Supporting Information

Computational Investigation of Acene-Modified Zinc-Porphyrin Based Sensitizers for Dye-Sensitized Solar Cells

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Table S5. Experimental [1] and Theoretical vertical excitation energies ΔE(eV) in the THF solution for the LAC dyes. The TDDFT calculations were carried out at the CAM-B3LYP/6-31G*, ω B97XD/6-31G*, LC-ωPBE /6-31G* and M062X /6-31G* levels in GAUSSIAN 09 and at the PBE/SVP, B3LYP/SVP, BH&HLYP /SVP levels in ORCA, respectively. All of the values are in eV. Within parentheses we also report the corresponding values of oscillator strength.

Table S6. Computational ESOP (eV) for the LAC dyes in the THF solution (left) and in gas phase (right) at different computational levels.

Table S7. The values of the important internal coordinates at the optimized geometries of LAC-1，LAC-3 and LAC-5 in gas phase and implicit solvent at B3LYP/SVP level. The definition of a, b, c, d and e are found in the figure caption of Figure S7.

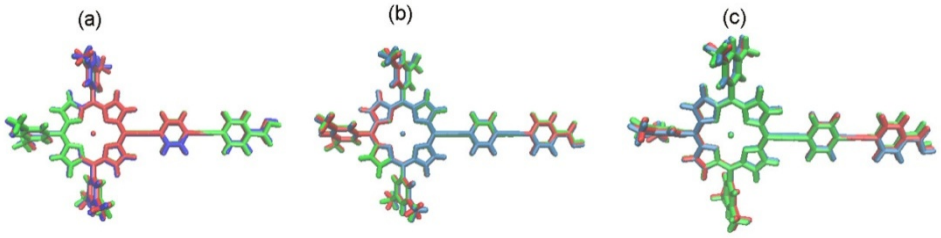

Figure S1. Optimized structures for the LAC-1 dye in THF solution at the B3LYP/SVP (blue), BH&HLYP/SVP (red) and ωB97XD /SVP (green) levels, respectively. (a) neutral ground state; (b) oxidized ground state;(c) reduced ground state.

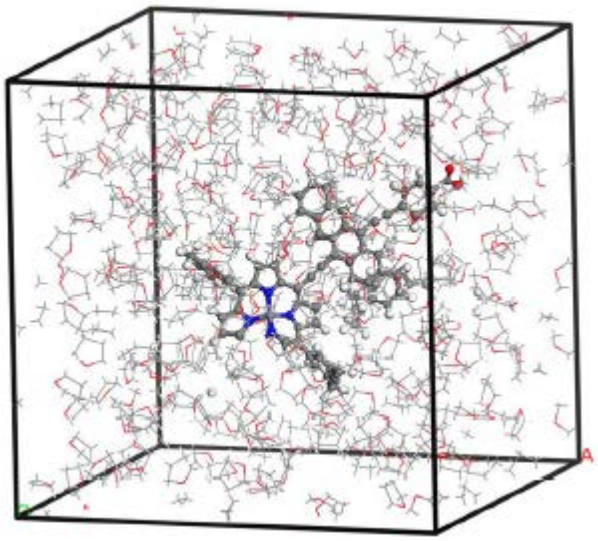

Figure S2. The initial configuration was obtained by randomly disposing the LAC and THF molecules in a cubic box.

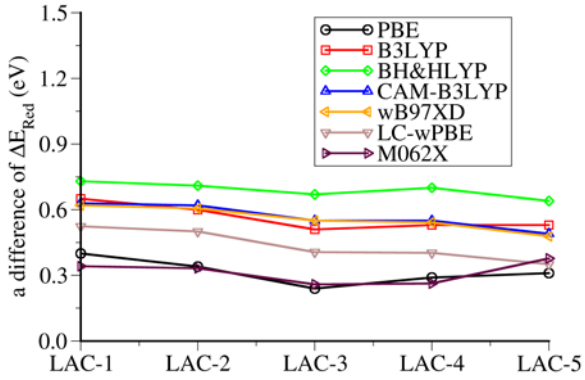

Figure S3. The differences between Experimental [1] and computational ΔE_{red} (eV) values at different computational levels.

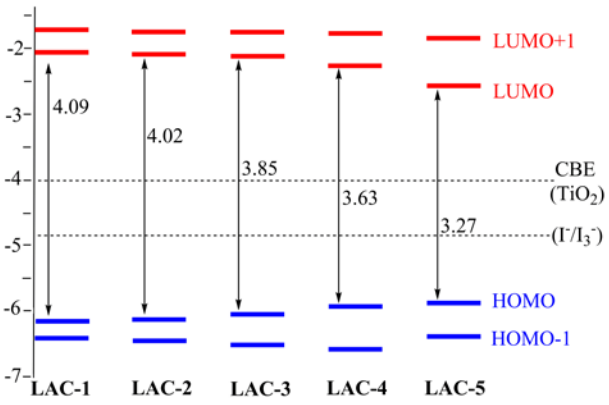

Figure S4. Computed MO levels and HOMO-LUMO gaps for LAC dyes at the CAM-B3LYP /6-31G* level. The horizontal dashed lines indicate the levels of the conduction band minimum (CBM) of the anatase TiO_2 surface (-4.0 eV) and the potential of I^-/I^{3-} (-4.8 eV) in the electrolyte solutions.

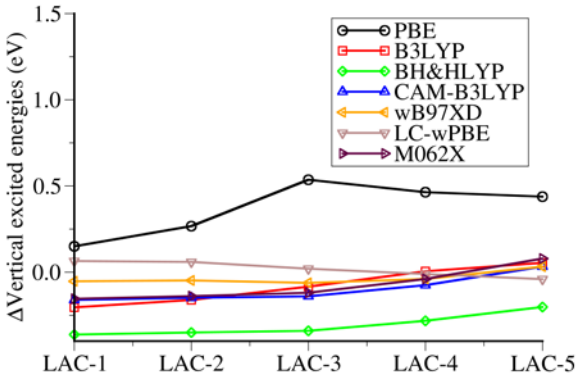

Figure S5. The differences between Experimental [1] and computational vertical excitation energies (eV) at different computational levels.

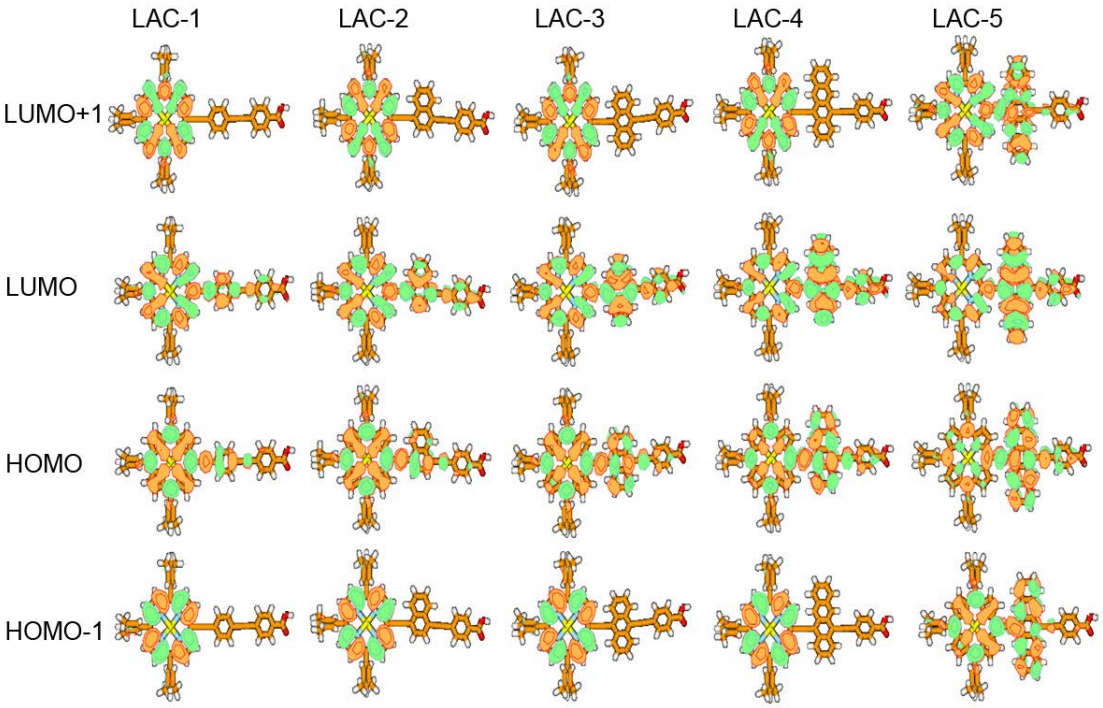

Figure S6. Frontier molecular orbitals of LAC dyes at the CAM-B3LYP/6-31G* level.

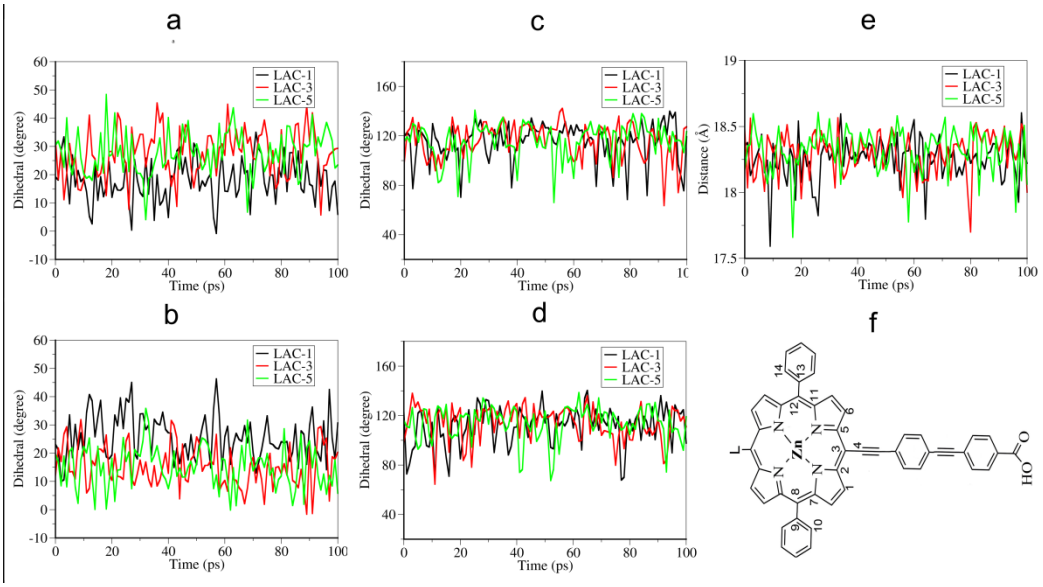

Figure S7. The evolution of dihedral angles: (a:∠1234), (b :∠6534), c (∠7-8-9-10), d (∠11-12-13-14) and the distance: e (Zn-C_{COOH}); f is the scheme of the LAC dye.

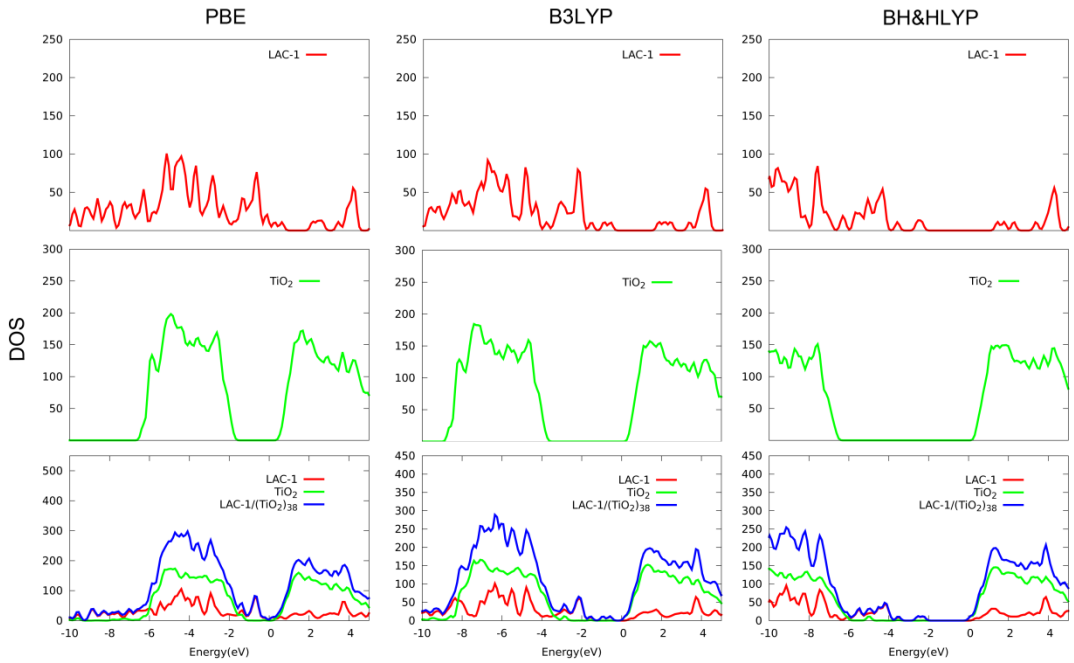

Figure S8. DOS and PDOS of LAC-1@$(TiO_2)_{38}$ at the PBE/SVP, B3LYP/SVP and BH&HLYP/SVP levels, respectively.

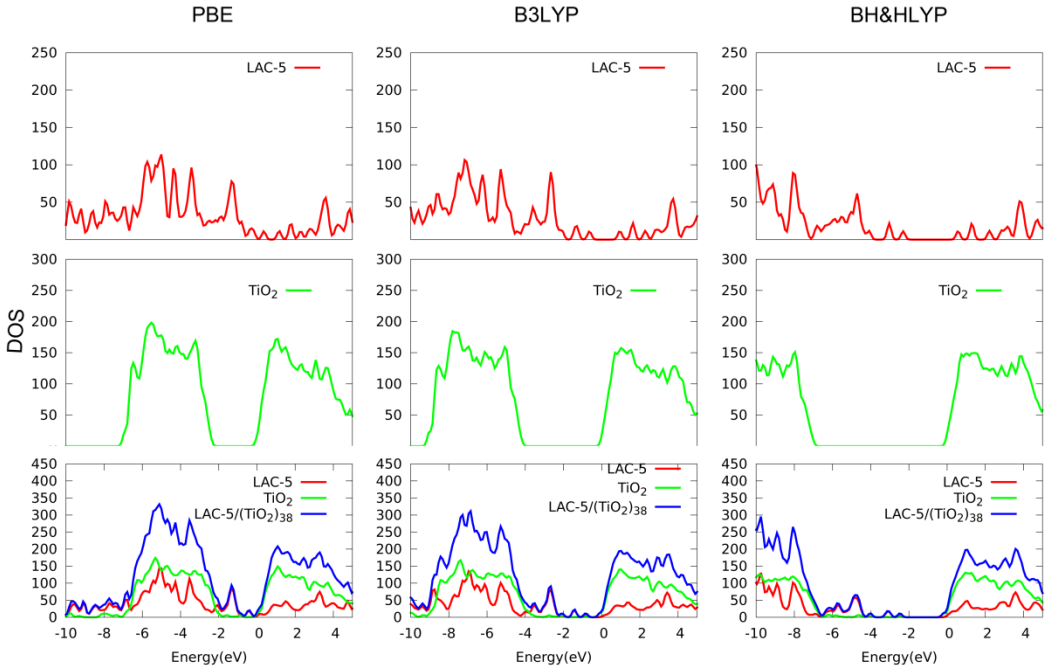

Figure S9. DOS and PDOS of LAC-5@$(TiO_2)_{38}$ at the PBE/SVP, B3LYP/SVP and BH&HLYP/SVP levels, respectively.

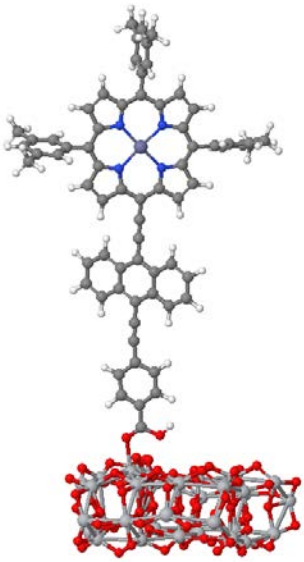

Figure S10. Optimized single-bridge structure of the LAC-3@$(TiO2)_{38}$ system with the LAC-3 dye adsorbed on the TiO_2(101) surface.

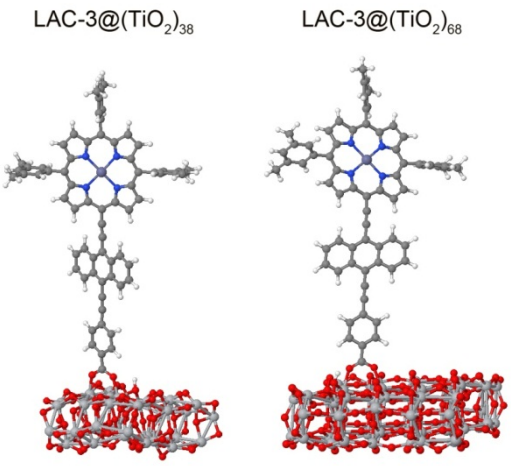

Figure S11. Optimized structure of the LAC-3@$(TiO_2)_{38}$ and LAC-3@$(TiO_2)_{68}$ systems with the LAC-3 dye adsorbed on the TiO_2(101) surface at PBE/SVP level.

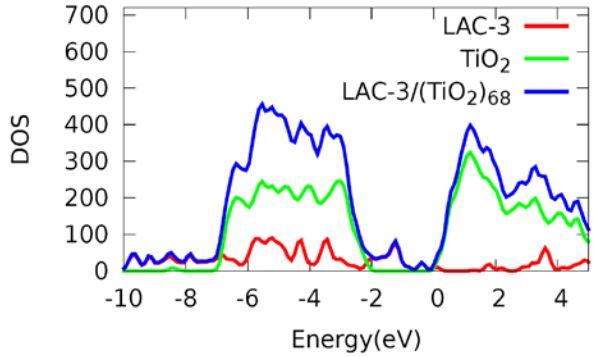

Figure S12. DOS and PDOS of LAC-3@$(TiO_2)_{68}$ at the PBE/SVP level.

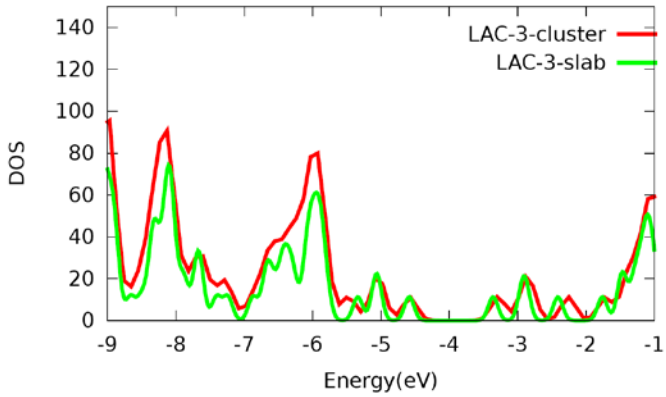

Figure S13. The DOS for the isolated LAC-3 within the cluster (red) and the periodic models (green).

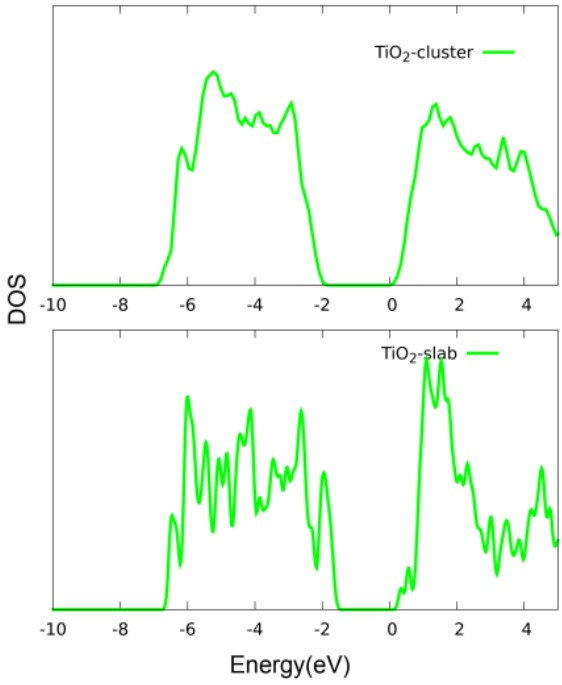

Figure S14. The DOS for the pure TiO_2 within the cluster (up) and the periodic models (down).

Table S1. (a) The RMSD (Å) for the optimized structures of the LAC-1 dye at BH&HLYP and ωB97XD level, compared with the results at B3LYP level. (ne) neutral ground state; (ox) oxidized ground state; (red) reduced ground state.

States	BH&HLYP/SVP	ωB97XD /SVP
ne	0.14	0.44
ox	0.14	0.15
red	0.20	0.40
Aver	0.16	0.33

(b) Calculated GSOP and GSRP (eV) for the LAC-1 dye at BH&HLYP and ωB97XD level, compared with the results at B3LYP level.

	BH&HLYP/SVP	ωB97XD /SVP
GSOP	0.05	-0.11
GSRP	0.14	-0.02

Table S2. (a) Calculated GSOP and GSRP for the LAC-1 dye by using the COSMO (ORCA) and PCM (Gaussian) solvent models.

Dye		PBE/TZVP		B3LYP/TZVP		BH&HLYP/TZVP	
		COSMO	PCM	COSMO	PCM	COSMO	PCM
LAC-1	GSOP	5.17	5.09	5.19	5.20	5.19	5.08
	GSRP	3.12	3.14	2.87	2.99	2.79	2.80

(b) Computational ΔE_{ox}(eV) for the LAC dyes in the THF solution (left) and in gas phase (right). Within parentheses we also report the corresponding values for $-\varepsilon_{HUMO}$ (eV), calculated for the neutral species at its equilibrium geometry in gas phase and in THF solution.

dyes	PBE		B3LYP		BH&HLYP		CAM-B3LYP		ωB97XD		LC-ωPBE		M062X	
	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS
LAC-1	5.17 (4.90)	5.85 (4.76)	5.19 (5.25)	5.92 (5.12)	5.19 (5.98)	5.95 (5.81)	5.18 (6.15)	6.02 (6.02)	5.17 (6.64)	6.00 (6.49)	5.27 (7.11)	6.11 (6.95)	5.39 (6.16)	6.20 (6.01)
LAC-2	5.12 (4.87)	5.80 (4.73)	5.15 (5.22)	5.87 (5.09)	5.16 (5.94)	5.91 (5.78)	5.17 (6.12)	5.99 (6.00)	5.16 (6.61)	5.98 (6.47)	5.26 (7.09)	6.09 (6.93)	5.39 (6.13)	6.18 (6.93)
LAC-3	5.03 (4.80)	5.70 (4.67)	5.07 (5.14)	5.76 (5.02)	5.10 (5.85)	5.80 (5.70)	5.14 (6.06)	5.90 (5.93)	5.14 (6.54)	5.90 (6.41)	5.19 (7.03)	5.98 (6.87)	5.37 (6.08)	6.09 (6.87)
LAC-4	4.95 (4.70)	5.59 (4.57)	4.97 (5.02)	5.64 (4.90)	4.99 (5.71)	5.66 (5.56)	5.05 (5.97)	5.78 (5.82)	5.06 (6.47)	5.78 (6.31)	5.04 (6.94)	5.81 (6.77)	5.29 (5.98)	5.97 (6.77)
LAC-5	4.82 (4.56)	5.46 (4.43)	4.80 (4.82)	5.48 (4.74)	4.79 (5.51)	5.44 (5.37)	4.88 (5.80)	5.59 (5.65)	4.91 (6.31)	5.59 (6.14)	4.79 (6.77)	5.55 (6.59)	5.13 (5.81)	5.80 (6.59)

Table S3. Computational ΔE_{red}(eV) for the LAC dyes in gas phase (left) and in the THF solution (right). Within parentheses we also report the corresponding values for $-\varepsilon_{LUMO}$ (eV), calculated for the neutral species at its equilibrium geometry in gas phase and in THF solution. All experimental values refer to the relative value with respect to the potential of the normal hydrogen electrode (NHE), setting as 4.44 eV below the vacuum level. [1]

dyes	PBE		B3LYP		BH&HLYP		CAM-B3LYP		ωB97XD		LC-ωPBE		M062X		exp.
	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS	
LAC-1	3.12 (3.37)	2.19 (3.23)	2.87 (2.86)	1.91 (2.72)	2.79 (2.21)	1.70 (2.03)	2.89 (2.06)	1.78 (1.90)	2.90 (1.59)	1.76 (1.42)	3.00 (1.56)	1.99 (1.36)	3.18 (2.40)	1.87 (2.22)	3.52
LAC-2	3.19 (3.42)	2.27 (3.27)	2.93 (2.90)	1.99 (2.76)	2.82 (2.25)	1.76 (2.07)	2.91 (2.10)	1.84 (1.94)	2.92 (1.64)	1.82 (1.46)	3.03 (1.60)	2.05 (1.40)	3.20 (2.45)	1.95 (1.40)	3.53
LAC-3	3.31 (3.53)	2.38 (3.38)	3.04 (3.01)	2.11 (2.87)	2.88 (2.35)	1.88 (2.18)	3.00 (2.21)	1.97 (2.04)	3.00 (1.74)	1.95 (1.56)	3.14 (1.69)	2.18 (1.48)	3.29 (2.56)	2.09 (1.48)	3.55
LAC-4	3.40 (3.64)	2.49 (3.50)	3.16 (3.13)	2.23 (3.00)	2.99 (2.47)	2.01 (2.31)	3.14 (2.34)	2.11 (2.18)	3.15 (1.87)	2.09 (1.69)	3.29 (1.80)	2.36 (1.60)	3.43 (2.70)	2.24 (1.60)	3.69
LAC-5	3.52 (3.77)	2.61 (3.63)	3.30 (3.28)	2.38 (3.15)	3.19 (2.65)	2.21 (2.49)	3.34 (2.53)	2.30 (2.36)	3.35 (2.05)	2.29 (1.87)	3.48 (2.00)	2.53 (1.79)	3.45 (2.89)	2.42 (1.79)	3.83

Table S4. (a) Excitation energies (λ), main electronic transitions and corresponding oscillator strengths (f) for LAC dyes in the gas phase.

dyes	λ/nm(eV)	f	Transition
LAC-1			
PBE	636.3	0.244	HOMO -> LUMO
	623.1	0.009	HOMO -> LUMO+1
	569.7	0.001	HOMO -> LUMO+2
	535.5	0.001	HOMO-1 -> LUMO+2
B3LYP	568.4	0.261	HOMO -> LUMO
	560.5	0.022	HOMO -> LUMO+1
	455.2	0.316	HOMO -> LUMO+2
	418.4	0.280	HOMO-2 -> LUMO
BH&HLYP	530.4	0.329	HOMO -> LUMO
	522.6	0.001	HOMO-1 -> LUMO
	376.6	3.823	HOMO-1 -> LUMO+1
	332.4	1.645	HOMO-1 -> LUMO
CAM-B3LYP	591.55	0.299	HOMO -> LUMO
	577.14	0.000	HOMO -> LUMO+1
	404.72	2.906	HOMO-1 -> LUMO+1
ωB97XD	583.76	0.257	HOMO -> LUMO
	571.15	0.000	HOMO-1 -> LUMO
	393.12	2.946	HOMO-1 -> LUMO+1
LC-ωPBE	620.27	0.144	HOMO -> LUMO

	612.96	0.000	HOMO-1 -> LUMO
	376.47	3.000	HOMO-1 -> LUMO+1
M062X	553.91	0.340	HOMO -> LUMO
	541.99	0.000	HOMO-1 -> LUMO
	398.70	2.867	HOMO-1 -> LUMO+1
LAC-2			
PBE	664.0	1.135	HOMO -> LUMO
	642.3	0.003	HOMO -> LUMO+1
	600.3	0.170	HOMO -> LUMO+2
	563.6	0.044	HOMO-1 -> LUMO+2
B3LYP	583.2	0.978	HOMO -> LUMO
	566.7	0.021	HOMO -> LUMO+1
	479.2	0.534	HOMO -> LUMO+2
	453.6	1.163	HOMO-2 -> LUMO
BH&HLYP	536.7	0.445	HOMO -> LUMO
	524.9	0.000	HOMO-1 -> LUMO
	401.1	3.051	HOMO-1 -> LUMO+1
	347.0	0.020	HOMO-2 -> LUMO
CAM-B3LYP	578.20	0.371	HOMO -> LUMO
	562.17	0.000	HOMO-1 -> LUMO
	418.77	2.579	HOMO-1 -> LUMO+1
	380.41	1.230	HOMO -> LUMO+1

ωB97XD	589.21	0.317	HOMO -> LUMO
	573.00	0.001	HOMO-1 -> LUMO
	410.94	2.735	HOMO-1 -> LUMO+1
LC-ωPBE	624.30	0.169	HOMO -> LUMO
	614.75	0.000	HOMO-1 -> LUMO
	389.46	3.019	HOMO-1 -> LUMO+1
M062X	560.86	0.440	HOMO -> LUMO
	544.20	0.000	HOMO-1 -> LUMO
	418.31	2.473	HOMO-1 -> LUMO+1
LAC-3			
PBE	727.8	0.944	HOMO -> LUMO
	690.7	0.003	HOMO -> LUMO+1
	683.3	0.534	HOMO -> LUMO+2
	634.1	0.025	HOMO-2 -> LUMO
B3LYP	621.3	1.437	HOMO -> LUMO
	580.3	0.002	HOMO -> LUMO+1
	537.1	0.000	HOMO -> LUMO+2
	498.7	0.737	HOMO-1 -> LUMO+1
BH&HLYP	552.2	0.852	HOMO -> LUMO
	527.6	0.000	HOMO-1 -> LUMO
	449.8	1.740	HOMO -> LUMO+2
	394.4	0.002	HOMO-2 -> LUMO

CAM-B3LYP	592.83	0.648	HOMO -> LUMO
	563.98	0.000	HOMO-1 -> LUMO
	475.70	1.332	HOMO-2 -> LUMO
	387.04	0.993	HOMO -> LUMO+1
ωB97XD	600.32	0.520	HOMO -> LUMO
	574.11	0.000	HOMO -> LUMO+1
	470.07	1.471	HOMO-2 -> LUMO
LC-ωPBE	630.19	0.249	HOMO -> LUMO
	615.49	0.000	HOMO-1 -> LUMO
	441.88	1.966	HOMO -> LUMO
M062X	578.76	0.782	HOMO -> LUMO
	546.59	0.000	HOMO -> LUMO+1
	471.38	1.187	HOMO-1 -> LUMO+1
LAC-4			
PBE	795.2	0.439	HOMO-1 -> LUMO
	782.2	0.955	HOMO -> LUMO
	755.1	0.003	HOMO -> LUMO+1
	699.1	0.014	HOMO-2 -> LUMO
B3LYP	678.5	1.569	HOMO -> LUMO
	602.9	0.002	HOMO -> LUMO+1
	600.1	0.001	HOMO-1 -> LUMO
	535.0	0.042	HOMO-2 -> LUMO

BH&HLYP	586.7	1.377	HOMO -> LUMO
	532.2	0.000	HOMO-1 -> LUMO
	490.8	0.478	HOMO-1 -> LUMO+1
	434.9	0.018	HOMO-2 -> LUMO
CAM-B3LYP	654.21	1.273	HOMO -> LUMO
	570.39	0.000	HOMO-1 -> LUMO
	537.52	0.203	HOMO -> LUMO+2
	423.12	0.187	HOMO-2 -> LUMO
ωB97XD	627.64	0.884	HOMO -> LUMO
	576.11	0.000	HOMO-1 -> LUMO
	529.49	0.421	HOMO -> LUMO+2
LC-ωPBE	642.20	0.411	HOMO -> LUMO
	616.81	0.000	HOMO-1 -> LUMO
	505.78	1.039	HOMO -> LUMO+2
M062X	622.93	1.123	HOMO -> LUMO
	550.52	0.000	HOMO-1 -> LUMO
	519.82	0.155	HOMO-2 -> LUMO
LAC-5			
PBE	897.2	0.237	HOMO -> LUMO+1
	875.8	1.053	HOMO -> LUMO
	839.8	0.004	HOMO -> LUMO+2
	765.0	0.010	HOMO-2 -> LUMO

B3LYP	770.0	1.420	HOMO -> LUMO
	669.1	0.025	HOMO-1 -> LUMO
	641.2	0.003	HOMO -> LUMO+2
	584.9	0.028	HOMO-2 -> LUMO
BH&HLYP	665.5	1.441	HOMO -> LUMO
	540.5	0.000	HOMO-1 -> LUMO
	521.5	0.005	HOMO-1 -> LUMO+2
	479.9	0.018	HOMO -> LUMO+1
CAM-B3LYP	730.37	0.973	HOMO -> LUMO
	572.32	0.000	HOMO-2 -> LUMO
	564.34	0.006	HOMO-1 -> LUMO
	459.03	0.028	HOMO-1 -> LUMO
ωB97XD	714.65	0.978	HOMO -> LUMO
	579.58	0.001	HOMO -> LUMO+2
	570.11	0.001	HOMO -> LUMO+1
LC-ωPBE	686.23	0.821	HOMO -> LUMO
	619.10	0.000	HOMO-1 -> LUMO+1
	576.92	0.231	HOMO -> LUMO+1
M062X	731.50	0.945	HOMO -> LUMO
	557.57	0.000	HOMO-2 -> LUMO
	552.44	0.0292	HOMO-1 -> LUMO

(b) Excitation energies (λ), main electronic transitions and corresponding oscillator strengths (f) for LAC dyes in

THF solution.

dyes	λ/nm(eV)	f	Transition
LAC-1			
PBE	681.2	0.975	HOMO -> LUMO
	623.8	0.003	HOMO -> LUMO+1
	582.8	0.003	HOMO -> LUMO+2
	574.7	0.019	HOMO-3 -> LUMO
B3LYP	681.2	0.975	HOMO -> LUMO
	623.8	0.003	HOMO -> LUMO+1
	582.8	0.004	HOMO -> LUMO+2
	574.7	0.019	HOMO-3 -> LUMO
BH&HLYP	531.6	0.342	HOMO -> LUMO
	522.7	0.000	HOMO-1 -> LUMO
	375.0	3.844	HOMO-1 -> LUMO+1
	332.0	1.780	HOMO-1 -> LUMO
CAM-B3LYP	581.78	0.412	HOMO -> LUMO
	563.14	0.000	HOMO-1 -> LUMO
	411.84	3.017	HOMO-1 -> LUMO+1
	394.48	1.605	HOMO -> LUMO+1
ωB97XD	593.79	0.360	HOMO -> LUMO
	574.50	0.000	HOMO-1 -> LUMO
	406.50	3.032	HOMO-1 -> LUMO+1
LC-ωPBE	628.35	0.198	HOMO -> LUMO

	617.13	0.000	HOMO-1 -> LUMO
	391.31	3.085	HOMO-1 -> LUMO+1
M062X	564.33	0.481	HOMO -> LUMO
	545.07	0.000	HOMO-1 -> LUMO
	411.15	2.947	HOMO-1 -> LUMO+1
LAC-2			
PBE	736.7	1.055	HOMO -> LUMO
	644.9	0.004	HOMO -> LUMO+1
	619.3	0.129	HOMO -> LUMO+2
	584.1	0.047	HOMO-1 -> LUMO+2
B3LYP	587.3	0.981	HOMO -> LUMO
	568.5	0.004	HOMO -> LUMO+1
	515.1	0.453	HOMO -> LUMO+2
	483.3	1.132	HOMO-2 -> LUMO
BH&HLYP	539.2	0.472	HOMO -> LUMO
	525.7	0.000	HOMO-1 -> LUMO
	400.1	3.045	HOMO-1 -> LUMO+1
	347.5	0.000	HOMO-2 -> LUMO
CAM-B3LYP	590.7	0.536	HOMO -> LUMO
	565.96	0.001	HOMO-1 -> LUMO
	429.87	2.742	HOMO-1 -> LUMO+1
	398.17	1.539	HOMO -> LUMO+1

ωB97XD	601.53	0.457	HOMO -> LUMO
	577.07	0.001	HOMO -> LUMO+1
	422.48	2.913	HOMO-1 -> LUMO+1
LC-ωPBE	633.48	0.243	HOMO -> LUMO
	619.44	0.001	HOMO-1 -> LUMO
	402.72	3.202	HOMO-1 -> LUMO+1
M062X	583.67	0.496	HOMO -> LUMO
	560.66	0.000	HOMO -> LUMO+1
	417.77	2.939	HOMO-1 -> LUMO+1
LAC-3			
PBE	915.8	0.775	HOMO -> LUMO
	701.8	0.003	HOMO -> LUMO+1
	831.6	0.441	HOMO -> LUMO+2
	643.4	0.026	HOMO-2 -> LUMO
B3LYP	628.0	1.456	HOMO -> LUMO
	582.6	0.003	HOMO -> LUMO+1
	539.8	0.000	HOMO -> LUMO+2
	500.1	0.720	HOMO-1 -> LUMO+1
BH&HLYP	556.1	0.898	HOMO -> LUMO
	528.6	0.000	HOMO-1 -> LUMO
	449.5	1.677	HOMO -> LUMO+2
	396.0	0.000	HOMO-2 -> LUMO

CAM-B3LYP	610.73	0.917	HOMO -> LUMO
	567.93	0.000	HOMO -> LUMO+1
	486.12	1.2889	HOMO-1 -> LUMO+1
	403.32	1.3415	HOMO -> LUMO+1
ωB97XD	616.85	0.752	HOMO -> LUMO
	578.30	0.000	HOMO -> LUMO+1
	481.26	1.467	HOMO -> LUMO+2
LC-ωPBE	641.17	0.372	HOMO -> LUMO
	620.15	0.000	HOMO-1 -> LUMO
	454.34	2.102	HOMO -> LUMO
M062X	598.23	1.075	HOMO -> LUMO
	550.64	0.001	HOMO -> LUMO+1
	480.48	1.123	HOMO-1 -> LUMO+1
LAC-4			
PBE	914.1	0.241	HOMO-1 -> LUMO
	890.9	0.994	HOMO -> LUMO
	839.3	0.003	HOMO -> LUMO+1
	763.3	0.013	HOMO-2 -> LUMO
B3LYP	683.2	1.567	HOMO -> LUMO
	605.0	0.004	HOMO-1 -> LUMO
	605.2	0.002	HOMO -> LUMO+1
	536.6	0.086	HOMO -> LUMO+2

BH&HLYP	589.9	1.387	HOMO -> LUMO
	532.6	0.000	HOMO-1 -> LUMO
	491.3	0.437	HOMO-1 -> LUMO+1
	436.9	0.029	HOMO-2 -> LUMO
CAM-B3LYP	629.55	1.035	HOMO -> LUMO
	567.00	0.000	HOMO-1 -> LUMO
	529.46	0.266	HOMO -> LUMO+2
	418.86	0.051	HOMO-2 -> LUMO
ωB97XD	650.16	1.135	HOMO -> LUMO
	579.77	0.001	HOMO -> LUMO+1
	538.83	0.340	HOMO -> LUMO+2
LC-ωPBE	656.01	0.598	HOMO -> LUMO
	620.99	0.000	HOMO-1 -> LUMO
	518.75	1.017	HOMO-2 -> LUMO
M062X	648.59	1.345	HOMO -> LUMO
	553.95	0.001	HOMO -> LUMO+1
	527.26	0.110	HOMO-2 -> LUMO
LAC-5			
PBE	1022.9	0.174	HOMO -> LUMO+1
	1011.8	0.955	HOMO -> LUMO
	1053.1	0.003	HOMO -> LUMO+2
	932.5	0.008	HOMO-2 -> LUMO

B3LYP	776.9	1.412	HOMO -> LUMO
	677.6	0.036	HOMO-1 -> LUMO
	653.0	0.003	HOMO -> LUMO+2
	588.4	0.038	HOMO -> LUMO+1
BH&HLYP	669.4	1.436	HOMO -> LUMO
	540.5	0.000	HOMO-2 -> LUMO
	522.6	0.002	HOMO-1 -> LUMO
	482.5	0.025	HOMO -> LUMO+1
CAM-B3LYP	766.58	1.127	HOMO -> LUMO
	575.28	0.000	HOMO-2 -> LUMO
	572.61	0.019	HOMO-1 -> LUMO
	463.35	0.077	HOMO-1 -> LUMO
ωB97XD	749.47	1.134	HOMO -> LUMO
	582.85	0.001	HOMO-2 -> LUMO+1
	578.19	0.002	HOMO-1 -> LUMO
LC-ωPBE	713.73	1.035	HOMO -> LUMO
	622.78	0.000	HOMO-1 -> LUMO+1
	586.16	0.149	HOMO -> LUMO+1
M062X	767.41	1.100	HOMO -> LUMO
	561.86	0.056	HOMO-1 -> LUMO
	560.52	0.001	HOMO-2 -> LUMO

Table S5. Experimental [1] and Theoretical vertical excitation energies ΔE(eV) in the THF solution for the LAC dyes. The TDDFT calculations were carried out at the CAM-B3LYP/6-31G*, ω B97XD/6-31G*, LC-ωPBE /6-31G* and M062X /6-31G* levels in GAUSSIAN 09 and at the PBE/SVP, B3LYP/SVP, BH&HLYP /SVP levels in ORCA, respectively. All of the values are in eV. Within parentheses we also report the corresponding values of oscillator strength.

dye	PBE	B3LYP	BH&HLYP	CAM-B3LYP	ωB97XD	LC-ωPBE	M062X	exp.
LAC-1	1.82 (0.975)	2.17 (0.709)	2.33 (0.342)	2.13 (0.411)	2.09(0.360)	1.97(0.198)	2.20(0.481)	1.97
LAC-2	1.68 (1.055)	2.11 (0.981)	2.30 (0.472)	2.10 (0.536)	2.06(0.448)	1.96(0.243)	2.16(0.636)	1.95
LAC-3	1.35 (0.775)	1.97 (1.456)	2.23 (0.898)	2.03 (0.917)	2.01(0.752)	1.93(0.372)	2.07(1.076)	1.89
LAC-4	1.36 (0.241)	1.82 (1.567)	2.10 (1.387)	1.90 (1.273)	1.91(1.136)	1.89(0.598)	1.91(1.346)	1.82
LAC-5	1.21 (0.174)	1.60 (1.412)	1.85(1.436)	1.62 (1.127)	1.65(1.135)	1.73(1.036)	1.62(1.100)	1.65

Table S6. Computational ESOP (eV) for the LAC dyes in the THF solution (left) and in gas phase (right) at different computational levels.

Dyes	PBE		B3LYP		BH&HLYP		CAM-B3LYP		ωB97XD		LC-ωPBE		M062X	
	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS	THF	GAS
LAC-1	3.35	3.90	3.02	3.74	2.86	3.61	3.05	3.92	3.08	3.88	3.30	4.11	3.19	3.96
LAC-2	3.44	3.93	3.04	3.74	2.86	3.60	3.07	3.85	3.10	3.88	3.29	4.10	3.23	3.97
LAC-3	3.68	4.00	3.10	3.76	2.87	3.55	3.11	3.81	3.13	3.83	3.26	4.01	3.30	3.95
LAC-4	3.59	4.03	3.15	3.81	2.89	3.55	3.15	3.81	3.15	3.80	3.15	3.88	3.38	4.98
LAC-5	3.61	4.08	3.20	3.87	2.94	3.58	3.26	3.89	3.26	3.86	3.06	3.74	3.51	4.11

Table S7. The values of the important internal coordinates at the optimized geometries of LAC-1，LAC-3 and LAC-5 in gas phase and implicit solvent at B3LYP/SVP level. The definition of a, b, c, d and e are found in the figure caption of Figure S7.

dye	a (º)		b (º)		c (º)		d (º)		e (Å)	
	Gas	THF	Gas	THF	Gas	THF	Gas	THF	Gas	THF
LAC-1	1.2	1.2	1.4	1.4	104.5	106.5	107.7	108.5	18.8	18.8
LAC-3	3.9	2.9	1.0	2.3	109.8	110.5	108.3	111.0	18.8	18.7
LAC-5	3.8	4.1	1.9	1.6	111.3	112.7	110.2	109.7	18.8	18.8

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