Computational investigation of tuning the electron donating ability in metal-free organic dyes featuring an azobenzene spacer for dye-sensitized solar cells

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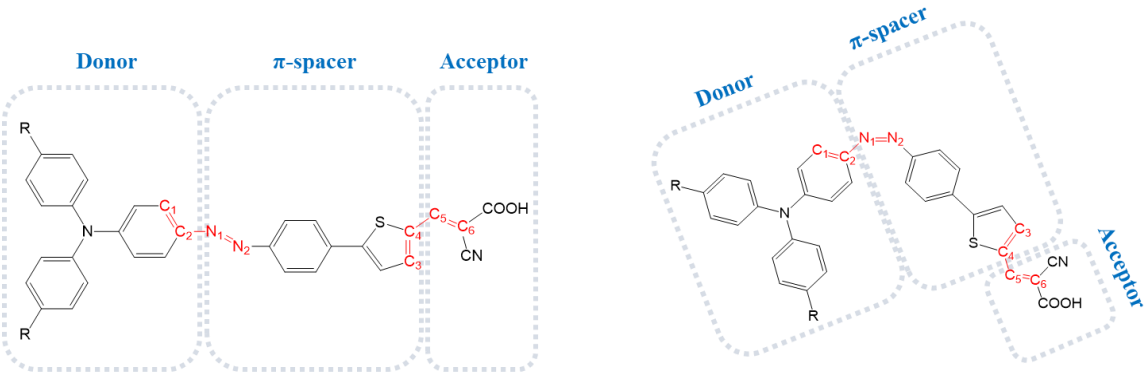
Table S1. Conjugative interaction energies ($\Delta E^{(2)}$, in kcal/mol) between the π and π* orbitals in the azo-benzene based dyes from the second-order perturbation theory analysis within NBO analysis.



Dyes	Donor orbital (π)	Acceptor orbital (π*)	$\Delta E^{(2)}$ [kcal mol^{-1}]	E_{acc}-E_{don} [a.u]	F(acc, don) [a,u]
(*E*)-DAC1	π(C_1≡C_2)	π*(N_1=N_2)	24.06	0.23	0.069
	π(C_3=C_4)	π*(C_5=C_6)	23.25	0.30	0.075
(*E*)-DAC2	π(C_1≡C_2)	π*(N_1=N_2)	24.55	0.23	0.069
	π(C_3=C_4)	π*(C_5=C_6)	23.36	0.30	0.075
(*E*)-DAC3	π(C_1≡C_2)	π*(N_1=N_2)	25.13	0.23	0.070
	π(C_3=C_4)	π*(C_5=C_6)	23.49	0.30	0.075
(*E*)-DAC4	π(C_1≡C_2)	π*(N_1=N_2)	26.27	0.22	0.071
	π(C_3=C_4)	π*(C_5=C_6)	23.77	0.30	0.075
(*Z*)-DAC1	π(C_1≡C_2)	π*(N_1=N_2)	15.53	0.24	0.057
	π(C_3=C_4)	π*(C_5=C_6)	23.37	0.30	0.075
(*Z*)-DAC2	π(C_1≡C_2)	π*(N_1=N_2)	16.26	0.24	0.058
	π(C_3=C_4)	π*(C_5=C_6)	23.48	0.30	0.075
(*Z*)-DAC3	π(C_1≡C_2)	π*(N_1=N_2)	17.61	0.24	0.061
	π(C_3=C_4)	π*(C_5=C_6)	23.62	0.30	0.075
(*Z*)-DAC4	π(C_1≡C_2)	π*(N_1=N_2)	19.48	0.23	0.063
	π(C_3=C_4)	π*(C_5=C_6)	24.83	0.29	0.077

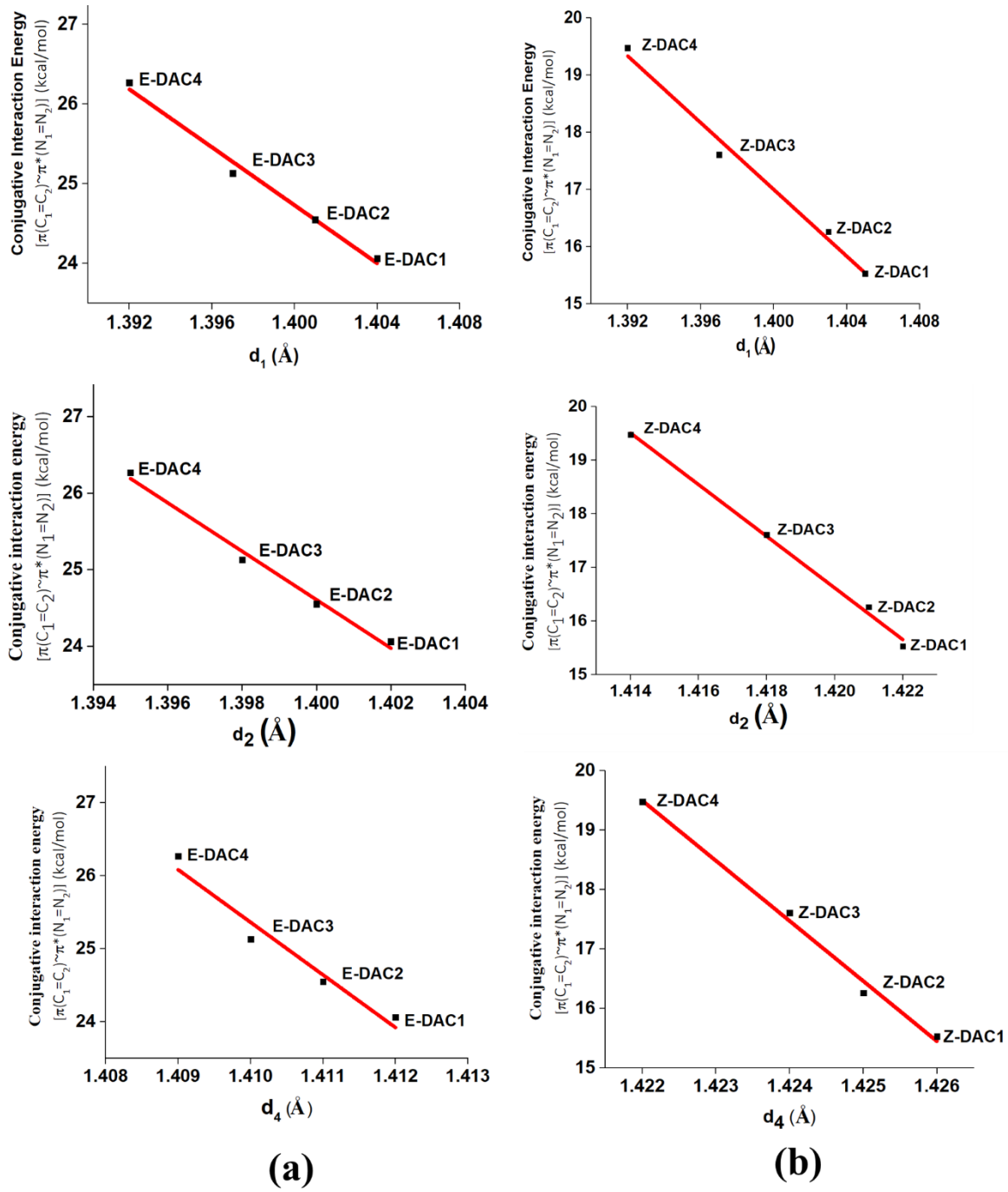


Figure S1 Conjugative interaction energies ($\Delta E^{(2)}$, in kcal/mol) between the π and π^* orbitals as a function of the d_1, d_2, and d_4 bond distance for (a) trans dyes, and (b) cis dyes.

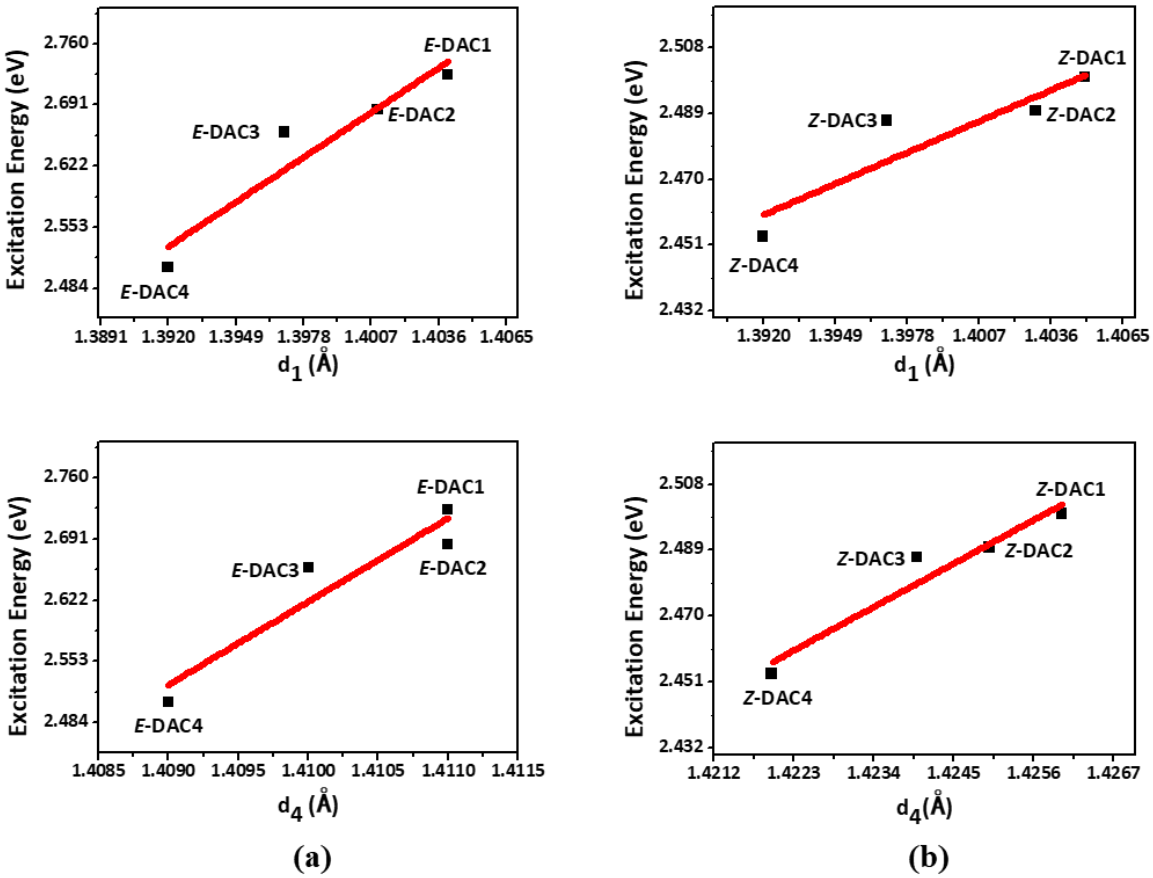


Figure S2 Plots of Excitation energy vs distance d_1, and d_4 for (a) trans dyes and (b) cis dyes.

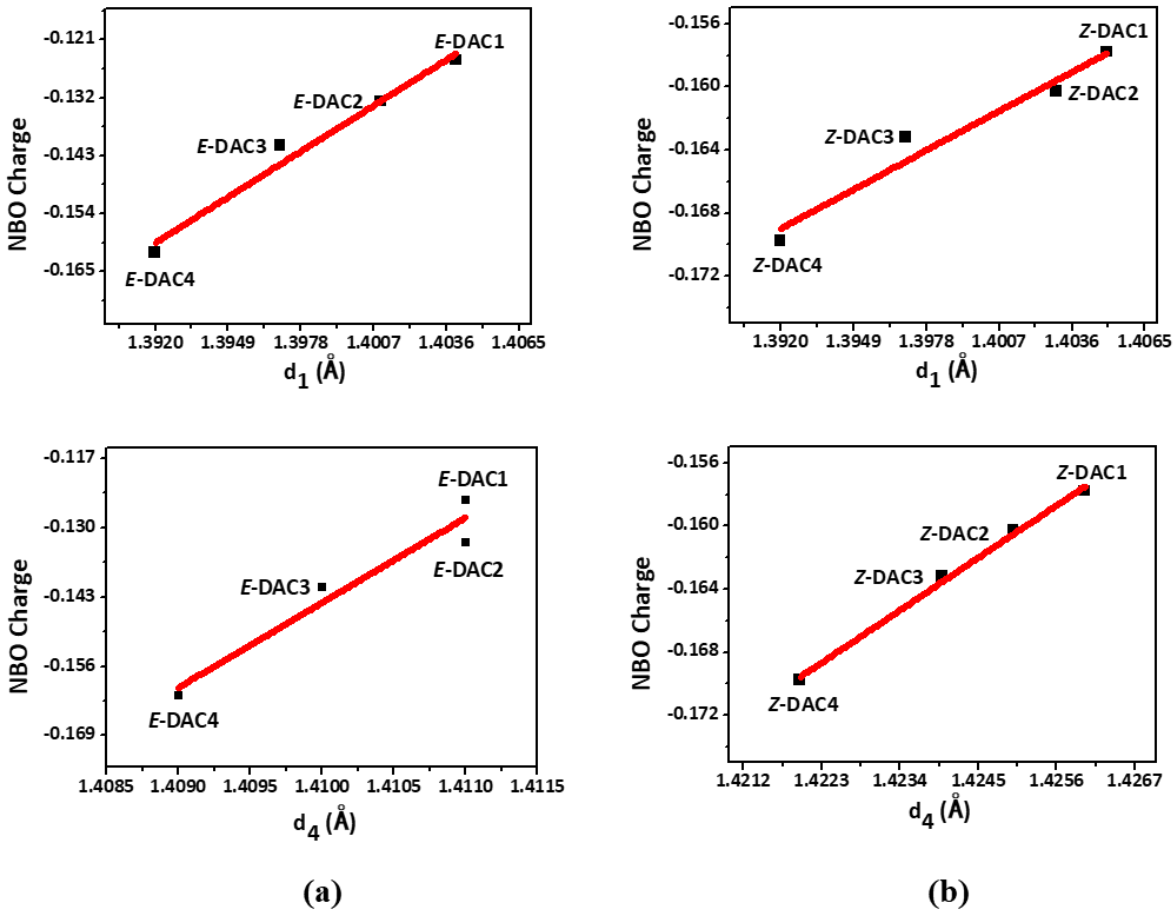


Figure S3 Plots of the NBO charges of π-spacer moiety vs distance d_1, and d_4 for (a) trans dyes and (b) cis dyes.

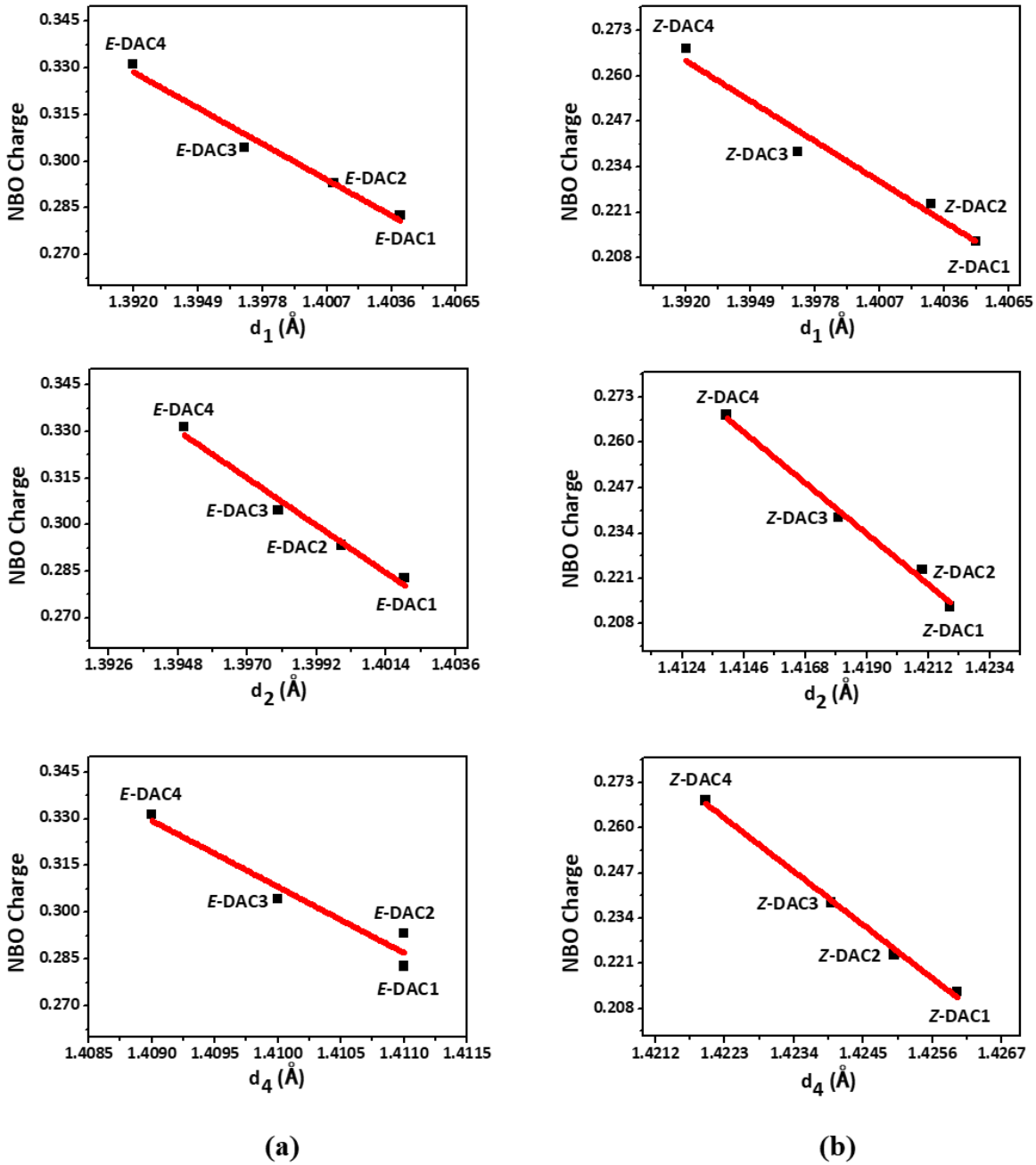


Figure S4 Plots of the NBO charges of donor moiety vs distance d_1, d_2 and d_4 for (a) trans dyes and (b) cis dyes.

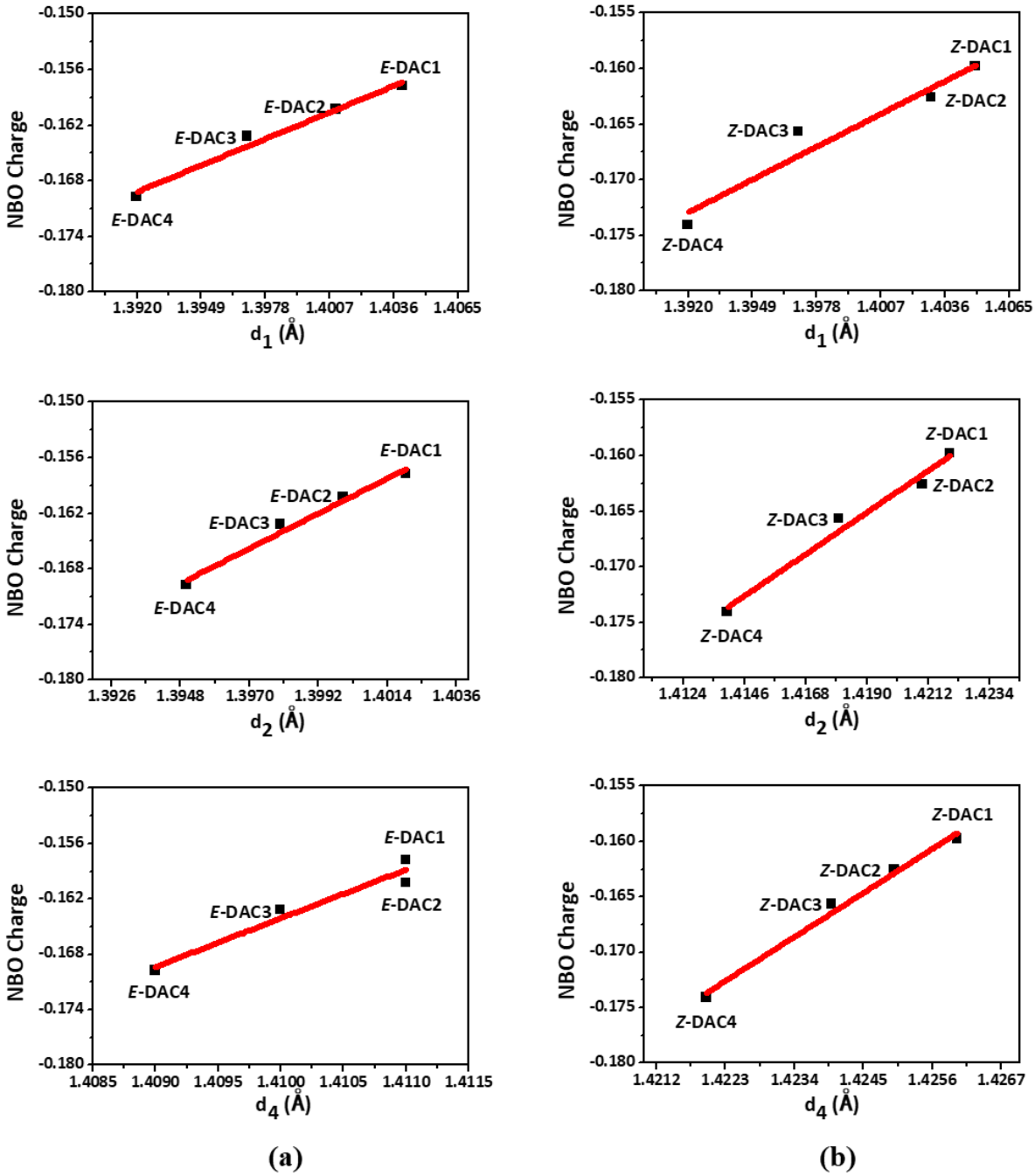


Figure S5 Plots of the NBO charges of acceptor moiety vs distance d_1, d_2 and d_4 for (a) trans dyes and (b) cis dyes.