Supporting Information

Modeling the effect of ionic additives on the optical and electronic properties of a dye-sensitized TiO_2 heterointerface: Absorption, charge injection and aggregation.

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Optimized Structures of the D102/additive adducts

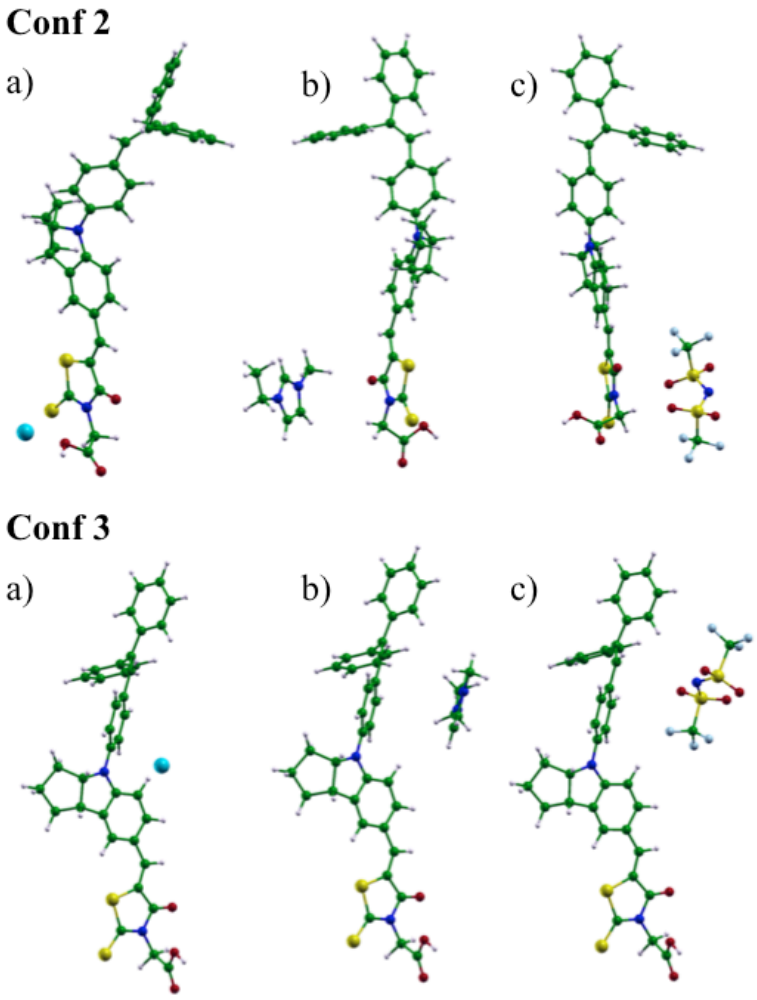

Figure S1. Optimized structures in acetonitrile of (a) D102/Li^+, (b) D102/$EMIM^+$, (c) D102/$TFSI^-$. Here, atom color for Carbon is green, Hydrogen is white, Nitrogen is blue, Oxygen is red, Fluorine is cyan, Sulfur is yellow and Lithium is cyan.

Calculated absorption spectra in solution

The calculated absorption maxima along with the calculated HOMO/LUMO energies and HOMO/LUMO gaps are listed in Table S1, while the simulated absorption spectra in acetonitrile are displayed in Figure S2.

Table S1. Experimental and theoretically calculated E_{max} and energy shifts compared to D102 dye and corresponding HOMO (H), LUMO (L) energies, and H–L gap (Δ_{HL}) in eV units.

Systems	***Exp***	***Acetonitrile***				
	E_{max}	E_{exc}	**Shift**	**H**	**L**	Δ_{HL}
D102	2.51	2.36	0.00	-5.34	-2.71	2.63
D102/Li^+	--	2.23	0.13	-5.49	-3.03	2.46
D102/$EMIM^+$	--	2.31	0.05	-5.41	-2.84	2.57
D102/$TFSI^-$	--	2.35	0.01	-5.26	-2.65	2.61
D102/Li-TFSI	2.49	2.23	0.13	-5.43	-2.98	2.45
D102/EMIM-TFSI	2.48	2.31	0.05	-5.33	-2.76	2.57

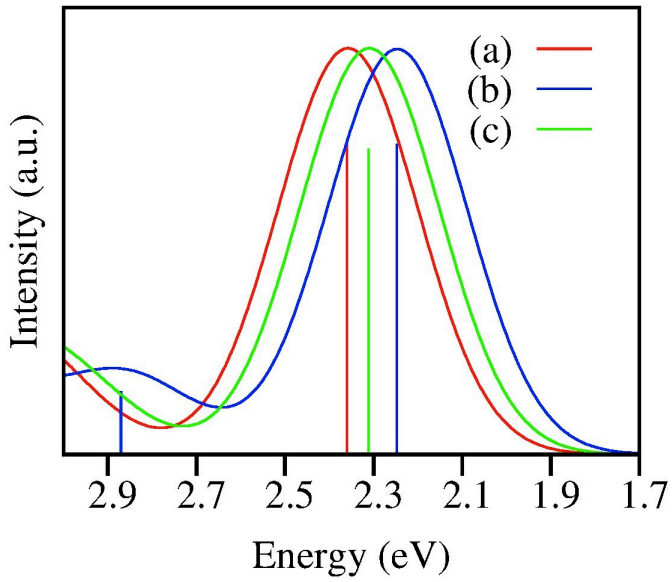

Figure S2. Calculated absorption spectra of (a) D102 (red line), (b) D102/Li^+ (blue line) and (c) D102/$EMIM^+$ (green line).

Calculated absorption spectra on TiO_2

Table S2. Experimental and calculated absorption maxima (λ_{max} in eV), calculated main vertical transitions energies (E_{exc} in eV), corresponding oscillator strengths and main single excitations contributing to the absorption band.

Systems	(Exp) λ_{max} (eV)	(Theo) λ_{max} (eV)	Main E_{exc} (osc. strength)	Main excitatio

				ns
D102@TiO_2	2.58	2.11	2.08 (0.122), 2.09 (0.202), 2.11 (0.262), 2.12 (0.112)	H->L+42 H->L+47
D102/Li^+@TiO_2	2.54	2.00	2.00 (0.817)	H->L+20
D102/$EMIM^+$@TiO_2	2.61	2.10	2.10 (0.372), 2.11 (0.269)	H->L+45 H->L+46