Supporting Information

Can Polypyridyl Cu(I)-based Complexes Provide Promising Sensitizers for Dye-Sensitized Solar Cells? A Theoretical Insight into Cu(I) Vs Ru(II) Sensitizers

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Figure S1: The calculated absorption spectra of $[CuLL']^+$ (L = L' = 6,6′-dimethyl-2,2′-bipyridine-4,4′-dimethylformate) using the B3LYP and B3PW91 funtionals with 6-31G* basis set in both the gas phase and MeCN solution.

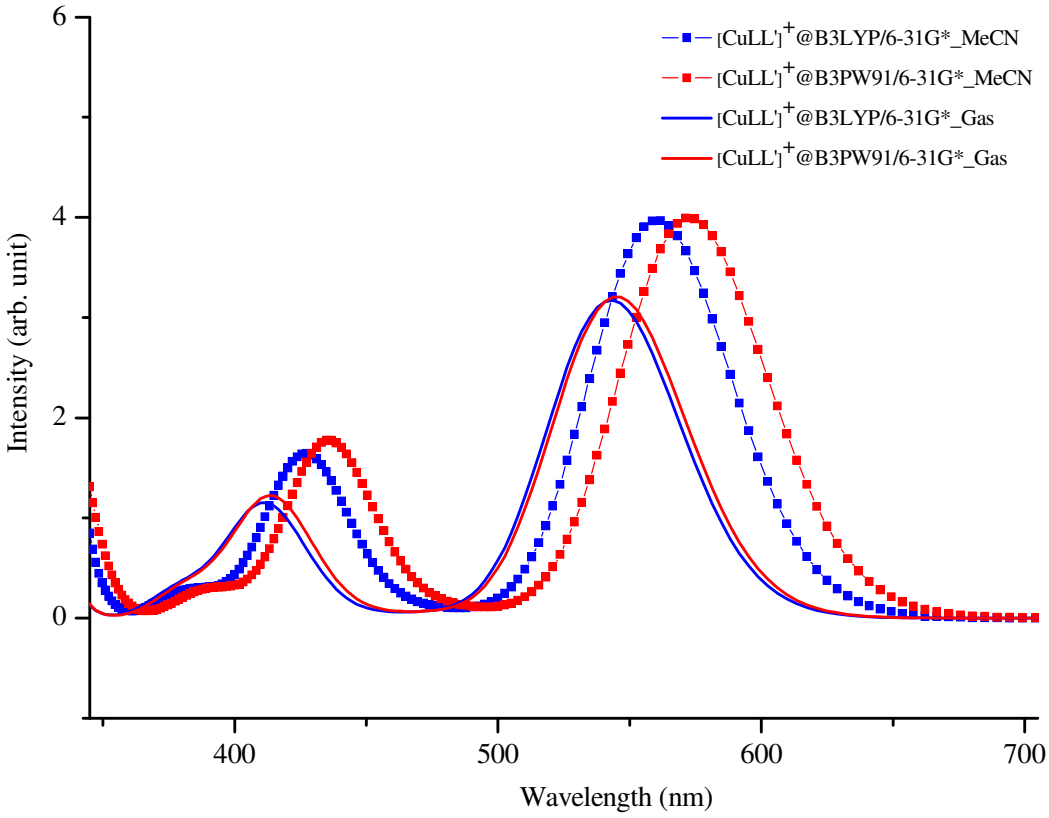

Figure S2: Energy levels and lowest TD-DFT excitation energies for $[CuLL']^+$ calculated at the B3LYP/6-31G* level in the gas phase.

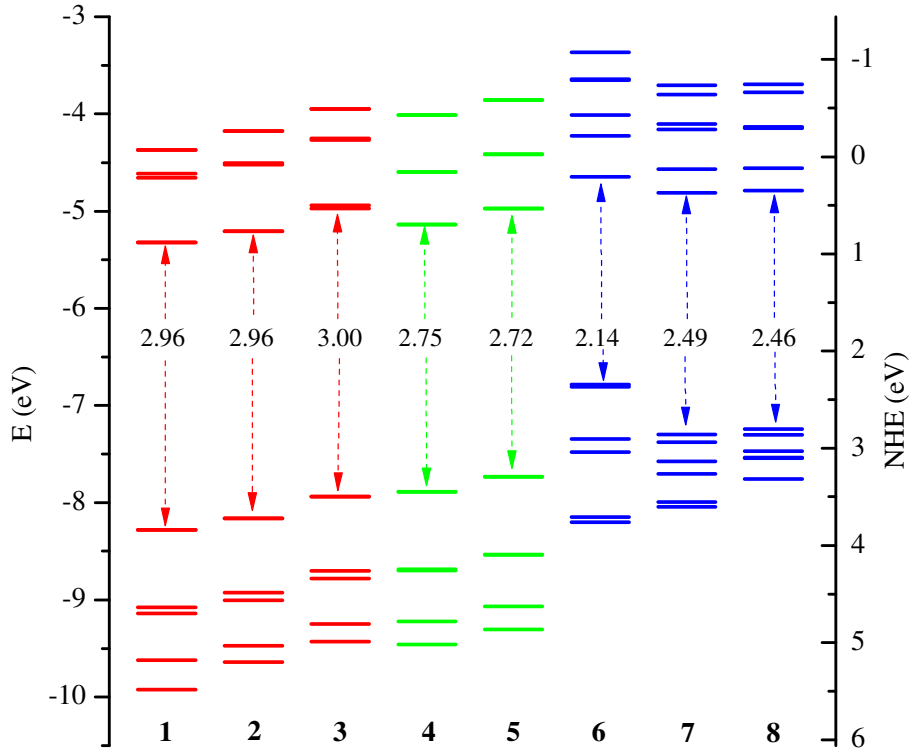

Figure S3: Simulated absorption spectra for $[CuLL']^+$ at the B3LYP/6-31G* (blue) and B3LYP/DZVP (red) levels in both gas phase (solid lines) and MeCN solution (solid lines with square symbol) and **N3** and **CYC-B11** at the B3LYP/SDD (blue) and B3LYP/3-21G* (red) levels in MeCN solution.

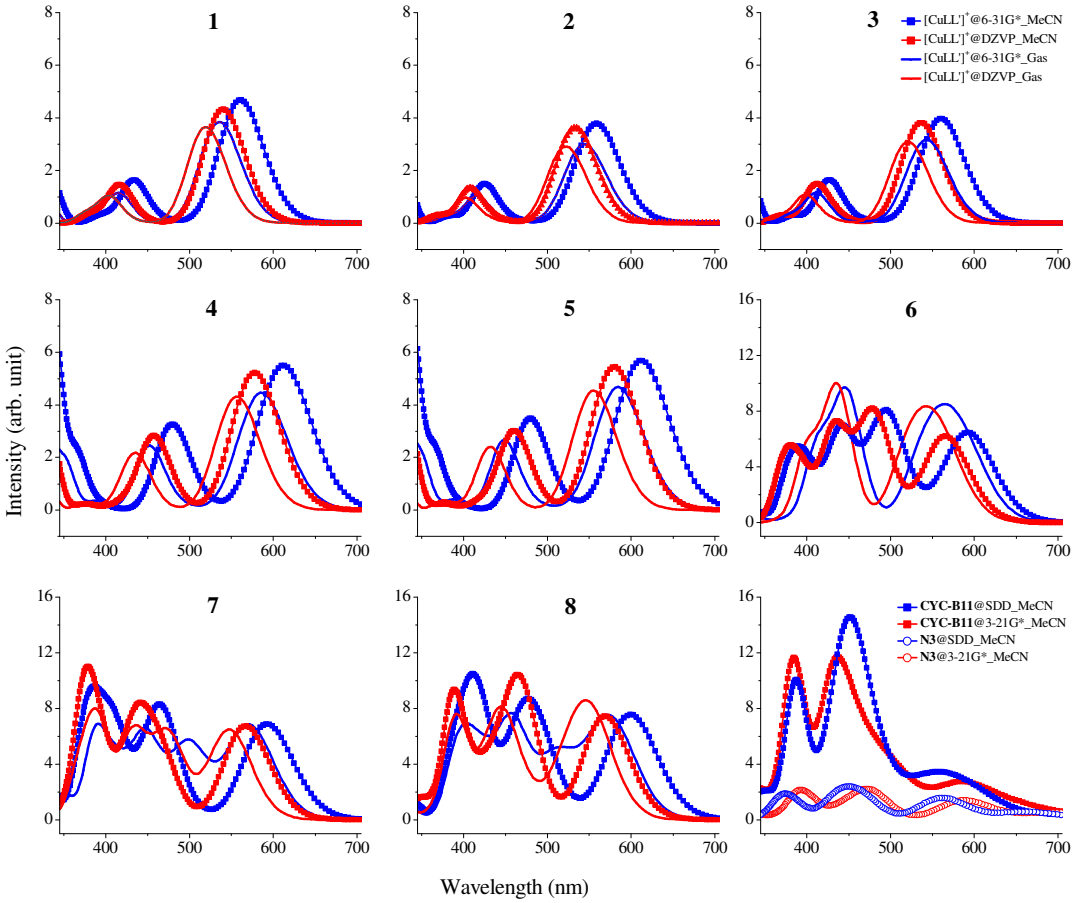

Figure S4: The frontier molecular orbitals of **CYC-B11** calculated at the B3LYP/SDD level in MeCN solution. Isodensity contour = 0.02.

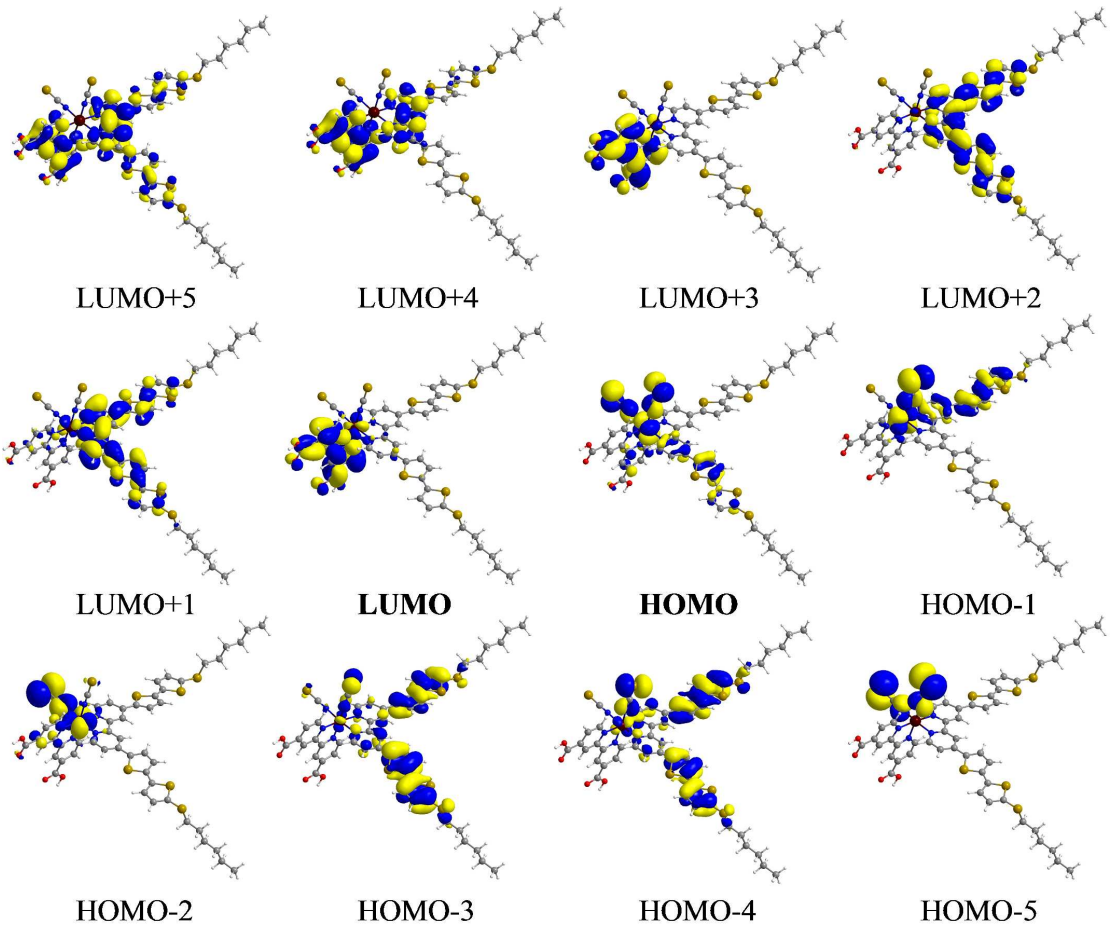

TABLE S1: Geometrical Parameters of $[CuLL']^+$ Calculated at the B3LYP/DZVP Level in MeCN Solution. Bond Lengths are in Angstroms, and Angles are in Degrees.

Parameters	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
R_{Cu-N1}	2.030	2.024	2.031	2.030	2.030	2.035	2.034	2.034
R_{Cu-N2}	2.030	2.037	2.030	2.030	2.030	2.035	2.034	2.034
R_{Cu-N3}	2.030	2.032	2.031	2.030	2.030	2.026	2.028	2.027
R_{Cu-N4}	2.030	2.029	2.031	2.030	2.030	2.026	2.027	2.027
R_{C1-O1}	1.232	1.231	1.231	1.232	1.233	1.229	1.229	1.229
R_{C1-O2}	1.357	1.357	1.363	1.374	1.373	1.367	1.367	1.367
∠N1-Cu-N2	81.9	81.7	81.8	81.5	81.5	81.4	81.5	81.5
∠N2-Cu-N3	124.6	124.7	124.9	125.0	125.0	125.1	124.9	125.2
∠N3-Cu-N4	81.9	81.7	81.8	81.5	81.5	81.8	81.6	81.7
∠N2-Cu-N4	125.0	124.4	124.9	125.0	125.0	124.8	125.1	124.8
∠N1-N2-N3-N4	-80.6	-81.2	-80.9	-81.0	-81.0	-81.2	-80.8	-80.6

TABLE S2: Selected Excitation Energies (E, nm), Oscillator Strengths (f), and Relative Orbital Contributions for the Optical Transitions between 350 and 700 nm of **5** and **7** at the B3LYP/6-31G* Level in the Gas Phase.

E	f	composition[a]
		5
584.6	0.430	H-1 → L+1 (44%) H-0 → L+0 (44%)
448.3	0.120	H-0 → L+3 (60%) H-1 → L+2 (30%)
448.3	0.120	H-1 → L+3 (60%) H-0 → L+2 (30%)
389.3	0.036	H-1 → L+4 (43%) H-0 → L+5 (43%)
349.6	0.182	H-3 → L+3 (97%)
		7
571.7	0.619	H-2 → L+0 (52%) H-0 → L+1 (37%)
511.7	0.089	H-6 → L+0 (83%) H-1 → L+1 (10%)
498.6	0.396	H-1 → L+1 (86%)
485.3	0.035	H-0 → L+1 (55%) H-2 → L+0 (31%)
478.6	0.015	H-0 → L+2 (66%) H-3 → L+2 (25%)
448.3	0.079	H-2 → L+2 (86%)
448.1	0.453	H-0 → L+3 (87%)
446.9	0.016	H-3 → L+1 (82%)
414.8	0.296	H-1 → L+3 (75%) H-5 → L+1 (11%)
404.3	0.030	H-0 → L+5 (46%) H-2 → L+4 (42%)
389.2	0.308	H-5 → L+1 (64%) H-1 → L+3 (16%)
387.4	0.185	H-3 → L+3 (63%) H-4 → L+1 (19%)
378.5	0.085	H-1 → L+5 (91%)
350.7	0.106	H-4 → L+3 (81%)

[a] Only oscillator strength f > 0.02 and orbital percentage > 10% are reported, where H = HOMO and L = LUMO.

TABLE S3: Selected Excitation Energies (E, nm), Oscillator Strengths (f), and Relative Orbital Contributions for the Optical Transitions between 350 and 700 nm of **CYC-B11** at the B3LYP/SDD Level in MeCN Solution.

E	f	composition[a]
608.8	0.117	H-0 → L+1 (83%)
570.2	0.179	H-2 → L+0 (73%) H-1 → L+1 (13%)
541.5	0.091	H-1 → L+1 (46%) H-2 → L+1 (35%)
528.2	0.108	H-2 → L+1 (56%) H-1 → L+1 (24%)
491.5	0.183	H-0 → L+2 (64%) H-0 → L+3 (29%)
475.7	0.226	H-0 → L+3 (41%) H-0 → L+2 (28%)
463.5	0.199	H-3 → L+0 (89%)
455.4	0.083	H-4 → L+0 (69%) H-1 → L+2 (13%)
452.5	0.472	H-1 → L+2 (51%) H-4 → L+0 (15%) H-3 → L+1 (12%)
446.9	0.105	H-0 → L+4 (38%) H-5 → L+0 (27%) H-3 → L+1 (20%)
446.1	0.153	H-5 → L+0 (59%) H-3 → L+1 (27%)
443.9	0.095	H-0 → L+4 (36%) H-3 → L+1 (32%) H-1 → L+2 (16%)
442.1	0.023	H-2 → L+3 (71%) H-0 → L+4 (11%)
430.3	0.313	H-4 → L+1 (92%)
420.9	0.047	H-0 → L+5 (90%)
394.3	0.034	H-1 → L+5 (88%)
389.5	0.348	H-3 → L+2 (55%) H-8 → L+0 (31%)
386.4	0.183	H-3 → L+2 (36%) H-8 → L+0 (27%) H-6 → L+0 (16%)
385.5	0.334	H-4 → L+2 (92%)
363.9	0.027	H-10 → L+0 (36%) H-5 → L+3 (17%) H-6 → L+1 (13%)
350.5	0.053	H-7 → L+1 (33%) H-7 → L+0 (22%) H-3 → L+4 (17%)

[a] Only oscillator strength f > 0.02 and orbital percentage > 10% are reported, where H = HOMO and L = LUMO.