Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2018

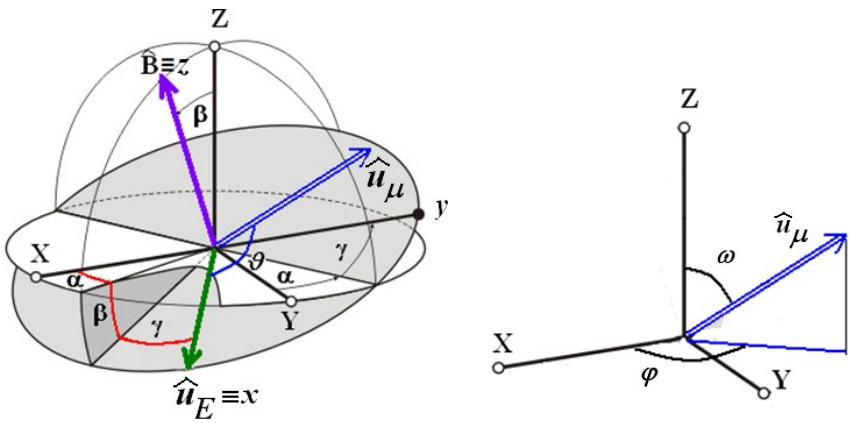
Electronic Supplementary Information

Precise Determination of the Orientation of the Transition Dipole Moment in a Bodipy Derivative by Analysis of the Magnetophotoselection Effect

*Antonio Toffoletti,[a] Zhijia Wang[b], Jianzhang Zhao[b], Matteo Tommasini[c] and Antonio Barbon[a]**

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo, 1, 35131 Padova, Italy. E-mail: antonio.barbon@unipd.it*
[b] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, E-208 West Campus, 2 Ling-Gong Road, Dalian 116024, People's Republic of China*
[c] *Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*

1. Determination of the orientational probability



Scheme S1. (left) definition of the polar angles for the Euler angles in the ZFS frame (*X, Y, Z*) for the orientation of the laboratory frame (*x, y, z*; the magnetic field defining *z*). The polarization field was consider either parallel to *B*, or, like in the figure, aligned along the transformed *x* axis. The angle ϑ between the transition dipole moment $\vec{\mu} = \mu \cdot \hat{u}_\mu$ and the polarization field $\vec{E} = E \cdot \hat{u}_E$ is also indicated. (right) polar angles in the ZFS frame for the orientation of the transition dipole moment.

The orientational probability has been defined as proportional to (see eq. (1)):

$$\left(\hat{u}_\mu \cdot \hat{u}_E\right)^2 = \cos^2 \vartheta \qquad \text{(S1)}$$

The product was obtained from the product of the Cartesian components of the two versors relative to the transition dipole moment and to the polarization vector.
The Cartesian components, for the transition dipole moment versor the components were obtained as projection of the vector on the axes: by calling ω, φ the polar angles of the transition moment versor $\hat{u}_\mu$ (see Scheme S1), the Cartesian components are

$$\hat{u}_\mu = (\sin\omega\cos\phi; \quad \sin\omega\sin\phi; \quad \cos\omega) \qquad \text{(S2)}$$

For the Cartesian components of the polarization field, instead, we have to distinguish the case with parallel of perpendicular orientation of the polarization versor with respect to the magnetic field.

Case 1): polarization field <u>*parallel*</u> to the magnetic field ($\hat{u}_E = \hat{u}_{E,z}$)
The components of the versor in the molecular frame are obtained by the standard Euler matrix as [1]:

$$\hat{u}_{E,z} = (\cos\alpha\sin\beta; \quad \sin\alpha\sin\beta; \quad \cos\beta) \qquad \text{(S3)}$$

The non-normalized probability is then obtained by multiplying S2 and S3:

$$\left(\hat{u}_{\mu}\cdot\hat{u}_{E,z}\right)^2=\cos^2\vartheta=$$
$$=\left[(\cos\alpha\sin\beta;\ \ \sin\alpha\sin\beta;\ \ \cos\beta)\cdot(\sin\omega\cos\phi;\ \ \sin\omega\sin\phi;\ \ \cos\omega)\right]^2 \qquad \text{(S4)}$$
$$=\left[\sin\omega\sin\beta\left(\cos\alpha\cos\phi+\sin\alpha\sin\phi\right)+\ \cos\beta\cos\omega\right]^2$$

A simplification of the expression can be obtained by assuming the transition dipole moment along one of the principal directions of the ZFS tensor (along one of the axes of the molecular frame). We have chosen to orient along the *Z*-axis to obtain the simplest expressions. Please note that the labelling of the molecular axes is arbitrary, so that it is easy to orient the transition dipole moment along one of the ZFS principal directions just by an exchange of labels.
The components of the transition dipole moment versor are then $\hat{\mu}=(0;\ \ 0;\ \ 1)$, that is $\omega=0$. In this case expression S4 simplifies to:

$$\left(\hat{u}_{\mu}\cdot\hat{u}_{E,z}\right)^2=\cos^2\vartheta=$$
$$=\left[\cos\beta\right]^2 \qquad \text{(S5)}$$

Case 2): polarization field <u>*perpendicular*</u> to the magnetic field ($\hat{u}_E=\hat{u}_{E,x}$)

The components of the versor in the molecular frame are obtained by assuming $\hat{E}$ along the *x* axis. Like in case 1), we make use of the standard Euler matrix as [1]:

$$\hat{u}_{E,x}=(\cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma;\ \ \sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma;\ \ \text{-}\sin\beta\cos\gamma) \qquad \text{(S6)}$$

and the product in eq. S1 can then be obtained by multiplication of expressions S2 and S6:

$$\left(\hat{u}_{\mu}\cdot\hat{u}_{E,x}\right)^2=\cos^2\vartheta=$$
$$\left[(\cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma;\ \sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma;\ \text{-}\sin\beta\cos\gamma)\cdot(\sin\omega\cos\phi;\ \ \sin\omega\sin\phi;\ \ \cos\omega)\right]^2$$
(S7)

Like in the previous case, a simplification of the expression can be obtained by assuming the transition dipole moment along the *Z* principal directions of the ZFS tensor: in this case expression S7 simplifies to:

$$\left(\hat{u}_{\mu}\cdot\hat{u}_{E,x}\right)^2=\cos^2\vartheta=$$
$$\left[\text{-}\sin\beta\cos\gamma\right]^2 \qquad \text{(S8)}$$

2. NMR and HRMS characterization of 2-iodoBodipy

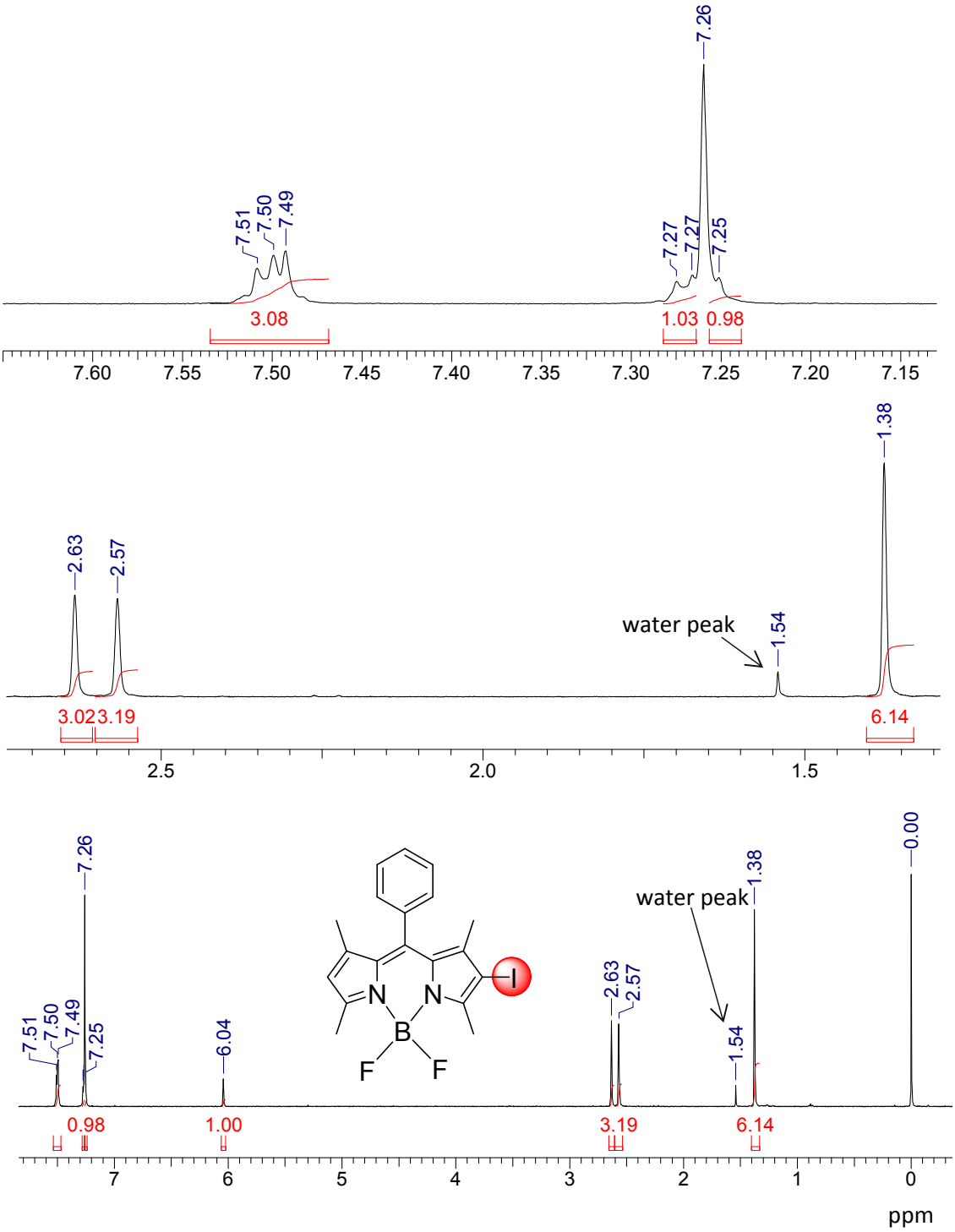


Figure S1. ^{1}H NMR of compound **2-iodoBodipy** (400 MHz, $CDCl_3$), 25°C.

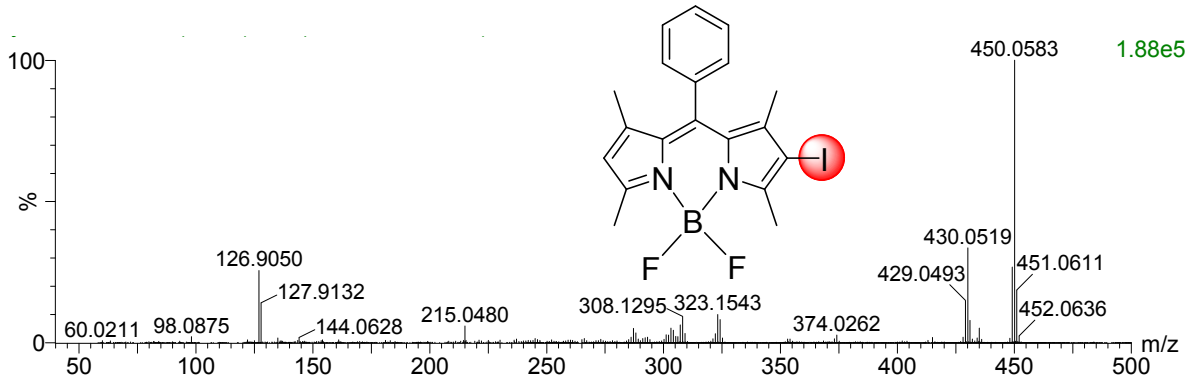


Figure S2. EI HRMS of **2-iodoBodipy**. 25°C.

3. $S_0 \rightarrow S_n$ Transition Dipole Moment calculation

Table S1: DFT Calculations of the $S_0 \rightarrow S_n$ transition dipole moments (TDM's) calculated by TDDFT with B3LYP functional and 6-31g(d) base functions; I-atom was parameterized with LANL2DZ. Geometry optimization was also performed. X, Y and Z are the components of the TDM in the ZFS frame, Dip is the square of the value of TDMs. (Dip = $\mu_{ABS}^2 = X^2 + Y^2 + Z^2$) and Oscill. is the oscillator strength. Note that the results are in "arbitrary units".

n-State	X	Y	Z	Dip	Oscill.
1	0.422	0.000	2.392	5.90	0.42
2	–0.635	0.004	–1.528	2.73	0.22
3	–0.479	–0.002	0.332	0.34	0.03

4. UV/visAbsorption spectrum

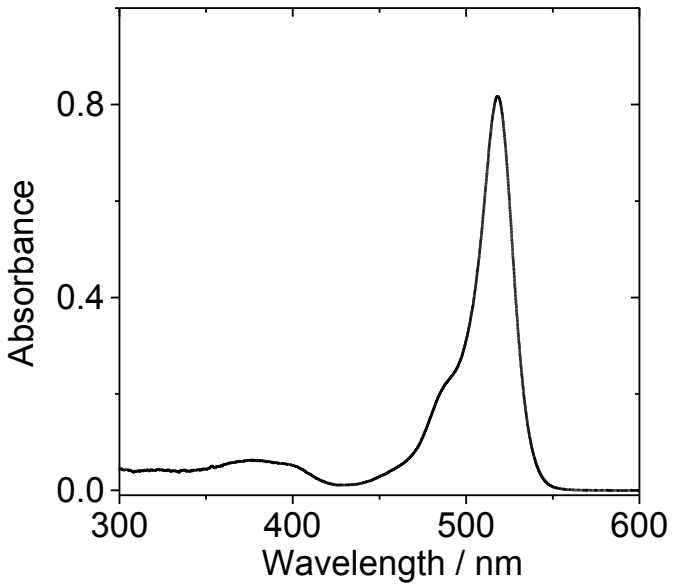


Figure S3: UV/vis absorption spectrum of 2-iodo-Bodipy, c = 1.0×10^{-5} M in toluene at 20 °C.

References

[1] A. Schweiger, G. Jeschke, Principles of Pulse Electron Paramagnetic Resonance, Oxford University Press, 2001.