Supporting information

Benzimidazolequinoxalines: Novel Fluorophores with Tuneable Sensitivity to Solvent Effects

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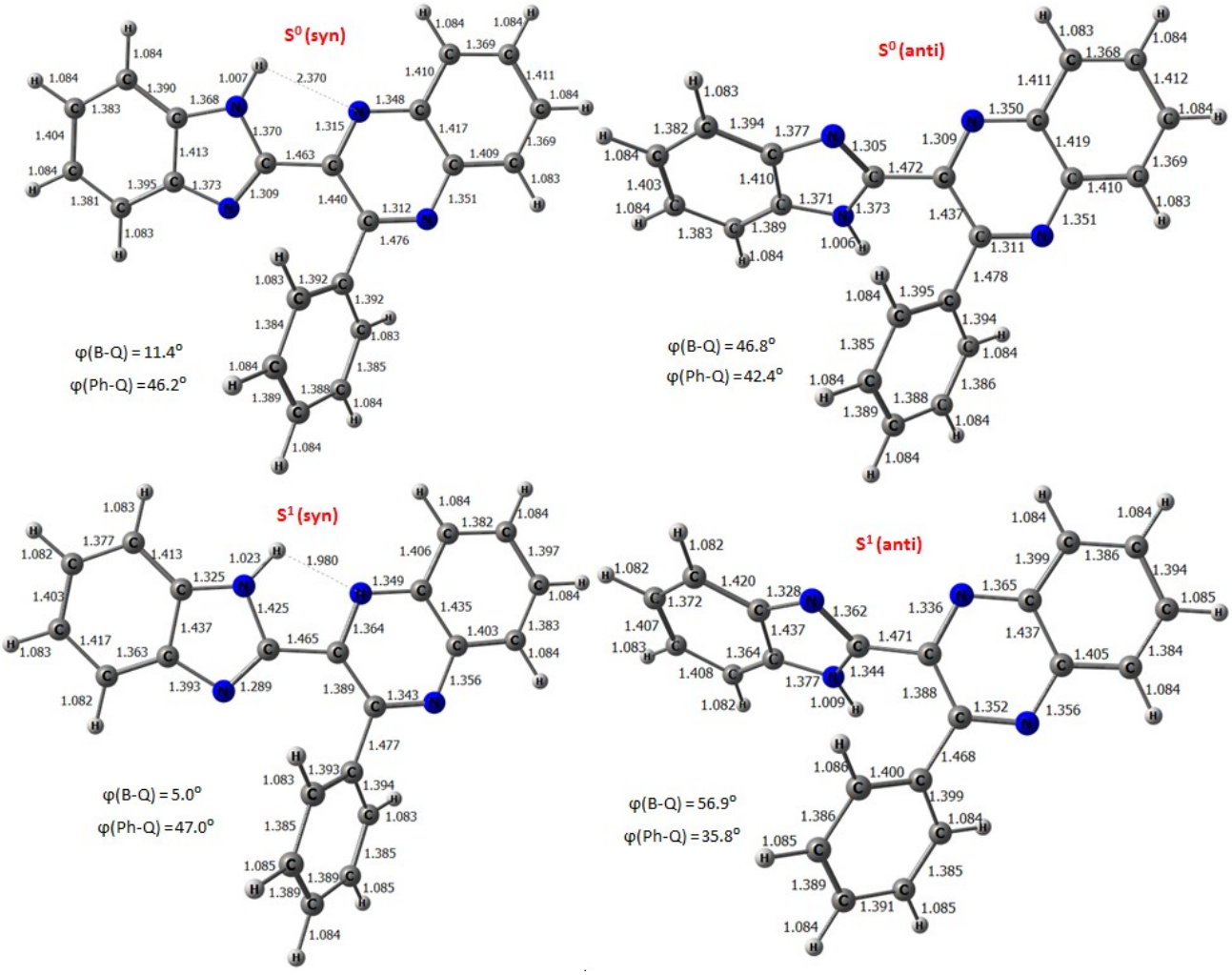
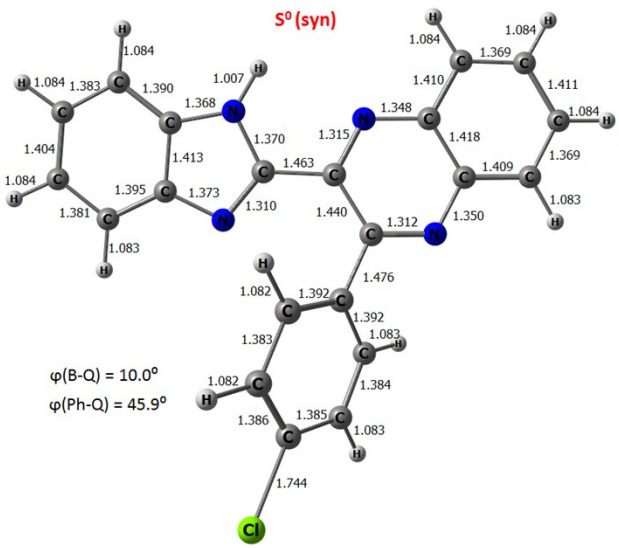
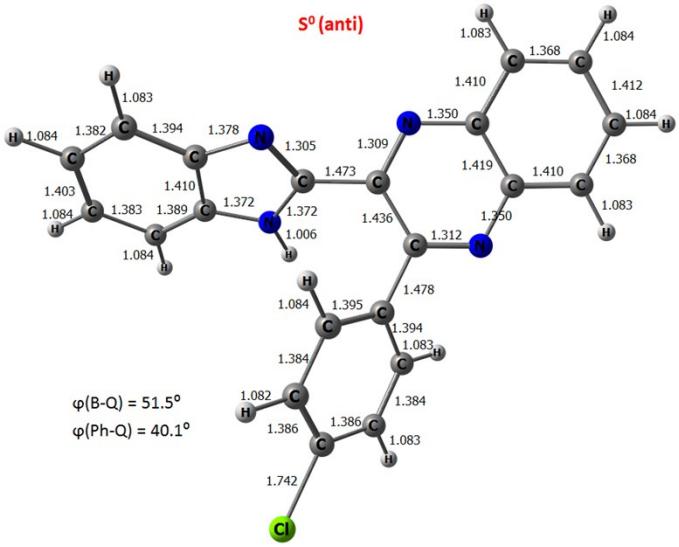
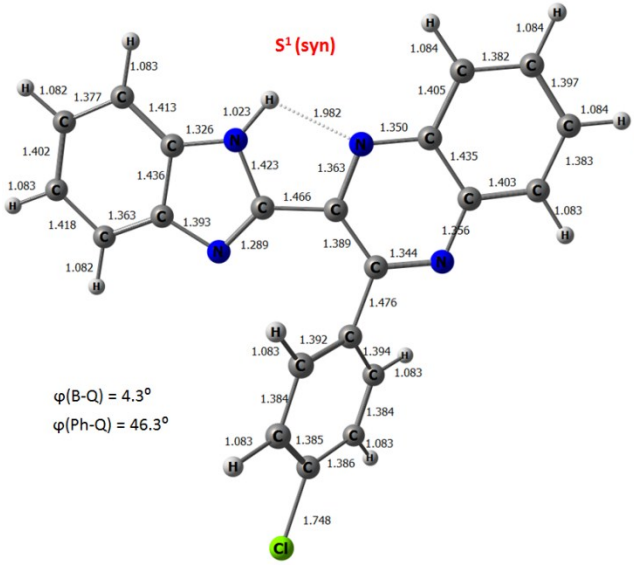
Figure 1S. The computed geometries of the *syn*- and *anti*-conformers of **1**, **4** and **6** in the ground state and in the excited state. Distances – in Å; φ - dihedral angles between the benzimidazole (B), quinoxaline (Q) and phenyl (Ph) rings.

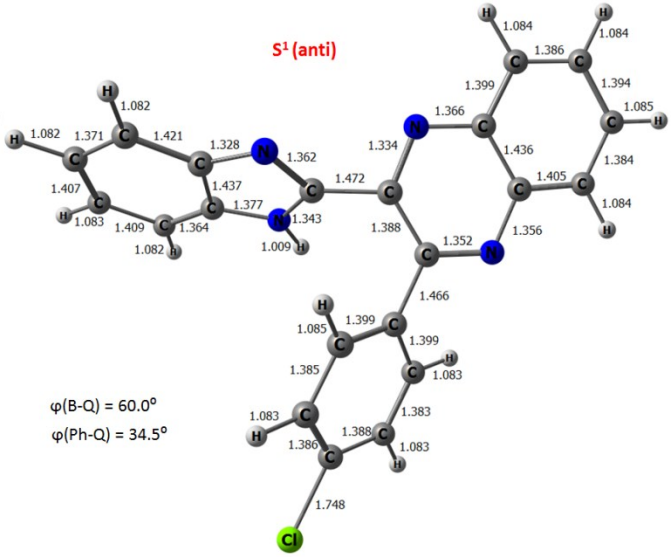


1

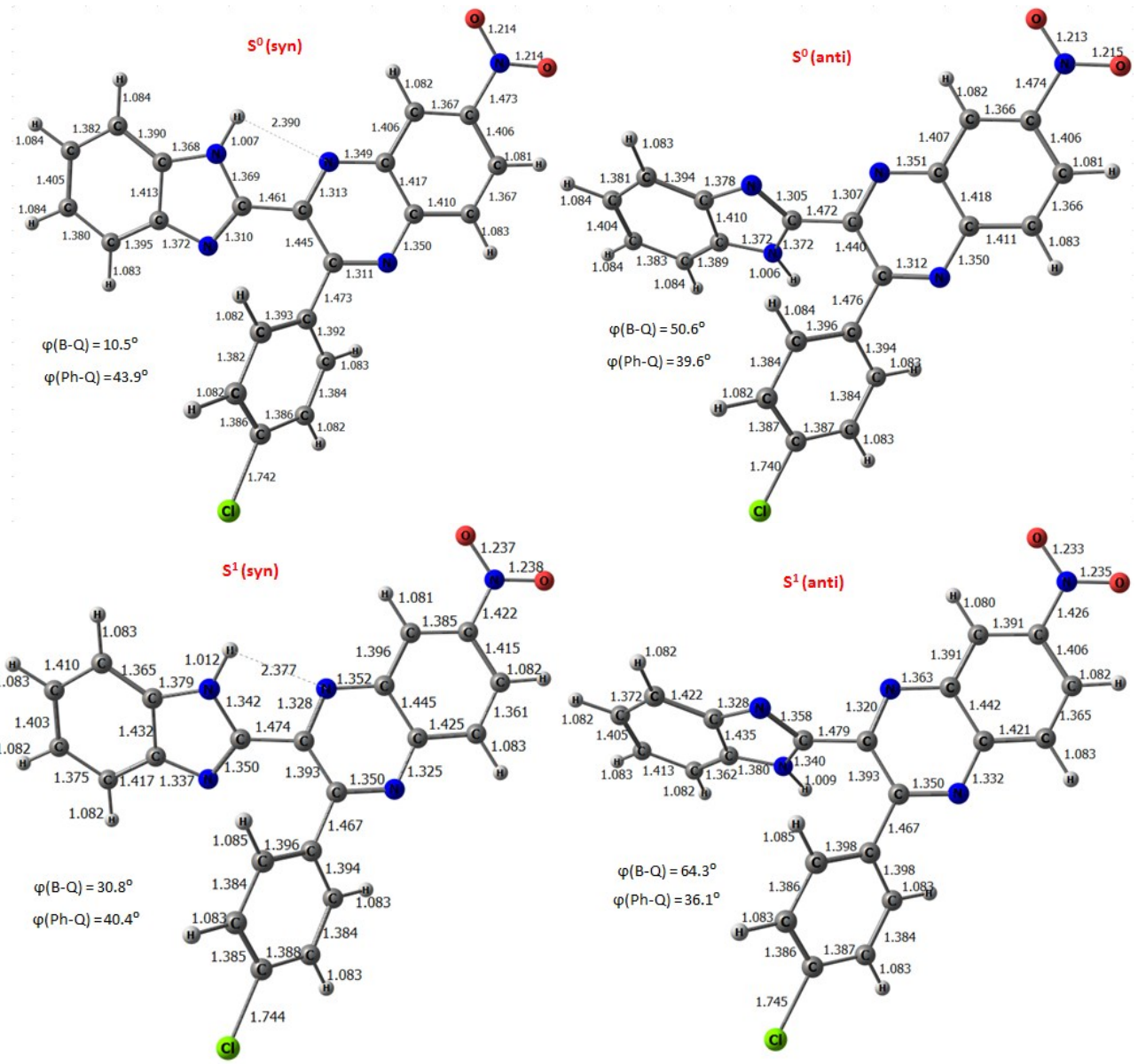

S⁰ (syn)
φ(B-Q) = 10.0°
φ(Ph-Q) = 45.9°


S⁰ (anti)
φ(B-Q) = 51.5°
φ(Ph-Q) = 40.1°


S¹ (syn)
φ(B-Q) = 4.3°
φ(Ph-Q) = 46.3°


S¹ (anti)
φ(B-Q) = 60.0°
φ(Ph-Q) = 34.5°

4


S0 (syn)
φ(B-Q) = 10.5°
φ(Ph-Q) = 43.9°
S0 (anti)
φ(B-Q) = 50.6°
φ(Ph-Q) = 39.6°
S1 (syn)
φ(B-Q) = 30.8°
φ(Ph-Q) = 40.4°
S1 (anti)
φ(B-Q) = 64.3°
φ(Ph-Q) = 36.1°

6

Figure 2S. TDDFT simulated absorption spectra of *syn*- (red lines) and *anti*-conformers (blue lines) of **2** in comparison with the experimental spectrum registered for **2** solutions in DCE (black line) and DMF (green line). The heights of the vertical straight lines correspond to the calculated oscillator strengths of the corresponding vertical transitions. Red and blue envelope curves are obtained by broadening of the vertical straight lines by Gaussian functions with a full-width at 1/e height of 0.4 eV.

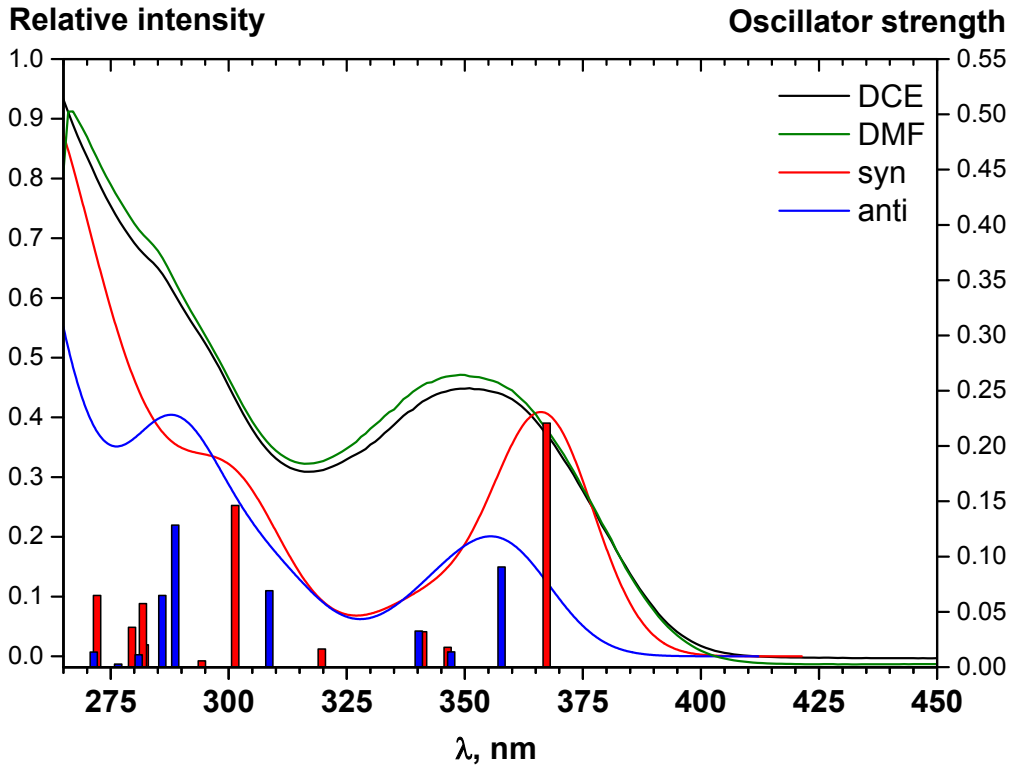
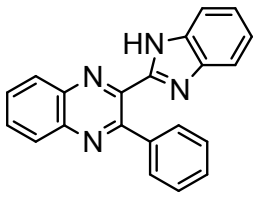
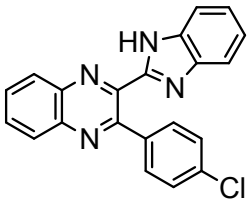
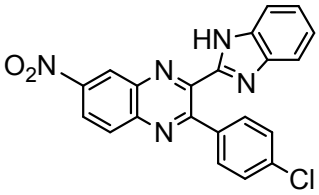


Table 1S. Structural parameters of intra- and intermolecular H-bonds or short contacts of **1, 4, 6** in ground (S_0) and excited (S_1) states. All bond lengths and their changes are given in Å.

Compound	Confor-mer	Bond length	1:1 H-complex with DMSO[a]		isolated molecules[b]	
			State		State	
			S_0	S_1	S_0	S_1
 **1**	*syn*	NH	1.0282	1.0746	1.0072	1.0234
		ΔNH	0.0211	0.0512		
		H···O	1.7649	1.5230		
		SO	1.5292	1.5528		
	anti	NH	1.0291	1.0845	1.0059	1.0091
		ΔNH	0.0232	0.0754		
		H···O	1.7340	1.4996		
		SO	1.5303	1.5540		
		$\Delta NH_{syn-anti}$	-	-	0.0012[c]	0.0143
 **4**	*syn*	NH	1.0285	1.0752	1.0072	1.0235
		ΔNH	0.0213	0.0517		
		H···O	1.7626	1.5203		
		SO	1.5293	1.5528		
	anti	NH	1.0285	1.0850	1.0057	1.0089
		ΔNH	0.0228	0.0762		
		H···O	1.7415	1.4963		
		SO	1.5303	1.5539		
		$\Delta NH_{syn-anti}$	-	-	0.0015[e]	0.0146
 **6**	*syn*	NH	1.0310	1.0849	1.0072	1.0120
		ΔNH	0.0238	0.0730		
		H···O	1.7380	1.4881		
		SO	1.5303	1.5539		
	anti	NH	1.0228	1.0871	1.0058	1.0089
		ΔNH	0.0171	0.0783		
		H···O	1.8170	1.4832		
		SO	1.5307	1.5531		
		$\Delta NH_{syn-anti}$	-	-	0.0014[f]	0.0031

[a]Strength of intermolecular H-bond N–H···O=S in 1:1 H-complex with DMSO is characterized by: i) elongation of N-H bond in the H-complex relative to isolated benzimidazolequinoxaline molecule, ΔNH; ii) H···O bond length; iii) S=O bond length. Increase in the H-bond strength results in increase of ΔNH and S=O bond length, and simultaneously in decrease of H···O bond length. [b]Relative strength of intramolecular N–H···N interaction is characterized by elongation of N-H bond of *syn*-conformer relative to *anti*-conformer, $\Delta NH_{syn-anti}$. [c]Relative change of frequency of stretching vibrations $\Delta\nu NH_{syn-anti}$ = -10 cm^{-1}; the corresponding change of IR intensity $\Delta I(\nu NH)_{syn-anti}$ = 21 $km \cdot mol^{-1}$. [d]$\Delta\nu NH_{syn-anti}$ = -14 cm^{-1}; $\Delta I(\nu NH)_{syn-anti}$ = 25 $km \cdot mol^{-1}$. [e]$\Delta\nu NH_{syn-anti}$ = -14 cm^{-1}; $\Delta I(\nu NH)_{syn-anti}$ = 24 $km \cdot mol^{-1}$. [f]$\Delta\nu NH_{syn-anti}$ = -13 cm^{-1}; $\Delta I(\nu NH)_{syn-anti}$ = 23 $km \cdot mol^{-1}$.

Table 2S. Experimental wavelengths (nm) of emission (emi) and the lowest-energy absorption (abs) maxima as compared with the corresponding wavelengths calculated for *syn*- and *anti*-conformers.

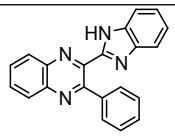
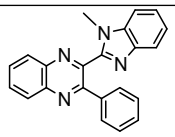
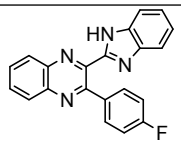
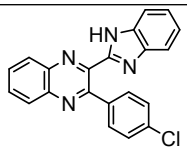
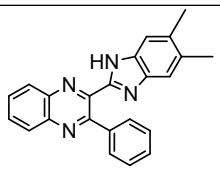
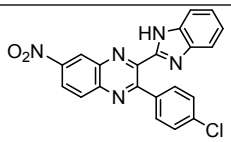
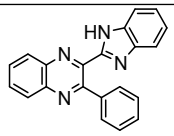
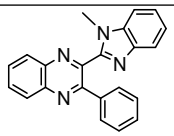
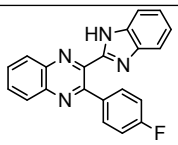
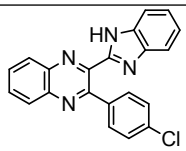
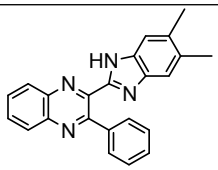
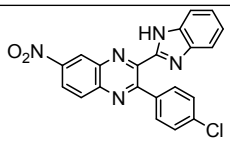
Compound	Type	Experiment			Calculations	
		DCE solution	DMF solution	DMSO solution	*syn*	*anti*
 **1**	abs	373	367	367	368	355
	emi	440	460	470	438	448
 **2**	abs	352	352	352	367	359
	emi	446	465	470	467	473
 **3**	abs	375	370	370	373	355
	emi	444	462	468	440	450
 **4**	abs	375	371	371	373	358
	emi	446	468	470	442	454
 **5**	abs	383	383	380	382	377
	emi	473	492	501	466	483
 **6**	abs	396	391	391	412	406
	emi	519	--	--	513	551

Table 3S. Calculated dipole moments (D) for S_0 and S_1 states of both *syn* and *anti* conformers.

Compound	conformer	Calculated dipole moments	
		S_0	S_1
 **1**	*syn*	2.80	12.04
	anti	3.37	14.23
 **2**	*syn*	3.15	14.25
	anti	3.73	15.18
 **3**	*syn*	4.45	12.23
	anti	2.97	14.23
 **4**	*syn*	4.80	12.51
	anti	2.97	13.78
 **5**	*syn*	2.79	14.56
	anti	3.17	17.81
 **6**	*syn*	2.43	18.49
	anti	6.12	21.97