

Electronic Supplementary Information

Influence of dye-TiO₂ interface on DSSC performance: a theoretical exploration with ruthenium dye[†]

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Choosing the proper functional is extremely important to obtain reasonable data in DFT calculation. At the very beginning of this project, we have tested the results of excited state based on the CAM-B3LYP¹ method. We found, however, there's no significant improvement in excited state properties. Recently, we have calculated the excited state properties by using LC-BLYP² in conjunction with LanL2DZ; 6-31G(d) basis set. All the parameters of excited states based on three methods are collected in Tab. ESI-1. In order to select a proper functional to estimate the excitation energy, we provide the experimental absorption spectrum of the dye, which is similar to **a** dye for comparison,³ as shown in Fig. ESI-1a. The simulated absorption spectra of the designed **a** dye by using different methods are given in Fig. ESI-1b. It is apparent that the simulated and experimental spectra resemble in profile, especially for the absorption band at around 400 - 500 nm base on the B3LYP⁴/LanL2DZ; 6-31G(d) level. Especially, the spectrum exhibits three strong absorption peaks at about 325, 386, and 434 nm when B3LYP/LanL2DZ; 6-31G(d) level is used, which are very close to the experimental values at 313, 388, and 438 nm. Whereas, the lowest-lying excitation energy of dye **a** calculated with CAM-B3LYP and LC-BLYP are about 458 and 420 nm, respectively, which is largely blue-shifted with respect to experimental values. In short, the B3LYP functional gives the best agreement with experimental trend on the absorption spectrum. Therefore, it is applied to calculate the excitation energy through out this work. Meanwhile, the B3LYP functional has been widely used to calculate the similar systems' absorption properties for Ru-based dyes.⁵⁻⁸

Table ESI-1 Main transitions ^a which contributes to electronic vertical excitation of **a**.

Functional	Major contribs ^b	ΔE (eV)	λ_{cal} (nm)	$\lambda_{expt.}$ ^c	f	
B3LYP	H-1→L (68%)	2.48	500	483	0.0367	
	H→L+2 (74%)	2.67	464		0.0454	
	H-1→L+1 (88%)	2.81	441		0.0384	
	H→L+1 (45%)	2.86	434	438	0.1449	
	H→L+3 (83%)	3.21	386	388	0.0680	
	H-2→L+2 (69%)	3.25	382		0.0677	
	H-1→L+6 (47%)	3.46	358		0.0284	
	H-5→L (41%)	3.79	327		0.0916	
	H-5→L (44%)	3.82	325	313	0.2431	
	H-6→L (50%)	3.87	320		0.0727	
	H-2→L+4 (48%)	4.11	302		0.0247	
	H-3→L+1 (49%)	4.26	291		0.0782	
	H-3→L+1 (46%)	4.29	289		0.0329	
	H-6→L+1 (88%)	4.30	288		0.1059	
	H-9→L (43%)	4.37	284		0.0615	
	H-5→L+3 (48%)	4.42	281		0.0655	
	H→L+7 (85%)	4.44	279		0.0656	
	H-2→L+5 (48%)	4.54	273		0.4577	
	H-5→L+3 (40%)	4.67	265		0.0296	
	H-8→L (39%)	4.76	260		0.0331	
CAM-B3LYP	H→L (85%)	2.71	458		0.0245	
	H-1→L (77%)	3.09	401		0.0937	
	H→L+2 (79%)	3.46	358		0.0309	
	H-1→L+2 (63%)	3.59	345		0.0228	
	H→L+1 (66%)	3.64	341		0.1707	
	H-1→L+1 (70%)	3.68	337		0.0260	
	H-2→L+2 (58%)	3.91	317		0.0361	
	H-2→L+1 (79%)	3.99	311		0.0210	
	H-4→L (49%)	4.16	298		0.0697	
	H-4→L (41%)	4.27	291		0.4671	
	H→L+3 (45%)	4.36	285		0.0431	
	H-1→L+3 (91%)	4.49	276		0.0607	
	H-3→L+2 (65%)	4.56	272		0.2035	
	H-5→L (92%)	4.68	265		0.0221	
	H→L+4 (70%)	4.82	257		0.2443	
	H→L+5 (70%)	4.94	251		0.2267	
	LC-BLYP	H-1→L (56%)	3.74	332		0.0623
		H-1→L+13 (36%)	4.22	293		0.1018
		H-4→L (55%)	4.48	277		0.1947
		H→L+1 (59%)	4.54	273		0.2336
H-1→L+2 (77%)		4.58	271		0.0832	
H-1→L+1 (69%)		4.71	263		0.3955	
H-2→L+2 (39%)		4.77	260		0.1545	
	H-3→L+2 (63%)	4.85	256		0.2545	

^a Only those excitations with oscillator strength $f > 0.0200$ are listed here.^b H represents for HOMO, L represents for LUMO. ESI-3^c The experimental absorption data are from ref.1.

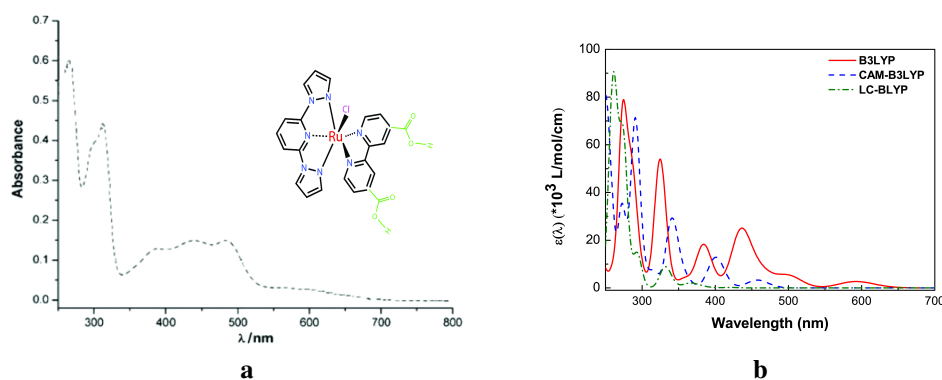


Fig. ESI-1 a. The experimental absorption spectrum of dye in DMSO solvent; b. The fitted absorption spectra of **a** dye based on B3LYP, CAM-B3LYP, and LC-BLYP with LanL2DZ and 6-31G(d) hybrid basis sets.

Additionally, Philippopoulos *et al.*³ have reported that this kind of Ru-dye can be used to assemble the DSSC, which therefore indicates that the HOMO energy level of **a** dye should be lower than the redox potential of I^-/I_3^- (-4.60 eV vs in vacuum) and higher than the valence band edge of TiO_2 (-7.20 eV vs in vacuum) while the LUMO energy level of a dye should be higher than the conduction band of TiO_2 (-4.00 eV vs in vacuum). It can be seen from Fig. ESI-2 that the long-range corrected functionals CAM-B3LYP and LC-BLYP both underestimate the energy of occupied orbital and overestimate the energy of virtual orbital as compared with the traditional B3LYP functional. Therefore, more reasonable HOMO-LUMO energy gap is predicated with B3LYP functional, but not in the long-range corrected functionals.

In regard to the above mentioned, we select B3LYP functional in conjunction with the LanL2DZ; 6-31G(d) basis set used in current work.

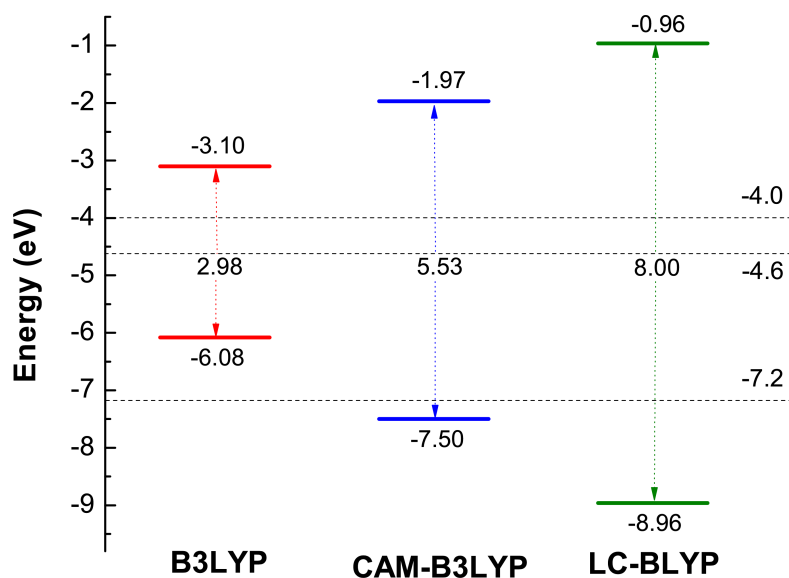


Fig. ESI-2 The HOMO and LUMO energy levels (in eV) of a dye based on B3LYP, CAM-B3LYP, and LC-BLYP with LanL2DZ and 6-31G(d) hybrid basis sets.

References

- [1] T. Yanai, D. P. Tew and N. C. Handy, *Chemical Physics Letters*, 2004, **393**, 51–57.
- [2] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai and K. Hirao, *The Journal of Chemical Physics*, 2004, **120**, 8425–8433.
- [3] A. I. Philippopoulos, A. Terzis, C. P. Raptopoulou, V. J. Catalano and P. Falaras, *European Journal of Inorganic Chemistry*, 2007, 5633–5644.
- [4] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

- [5] G. Li, L. Ray, E. N. Glass, K. Kovnir, A. Khoroshutin, S. I. Gorelsky and M. Shatruk, *Inorganic Chemistry*, 2012, **51**, 1614–1624.
- [6] G. Li, P. G. Bomben, K. C. D. Robson, S. I. Gorelsky, C. P. Berlinguette and M. Shatruk, *Chem. Commun.*, 2012, **48**, 8790–8792.
- [7] J. Wang, F.-Q. Bai, B.-H. Xia, L. Feng, H.-X. Zhang and Q.-J. Pan, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2206–2213.
- [8] J. Chen, F.-Q. Bai, J. Wang, L. Hao, Z.-F. Xie, Q.-J. Pan and H.-X. Zhang, *Dyes and Pigments*, 2012, **94**, 459 – 468.