Strong Intramolecular Charge Transfer Emission in Benzobisoxazole Cruciforms: Solvatochromic Dyes as Polarity Indicators

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Calculated HOMOs and LUMOs¹

Ground and first excited states were optimized at the Density Functional Theory (DFT) level, by means of the hybrid B3LYP method, and *ab initio* CIS method, respectively, using the double valence basis set (6-31g). Note that the optimized excited state is the Franck-Condon LE state. In general, all the geometries are fully planar and symmetric (dipole moment ~0 D). Shown below, for each examined cruciform, are: (*a*) the geometry of the ground state (left), (*b*) the HOMO (center) and LUMO (right) contour maps, (*c*) the respective spatial group and (*d*) the energies of the HOMO and the LUMO states—which are related to the Ionization Potential and Electron Affinity values, respectively.

Compound 1



Planar and symmetric (C2h)E(HOMO) = -8.30018 eV (ionization potential)

E(LUMO) = -1.54688 eV (electron affinity)



Planar and symmetric (Ci) E(HOMO) = -7.78140 eV (ionization potential)

E(LUMO) = -1.36657 eV (electron affinity)



Planar and symmetric (C2) E(HOMO) = -7.95514 eV (ionization potential)

E(LUMO) = -1.30441 eV (electron affinity)





Planar and symmetric (Ci) E(HOMO) = -7.62284 eV (ionization potential)

E(LUMO) = -1.13817 eV (electron affinity)





Planar and symmetric group (C2h)E(HOMO) = -8.52735 eV (ionization potential)

E(LUMO) = -1.83150 eV (electron affinity)



Planar and symmetric (C2h)E(HOMO) =-8.65897 eV (ionization potential)

E(LUMO) = -1.79492 eV (electron affinity)





Planar and symmetric (C2h)E(HOMO) = -8.93157 eV (ionization potential)

E(LUMO) = -2.07615 eV (electron affinity)





Planar and symmetric (Ci) E(HOMO) = -7.92708 eV (ionization potential)

E(LUMO) = -1.64451 eV (electron affinity)



Planar and symmetric (C2) E(HOMO) = -8.14821 eV (ionization potential)

 $E(LUMO) = -1.54381 \text{ eV} (electron affinity})$

Solvent Effects on the Absorption and Fluorescence of Compound 8²

The CIS method used to optimize the excited state and to simulate the transitions (CIS) does not predict the ICT states in the gas phase even in the compound **8**, which presents the most probable ICT transition.

Absorption

Excited State 1: Singlet-A,**324.91 nm**, f=2.3618 Excited State 2: Singlet-A, **259.84** nm, f=1.5343

Fluorescence

Excited State 1: Singlet-A, **342.60 nm** f=2.4697



However, if we consider the solvent effect, the quantum calculations describe better spectra of ICT transitions: Stokes shifts increase and the emission band is red shift in polar solvents respect to apolar or gas phase. The effect of the solvent is simulated in two solvents of very different nature (cyclohexane and methanol) using the Polarizable Continuum Model (PCM).

Absorption in cyclohexane

Excited State 1: Singlet-A, **347.14** nm, f=2.6136 $|\overline{M}| = 5.465$ (X= 5.3203, Y=1.2506; Z = 0) Excited State 2: Singlet-A, 271.26 nm, f=2.0102 $|\overline{M}| = 4.237$ (X= 1.4595, Y=3.9776; Z = 0)

Fluorescence in cyclohexane

Excited State 1: Singlet-A, **378.40** nm, f=2.6819 $|\overline{M}| = 5.780(X = 5.7033, Y = 0.9391; Z = 0)$

Absorption in methanol

Excited State 1: Singlet-A, **385.31** nm, f=2.8706 $|\overline{M}| = 6.03 \text{ (X} = 5.8522, \text{Y} = 1.4713; \text{Z} = 0)$ Excited State 2: Singlet-A, 290.03 nm, f=2.5980 $|\overline{M}| = 4.98 \text{ (X} = -1.9212, \text{Y} = -4.5951; \text{Z} = 0)$

Fluorescence in methanol

Excited State 1: Singlet-AM **457.01** nm, f=2.7273 $|\overline{M}| = 6.406 (X = 6.3399, Y = 0.9160; Z = 0)$





Additional Photophysical Data for Selected Cruciforms

Table S1. Main photophysical parameters of compound **1** in different solvents: absorption maxima (λ_{abs} , in nm), logarithm of molar absorption coefficient (lg ε_{max}), fluorescence wavelengths (λ_{fl} , in nm), Stokes shift ($\Delta \gamma_{st}$, in cm⁻¹), fluorescence quantum yield (φ_{fl}), lifetime (τ , in ns) and radiative (k_{fl} , in s⁻¹) and nonradiative deactivation (k_{nr} , in s⁻¹) rate constants.

Solvent	$\lambda_{abs}[nm]$	$\lg \varepsilon_{\max}$	$\lambda_{\mathrm{fl}}[\mathrm{nm}]$	$\Delta\gamma_{ m st}$ [cm ⁻¹]	$oldsymbol{arphi}_{\mathrm{fl}}$	τ [ns]	$k_{ m fl} \left[imes 10^8 { m s}^{-1} ight]$	$k_{ m nr}$ [×10 ⁸ s ⁻¹]
cyclohexane	366	4.89	400/424.5	2340	0.78	1.32	5.91	1.67
dioxane	366	4.89	400/424.5	2320	0.77	1.32	5.83	1.74
DCM	367	4.91	402.5/427	2400	0.77	1.43	5.38	1.61
MeCN	364	4.88	398/422	2350	0.73	1.56	4.68	1.73
EtOH	364.5	4.90	402.5/425	2590	0.73	1.61	4.53	1.68
F3Et*	359.5	_	405.5*	3160	0.72	2.16	3.33	1.30

*solubility problems in F3Et.

Table S2. Main photophysical parameters of compound **5** in different solvents: absorption maxima (λ_{abs} , in nm), logarithm of molar absorption coefficient (lg ε_{max}), fluorescence wavelengths (λ_{fl} , in nm), Stokes shift ($\Delta \gamma_{st}$, in cm⁻¹), fluorescence quantum yield (φ_{fl}), lifetime (τ , in ns) and radiative (k_{fl} , in s⁻¹) and nonradiative deactivation (k_{nr} , in s⁻¹) rate constants.

Solvent	$\lambda_{abs}[nm]$	$\lg \varepsilon_{\max}$	$\lambda_{\rm fl}[\rm nm]$	$\Delta \gamma_{\rm st} \left[{ m cm}^{-1} ight]$	$oldsymbol{arphi}_{\mathrm{fl}}$	τ [ns]	$k_{ m fl} \left[imes 10^8 { m s}^{-1} ight]$	$k_{ m nr}$ [×10 ⁸ s ⁻¹]
cyclohexane*	366	—	418	3400	0.62*	2.10	2.95	1.81
dioxane	367	4.80	427	3830	0.74	2.51	2.95	1.04
DCM	367	4.81	434	4210	0.64	2.48	2.58	1.45
MeCN	365	4.80	433	4300	0.65	2.95	2.20	1.19
EtOH	365	4.80	452	5270	0.67	3.61	1.86	0.91
F3Et	360.5	4.81	472	6550	0.01	—		—

*solubility problem in cyclohexane (high error in φ calculated due to the low absorbance at the excitation wavelength).

Table S3. Main photophysical parameters of compound **6** in different solvents: absorption maxima (λ_{abs} , in nm), logarithm of molar absorption coefficient (lg ε_{max}), fluorescence wavelengths (λ_{fl} , in nm), Stokes shift ($\Delta \gamma_{st}$, in cm⁻¹), fluorescence quantum yield (φ_{fl}), lifetime (τ , in ns) and radiative (k_{fl} , in s⁻¹) and nonradiative deactivation (k_{nr} , in s⁻¹) rate constants.

Solvent	$\lambda_{abs} [nm]$	$\lg \varepsilon_{\max}$	$\lambda_{\rm fl}[\rm nm]$	$\Delta \gamma_{\rm st} \left[{ m cm}^{-1} ight]$	$oldsymbol{arphi}_{\mathrm{fl}}$	τ[ns]	$k_{ m fl} \left[imes 10^8 { m s}^{-1} ight]$	$k_{ m nr}$ [×10 ⁸ s ⁻¹]
cyclohexane*	366	—	401	2380	0.75	1.56	4.81	1.60
dioxane	367	4.78	413	3030	0.73	2.01	3.63	1.34
DCM	368	4.79	415	3080	0.72	1.96	3.67	1.43
MeCN	366	4.79	418	3400	0.71	2.36	3.01	1.23
EtOH	368	4.75	418	3250	0.77	2.28	3.38	1.01
F3Et	362	4.82	426 ¹	3760	0.35	1.16 ²	2.16	6.46
			533 ¹			1.90 ²	1.05	4.21

*solubility problems in cyclohexane. ¹Emission maxima after deconvolution. ²Lifetimes recorded at both emission maxima (τ_1 correspond to 426 nm and τ_2 to 533 nm emission maxima, respectively)

Table S4. Main photophysical parameters of compound 7 in different solvents: absorption maxima (λ_{abs} , in nm), logarithm of molar absorption coefficient (lg ε_{max}), fluorescence wavelengths (λ_{fl} , in nm), Stokes shift ($\Delta \gamma_{st}$, in cm⁻¹), fluorescence quantum yield (φ_{fl}), lifetime (τ , in ns) and radiative (k_{fl} , in s⁻¹) and nonradiative deactivation (k_{nr} , in s⁻¹) rate constants.

Solvent	$\lambda_{abs}[nm]$	$\lg \varepsilon_{\max}$	$\lambda_{\rm fl}[\rm nm]$	$\Delta \gamma_{\rm st} [{\rm cm}^{-1}]$	$oldsymbol{arphi}_{\mathrm{fl}}$	τ [ns]	$k_{ m fl} \left[imes 10^8 { m s}^{-1} ight]$	$k_{ m nr}$ [×10 ⁸ s ⁻¹]
cyclohexane*	370	—	399	1960	0.81	1.63	4.97	1.17
ioxane	365	4.88	402	2520	0.79	1.92	4.11	1.09
DCM	366.5	5.06	404	2530	0.74	1.88	3.94	1.38
MeCN*	364	4.79	401	2535	0.77	2.16	3.56	1.06
EtOH	366	4.83	407	2750	0.79	2.34	3.34	0.90
F ₃ Et	363.5	4.87	409	3060	0.40	(1)		

*solubility problem in cyclohexane.

(1) multiexponetial behavior:

$\lambda_{\rm ex} / \lambda_{\rm em} [\rm nm]$	$ au_1(\%)$	$ au_2(\%)$	$ au_3(\%)$
370/450	0.12 (43)	1.08 (43)	2.76 (14)
370/550	0.18(A<0)	4.83	

Additional Absorption and Emission Spectra of Compounds 7 and 8



Figure S1. Height-normalized absorption and emission spectra of compound 7 in different solvents: cyclohexane (black), dioxane (red), DCM (green), MeCN (blue) and EtOH (cyan).



Figure S2. On the left, height-normalized absorption and emission spectra of compound **8** in different solvents: cyclohexane (black), dioxane (red) and DCM (green). On the right, color of the emission of compound **8** in cyclohexane (black), dioxane (red) and DCM(green) under UV light ($\lambda_{exc} = 365$ nm)

References

- 1 Overall, the HOMO-LUMO energy gaps are higher than the theoretically predicted energy of the absorption transition. This is a well-known feature; while the HOMO-LUMO gap should be related with the absorption transition, this is quite a rough estimation. A more accurate prediction of the absorption energy can be obtained by theoretical methods, wherein the absorption process is simulated as a vertical Franck-Condon transition. To this end, a single point calculation in the first singlet excited state is performed from the optimized ground state geometry. See: (a) J. B. Foresman and H. Frisch, in *Exploring Chemistry with Electronic Structure* Methods, Gaussian Inc., Pittsburgh, PA, 1996. Among the different methods available in the literature we have chosen the Configuration Interaction Singles (CIS), see: (b) J. B. Foresman, M. Head-Gordon, J. A. Pople and M. J. Frisch, J. Phys. Chem., 1992, 96, 135-149. This method was chosen because of its low computational cost (keeping in mind the high number of atoms of the fluorophores), and reasonably high accuracy. In addition, this method also allowed the optimization of the excited state geometry and could be combined with other methods which simulate the solvent effect, such as the Polarizable Continuum Model (PCM), see: (c) S. Miertus, E. Scrocco and J. Tomasi, Chem. Phys., 1981, 55, 117-129.
- 2 The Gaussian output file provides the absorption energy and wavelength, the transition dipole moment (M) and the probability by the oscillator strength (f). The GaussView program plots this information as a spectrum, where the electronic transitions are fitted to symmetric Gaussians. Therefore, the spectral line-widths are not very realistic with regard to the experimental recorded absorption spectra, but present an intuitive way to compare them with the theoretically predicted ones.