Supporting Information for

On the selective detection of duplex deoxyribonucleic acids by 2,1,3-benzothiadiazoles fluorophores

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Table S1. Selected bond angles and distances from x-ray data of compounds **3a** and **3b**.

selected atoms	d (Å) **3a**	d (Å) **3b**[1]	selected atoms	angle (deg) **3a**	angle (deg) **3b**[1]
C21-C1	1.439(2)	1.431(3)			
C1-C2	1.197(2)	1.200(3)			
C2-C3	1.427(2)	1.424(3)	N1-S1-N2	101.20(7)	
C3-C4	1.379(2)	1.371(3)	C7-N1-S1	106.61(10)	101.03(9)
C4-C5	1.414(2)	1.414(3)	C8-N2-S1	106.00(11)	107.25(15)
C5-C6	1.381(2)	1.377(3)	N1-C7-C8	112.65(13)	106.26(13)
C6-C7	1.438(2)	1.440(3)	N2-C8-C7	113.53(14)	111.55(17)
C7-C8	1.437(2)	1.438(3)	C21-C1-C2	172.16(17)	113.90(18)
C8-C3	1.430(2)	1.424(3)	C1-C2-C3	176.85(18)	174.90(2)
N1-C7	1.347(2)	1.356(2)			179.40(3)
N2-C8	1.347(2)	1.348(3)			
S1-N1	1.612(1)	1.609(2)			
S1-N2	1.615(1)	1.607(2)			

[1] mean values of three independent molecules

Table S2. Summary of the crystal data and structure refinement for **3a** and **3b**.

Parameter	**3a**	**3b**
Empirical formula	$C_{20}H_{13}N_3OS$	$C_{20}H_{13}N_3OS$
Formula weight	343.39	343.39
Temperature	200(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	6
Unit cell dimensions		
a (Å)	8.963(1)	7.4910(1)
b (Å)	9.048(1)	16.4275(3)
c (Å)	10.465(1)	21.0326(3)
α (deg)	111.391(2)	107.378(1)
β (deg)	90.220(2)	96.119(1)
γ (deg)	91.569(2)	97.804(1)
Volume	789.76(16) $Å^3$	2417.40(6) $Å^3$
Density (calculated)	1.44 g/cm^3	1.41 g/cm^3
Absorption coefficient	0.22 mm^{-1}	0.21 mm^{-1}
Crystal shape	polyhedron	polyhedron
Crystal size	0.36 x 0.29 x 0.24 mm^3	0.48 x 0.38 x 0.10 mm^3
Crystal colour	yellow	yellow
Theta range	2.1 to 28.3 deg.	1.9 to 27.5 deg.
Index ranges	$-11 \le h \le 11$ $-12 \le k \le 12$ $-13 \le l \le 13$	$-9 \le h \le 9$ $-21 \le k \le 21$ $-27 \le l \le 27$
Reflections collected	8197	24828
Independent reflections	3875 (R(int) = 0.0193)	10995 (R(int) = 0.0685)
Observed reflections	3307 ($I > 2\sigma(I)$)	6623 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max./min. transmission	0.95 / 0.93	0.98 / 0.90
Data/restraints/parameters	3875 / 0 / 227	10995 / 0 / 679
Goodness-of-fit on F^2	1.05	1.01
Final R indices ($I > 2\sigma(I)$)	R1 = 0.042, wR2 = 0.106	R1 = 0.051, wR2 = 0.120
Largest diff. peak and hole	0.34 and -0.26 $eÅ^{-3}$	0.25 and -0.39 $eÅ^{-3}$

Table S3. Spectrometric data of all tested compounds **1a-c**, **2a-b**, **3a-c.**

Dye	Log ε (ε)	λ_{abs}^{max} (nm)[a]	λ_{em}^{max} (nm)[a]	Stokes Shift (nm)	λ_{abs}^{max} (nm)[b]	λ_{em}^{max} (nm)[b]	Stokes Shift (nm)[b]	Φ_f	E_{gap}^{op} (eV)[d]
1a	4.35 (22342)	365	471	106	452	543	91	0.86	2.81
1b	3.76 (5790)	429	563	134	522	590	68	0.29	2.29
1c	3.81 (6482)	438	552	114	424	543	119	0.37	1.90
2a	3.22 (1644)	411	535	124	418	526	108	0.51	1.85
2b	3.33 (2150)	367	506	139	426	493	67	0.80	2.28
3a	3.97 (9152)	444	544	100	491	535	44	0.40	2.21
3b	3.78 (6076)	401	547	146	430	531	101	0.44	2.20
3c	4.01 (10208)	426	525	99	413	525	112	0.47	2.22

[a] In solution (phosphate buffer 10 μM, pH = 7.0). [b] Solid state. [c] Quantum yield of fluorescence in MeCN (quinine sulfate (Riedel) in 1 M H_2SO_4, $\Phi_f = 0.55$, as standard. [d] Determined in phosphate buffer 100 mM (pH = 7.0).

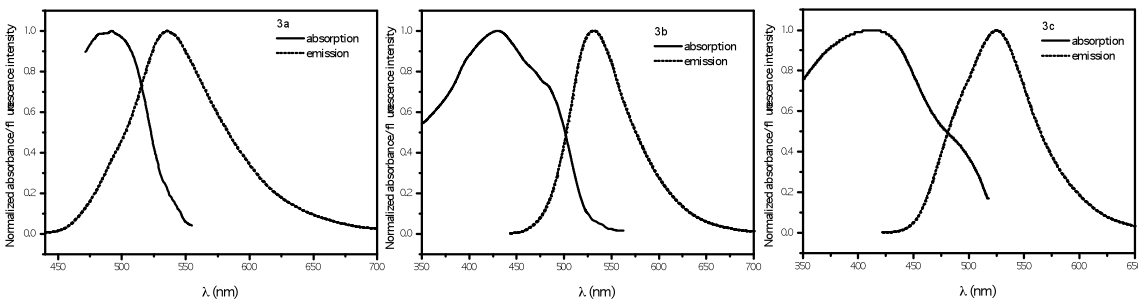

Figure S1. Solid-state (normalized) absorption and emission of dyes **3a-c**.

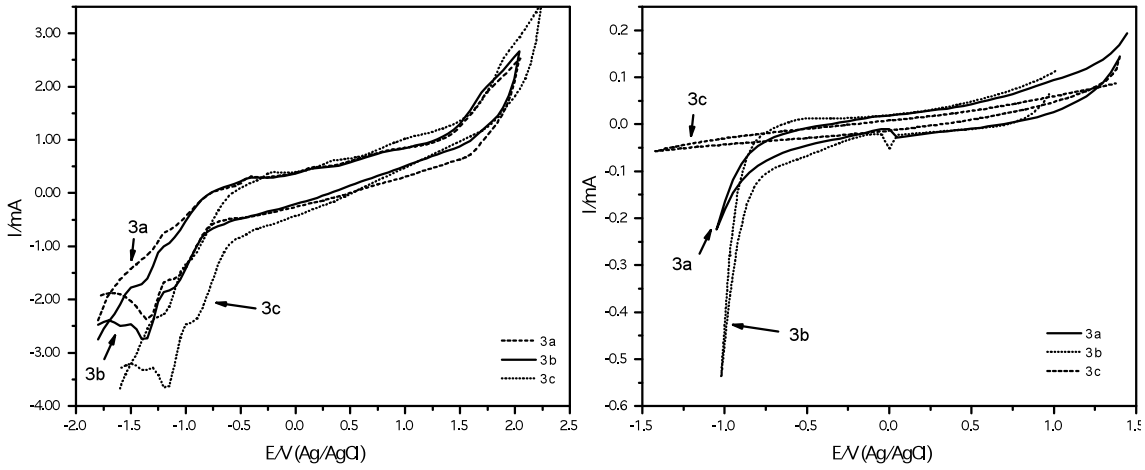

Figure S2. CV of compounds **3a-c** (1.00 mM) dissolved in a 0.10 M solution $TBAPF_6$ in MeCN recorded at a scan rate of 200 mV/s (left) and CV (thin film coated onto a Pt wire electrode) of compounds **3a-c** recorded at a scan rate of 40 mV/s in a 0.10 M solution of $TBAPF_6$ in MeCN (right).

All compounds exhibited a very similar electrochemical behavior and it was possible to observe quasi-reversible processes. Compounds **3a-c** presented a large electrochemical window, *i.e.*, from -2.0 V to 2.0 V (Ag/AgCl) for the anodic and cathodic potential sweeps, respectively. For **3a**, the related values were 0.89 V (and -0.34 V), 0.18 V (and -1.09 V) and -0.41 V (related to -1.35 V). For **3b**, we observed 0.76 V (and -0.35 V), 0.16 V (and -1.12 V) and -0.41 V (related to -1.38 V), as for **3b** at 0.76 V (and -0.35 V), 0.16 V (and -1.12 V) and -0.41 V (related to -1.38 V). In the case of **3c,** an anodic shift in the CV and the related observed values were 0.98 V (and -0.27 V), 0.38 V (and -0.91 V), and -0.20 V (related to -1.19 V). In the solid state, the dyes presented a good electrochemical stability. In the electrochemical window tested (-1.5-1.5 V), a well-defined reduction or oxidation peak was not observed, indicating a larger electrochemical window and stability than the limits of the solvent oxidation and reduction windows.

Table S4. *Ab initio* calculation of the HOMO-LUMO values for tested dyes and bases.

Structure		Hartree	eV	kJ/mol
	HOMO	-0.279	-7.59198	-732.515
3a	LUMO	0.03545	0.964644	93.07398
	GAP	0.31445	8.556625	825.5885
	HOMO	-0.27971	-7.6113	-734.379
3b	LUMO	0.03292	0.895799	86.43146
	GAP	0.31263	8.5071	820.8101
	HOMO	-0.27582	-7.50545	-724.165
3c	LUMO	0.03656	0.994849	95.98828
	GAP	0.31238	8.500297	820.1537
	HOMO	-0.28316	-7.70518	-743.437
3a'	LUMO	0.04817	1.310773	126.4703
	GAP	0.33133	9.015953	869.9069
	HOMO	-0.28439	-7.73865	-746.666
3b'	LUMO	0.04011	1.091449	105.3088
	GAP	0.32450	8.830099	851.9748
	HOMO	-0.28057	-7.6347	-736.637
3c'	LUMO	0.04514	1.228323	118.5151
	GAP	0.32571	8.863025	855.1516
	HOMO	-0.29852	-8.12315	-783.764
Adenine	LUMO	0.14434	3.927693	378.9647
	GAP	0.44286	12.05084	1162.729
	HOMO	-0.32146	-8.74738	-843.993
Cytosine	LUMO	0.13235	3.601429	347.4849
	GAP	0.45381	12.34881	1191.478
	HOMO	-0.28788	-7.83362	-755.829
Guanine	LUMO	0.15706	4.273822	412.361
	GAP	0.44494	12.10744	1168.19
	HOMO	-0.33245	-9.04643	-872.847
Thymine	LUMO	0.12834	3.492311	336.9567
	GAP	0.46079	12.53874	1209.804