to S_1 and is also dominated by an excitation localized on the BODIPY core, for all the systems investigated. Since the use of larger basis sets (see Table S4) leads to negligible differences in computed excitation energies, the following calculations were carried out with the 6-311G* basis set.

The quality of predicted excited states can be assessed by comparing computed absorption spectra in solution with the experimental data. To this end, we determined the cLR(NEQ) corrected excitation energy of S_1 (see Table S5), the state responsible for the main absorption band of BODIPY derivatives. The comparison between computed and experimental spectra is shown in Fig. 7 where a shift of 0.45 eV was applied to computed excitation energies to account for the systematic overestimation of S_1 excitation energy at TD-DFT level [17–19], as described in Sect. 2.2.

Fig. 7 Comparison between computed and observed absorption spectra of the four investigated BODIPY derivatives. PCM-TD-M06-2X/6-311G* level of theory including cLR(NEQ) solvent corrections. The computed excitation energies were shifted by 0.45 eV in accordance with the known systematic overestimate at TD-DFT level [18]

Interestingly, the spectral changes induced by different iodination are very well reproduced by the calculations.

It is instructive to analyze in more detail the results of different computational protocols for solvent corrections. Solvatochromism in absorption spectra is determined by the different dipole moment of ground and excited states. Calculations show that the dipole moment (see Table S6) is systematically lower in S_1 compared to the ground state, for all the BODIPY derivatives investigated. This implies that an inverted solvatochromism [37] should be observed, accompanied by a blue shift when moving from gas-phase (calculations in vacuo) to MeCN. In contrast (see Table S5), $S_0 \rightarrow S_1$ excitation energies computed in MeCN with the LR approach, decrease compared to gas-phase, while the expected excitation energy increase is predicted only by cLR(NEQ) calculations. Consider, for example the S_1 excitation energy computed at 2.97 eV in vacuo for BDP, which unexpectedly decreases to 2.87 eV in MeCN (LR) and correctly increases to 2.99 eV in MeCN (cLR(NEQ)). As a result of the incorrect LR description, the correspondingly computed spectra are red-shifted, in Figure S8, compared to those obtained including the cLR(NEQ) solvent correction. The overshooting of positive solvatochromism by the LR approach has been documented in previous work [21, 38]. Here, we underscore that, for BODIPY derivatives characterized by inverted solvatochromism, the inclusion of solvent correction at LR level, incorrectly predicts an excitation energy decrease and only cLR provides a physically sound description of gas phase to solvent excitation energy changes.

Fig. 8 Computed excitation energies (PCM-TD-M06-2X/6-311G*/LANL2DZ level, including cLR(EQ) solvent correction) of low-lying singlet and triplet excited states of BDP and iodinated derivatives

3.4.3 Predicted efficiency of ISC deactivation

Experimental data (Table 1) show that only *o*-I-BDP and I₂-BDP populate efficiently the lowest triplet state T_1 and exhibit relevant Φ_Δ values. Furthermore, the efficiency is greater for I₂-BDP with respect to *o*-I-BDP while population of T_1 is an inefficient process for *p*-I-BDP and BDP. According to the excited state calculations discussed in the previous section, two triplet states lie below (T_1) or close (T_2) to S_1 and should be considered to rationalize the experimental results. Because the ISC process is relatively slow [39] (of the order of 10^7 – 10^8 s⁻¹) compared to typical timescales of solvent reorganization [40] (picosecond, sub-picosecond), we can safely assume that solvent equilibration occurs. Thus, solvent-equilibrated excited state energies (cLR(EQ)) (see Fig. 8) are considered in the following discussion. As discussed above, the S_1 state (blue diamond, Fig. 8) is found between T_1 and T_2 states, and quite close to the latter. Therefore, the $S_1 \rightarrow T_2$ ISC cannot be ruled out. Indeed, in recent investigations on different BODIPY derivatives [41, 42] it has been proposed that the $S_1 \rightarrow T_2$ deactivation path can be a relevant ISC channel.

For radiationless transitions slower than vibrational relaxation [43], and for relatively large energy gaps ΔE_{S-T} between S_1/T_n states, the ISC process can be discussed in terms of a simplified relation (Eq. 1), where the rate constant (k_{ISC}) is proportional to the SOC matrix element $\langle T_n | \hat{H}_{SO} | S_1 \rangle$ and inversely proportional to the square of the energy gap ΔE_{S-T} between S_1/T_n states [41, 43–45]:

Table 3 Computed SOC magnitudes between S_1 and T_1/T_2 states of BDP and iodinated derivatives

Molecule	SOC @geometry PCM-B3LYP	
	S_1/T_1 [cm^{-1}] ^a (ΔE_{S-T} [eV]) ^b	S_1/T_2 [cm^{-1}] ^a (ΔE_{S-T} [eV]) ^b
<i>o</i> -I-BDP	1.09 (1.51)	0.14 (− 0.11)
<i>p</i> -I-BDP	0.00 (1.51)	0.00 (− 0.11)
I ₂ -BDP	2.64 (1.35)	11.70 (− 0.05)
BDP	0.00 (1.50)	0.00 (− 0.11)

^aSOC values calculated with the SOMF(1X) approach including relativistic corrections with ZORA, from TDA-M06-2X/ZORA-def2-TZVP/SARC-ZORA-TZVP calculations at PCM-B3LYP/6-31G* (BDP) and PCM-B3LYP/6-31G*/LANL2DZ (iodinated BDP) optimized geometries

^b ΔE_{S-T} from PCM-TD-M06-2X/6-311G* and PCM-TD-M06-2X/6-311G*/LANL2DZ levels, including cLR(EQ) solvent correction

$$k_{ISC} \propto \frac{|\langle T_n | \widehat{H}_{SO} | S_1 \rangle|^2}{(\Delta E_{S-T})^2} \quad (1)$$

The SOC between T_1 , T_2 and S_1 , computed at the optimized PCM-B3LYP (PCM-M06-2X) geometries are collected in Table 3 (Table S7 and S8). In the same table we also report the relevant ΔE_{S-T} values taken from cLR(EQ) calculations (Fig. 8, Table S5). Although the two sets of geometries display different degrees of orthogonality between the phenyl substituent and the BODIPY core and a different BF_2 out of plane tilt, it is interesting to note that both consistently suggest a similar decay pattern. The SOC computed for the two geometries of *o*-I-BDP are very similar since this is the only case in which the BODIPY derivative displays an orthogonal geometry also at PCM-M06-2X level. Concerning the magnitude of computed SOC, we note that these are negligible for BDP, both at PCM-B3LYP and PCM-M06-2X geometries. For *p*-I-BDP the computed SOC are also negligible for both sets of geometries, although slightly larger at the less symmetric PCM-M06-2X structure. A markedly different trend is documented for the remaining two iodinated derivatives. *o*-I-BDP displays, for both geometries, a relevant SOC between T_1 and S_1 and a non-negligible value between S_1 and T_2 . It is well known that the presence of a second triplet state in the vicinity of the excited singlet greatly enhances the rate of the intersystem crossing [46]. Since ΔE_{S-T} is considerably smaller for the T_2 state, we cannot rule out a contribution from the $S_1 \rightarrow T_2$ ISC to the efficient triplet formation. Finally, very large SOC are computed for I₂-BDP in perfect agreement with the remarkable effect experimentally documented for

iodine atoms directly linked to the BODIPY core. While both SOC between T_1 / S_1 and T_2 / S_1 are significant, we note that the less symmetric PCM-M06-2X structure leads to larger couplings, suggesting that vibronically induced effects might also be relevant. At the same time the $\langle T_2 | \widehat{H}_{SO} | S_1 \rangle$ couplings are much larger than those computed for *o*-I-BDP. This, coupled to a reduction of the S_1/T_2 energy difference in I₂-BDP, points to an even more relevant role of the $S_1 \rightarrow T_2$ ISC for this system.

Thus, based on the above considerations, we expect negligible triplet generation for BDP and *p*-I-BDP. The most efficient triplet generation is predicted for I₂-BDP while an intermediate efficiency is expected for *o*-I-BDP. A possible additional deactivation pathway via $S_1 \rightarrow T_2$ ISC is predicted for both, with an increased efficiency for I₂-BDP. These conclusions are in agreement with experimental data.

4 Conclusions

The purpose of this work was the synthesis of fully organic phosphorescent BODIPY derivatives. Given the improvements in the photophysical properties recently displayed by this class of molecules, the effort was aimed at the synthesis of BODIPYs that did not contain heavy metals, but relied on iodine atoms for the efficient population of their triplet states. Monoiodination in the *ortho* position of *meso* phenyl-BODIPY proved to be an effective way to gain access to the phosphorescent triplet state while maintaining fluorescent BODIPYs electrochemical properties. The molecules' photophysical and electrochemical properties are therefore decidedly influenced by the positions that iodine atoms occupy around the BODIPY core, and their rationalization was possible on the basis of the combined experimental and computational study.

Quantum chemical calculations were shown to support the remarkable changes in redox potentials of I₂-BDP and the relative shifts in absorption spectra along the series of BODIPY derivatives investigated. From a methodological point of view, it was shown that only the cLR approach correctly describes solvatochromic effects in BODIPY derivatives, when moving from gas-phase to solvent. Finally, the computed low-lying excited states and SOC were shown to be fully consistent with the inefficient triplet generation of BDP and *p*-I-BDP. The superior efficiency of I₂-BDP compared to *o*-I-BDP was demonstrated by large SOC for the two available ISC pathways: $S_1 \rightarrow T_2$ and $S_1 \rightarrow T_1$. While functionalization of iodine atoms at different positions in BDP does not affect substantially the nature of low-lying excited states, it modulates their relative energy. The tiny changes in wavefunctions induced by the presence and position of iodine atoms are nicely captured by the calculated SOC which provide a consistent interpretation of the experimental data.

These results are useful for the design of other BODIPY derivatives exhibiting highly efficient population of the lowest triplet state with potential applications in photocatalysis and photodynamic therapy.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43630-021-00152-5>.

Funding The National PRIN 2017 projects (ID: 20174SYJAF, SURSUMCAT and ID: 20172M3K5N, CHIRALAB) are acknowledged for financial support for this research. Fondazione CarisBo is acknowledged for the funding of the project “Tecnologie avanzate per il controllo e lo sviluppo di molecole innovative per la salute” (ID: #18668). The University of Bologna is gratefully acknowledged.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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