Electronic Supplementary Information (ESI)

Effect of functionalized π-bridge on porphyrin sensitizers for dye-sensitized solar cells: An in-depth analysis of electronic structure, spectrum, excitation, and intramolecular electron transfer†

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Fig. S1 Simulated absorption spectra of the reference sensitizers **SM315** and **SM371** at the B3LYP/6-31G(d), CAM-B3LYP/6-31G(d), PBE0/6-31G(d), and M06/6-31G(d) levels.

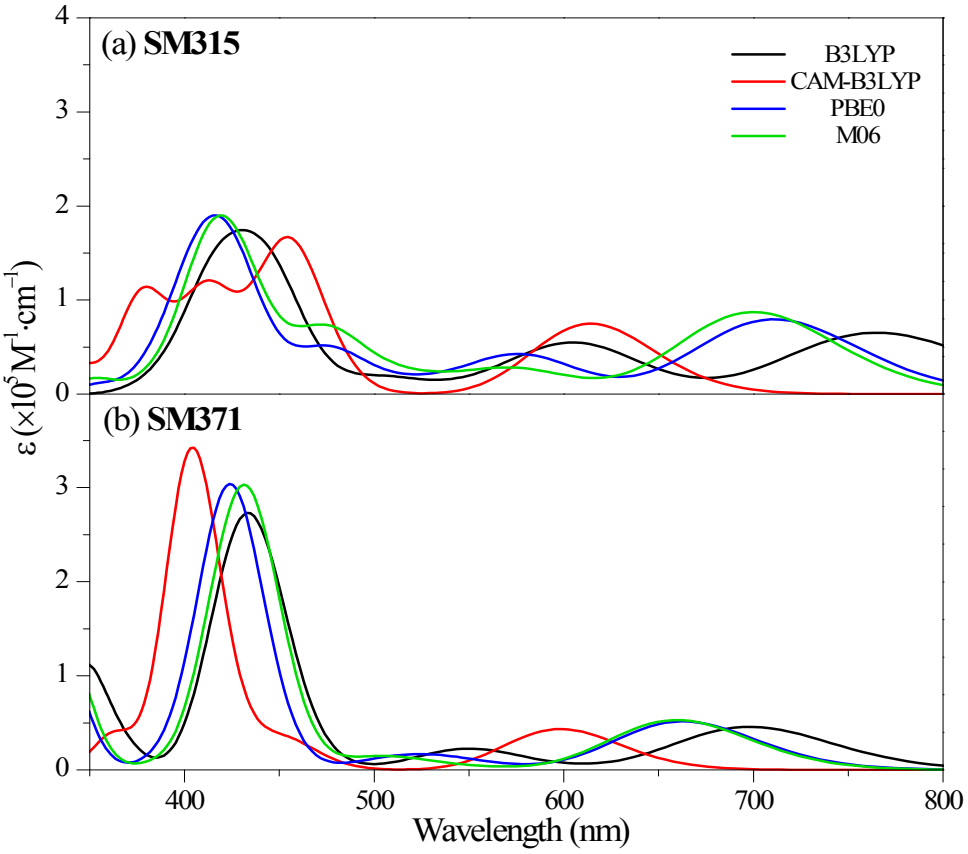

Fig. S2 The first three frontier molecular orbitals of other porphyrin sensitizers. Isodensity contour = 0.02.

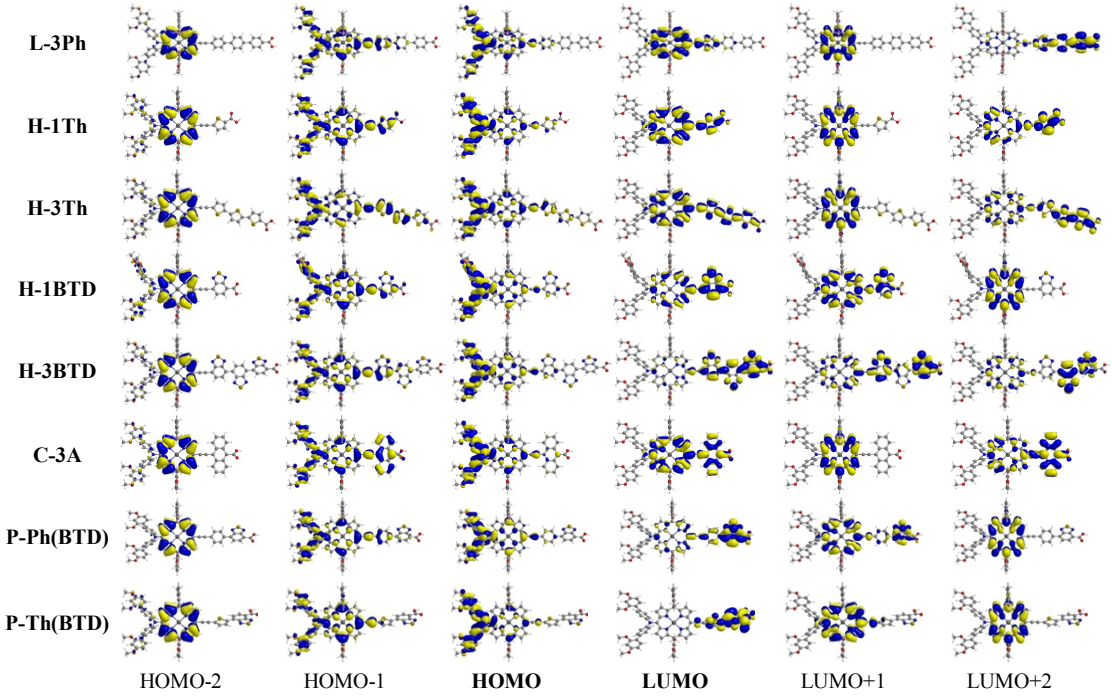

Table S1. The first three energy levels of all porphyrin sensitizers.

Sensitizers	H-2	H-1	HOMO	LUMO	L+1	L+2
SM315	-2.277	-2.317	-2.853	-4.775	-5.210	-5.328
P-Ph(BTD)	-2.231	-2.443	-2.765	-5.071	-5.495	-5.546
P-(BTD)Th	-2.285	-2.359	-2.988	-4.778	-5.203	-5.336
P-Th(BTD)	-2.279	-2.510	-2.949	-4.775	-5.307	-5.326
SM371	-1.599	-2.279	-2.611	-4.777	-5.246	-5.328
L-2Ph	-1.721	-2.260	-2.548	-4.754	-5.188	-5.309
L-3Ph	-1.771	-2.253	-2.526	-4.745	-5.165	-5.302
H-1Th	-1.757	-2.293	-2.675	-4.784	-5.236	-5.344
H-2Th	-2.051	-2.280	-2.674	-4.755	-5.140	-5.331
H-3Th	-2.210	-2.274	-2.671	-4.742	-5.069	-5.326
C-2A	-1.870	-2.285	-2.642	-4.789	-5.235	-5.331
C-3A	-2.096	-2.285	-2.681	-4.768	-5.153	-5.334
H-1BTD	-2.305	-2.356	-3.008	-4.813	-5.287	-5.353
H-2BTD	-2.310	-2.564	-3.067	-4.788	-5.227	-5.341
H-3BTD	-2.407	-2.719	-3.083	-4.777	-5.200	-5.331

Note: All energies are in eV, where H = HOMO and L = LUMO.

Table S2. Selected excitation energies (E, nm), oscillator strengths (*f*), and relative orbital contributions for the optical transition between 350 and 800 nm of other porphyrin sensitizers.

E	*f*	Compositions[a]	E	*f*	Compositions
		SM315	410.8	0.238	H→L+2(72%) H-2→L+1(13%)
700.2	0.801	H→L(87%)	365.1	0.233	H-2→L+2(91%)
576.4	0.229	H-1→L(83%)	354.9	0.083	H-9→L(48%) H-1→L+2(17%)
544.9	0.033	H→L+1(67%) H-2→L+2(15%)			H-16→L(13%)
516.7	0.152	H→L+2(47%) H-2→L(39%)	350.8	0.046	H-15→L(64%) H-4→L+1(14%)
		H-1→L+2(12%)	337.5	0.808	H→L+4(70%) H-16→L(13%)
475.1	0.576	H-1→L+1(38%) H-2→L+2(24%)	337.4	0.180	H-16→L(54%) H→L+4(17%)
		H→L+1(16%) H-1→L(10%)	328.6	0.033	H-10→L(89%)
473.0	0.038	H-1→L+2(40%) H-2→L+1(39%)			**H-3Th**
		H-2→L(15%)	681.7	1.106	H→L(89%)
454.8	0.015	H-3→L(93%)	573.5	0.361	H-1→L(88%)
429.6	0.992	H-1→L+1(37%) H-2→L+2(23%)	508.3	0.981	H→L+2(46%) H-2→L+1(27%)
		H-7→L(17%) H-4→L(16%)			H-1→L+2(10%)
412.3	0.947	H-2→L+1(47%) H-1→L+2(38%)	507.0	0.142	H-1→L+1(44%) H→L+1(28%)
407.6	0.012	H-5→L(92%)			H-2→L(22%)
400.5	0.212	H-4→L(46%) H-2→L+2(17%)	468.9	0.486	H→L+2(38%) H-4→L(36%)
389.9	0.012	H-8→L(42%) H-7→L(21%)			H-2→L+1(18%)
382.6	0.072	H-7→L(25%) H-9→L(14%)	450.8	0.432	H-1→L+1(42%) H-2→L(36%)
		H-8→L(12%) H-4→L(11%)	436.2	0.123	H-3→L(87%)
		H-3→L+2(10%)	430.8	0.045	H-1→L+2(75%) H-4→L(12%)
380.9	0.047	H-3→L+1(94%)	407.4	0.286	H-4→L(38%) H-2→L+1(37%)
355.8	0.039	H-15→L(66%)	406.3	0.094	H-2→L+2(80%) H-4→L+1(10%)
352.5	0.086	H-16→L(36%) H-4→L+1(19%)	374.4	0.533	H-4→L+1(75%) H-2→L+2(11%)
		H-7→L+1(18%)	373.9	0.193	H-4→L+2(41%) H→L+3(30%)
350.7	0.016	H-14→L(36%) H-4→L+2(20%)			H-7→L(11%)
345.2	0.013	H-4→L+1(33%) H-16→L(29%)	366.2	0.286	H-4→L+2(37%) H→L+3(31%)
		P-Ph(BTD)	365.3	0.014	H-5→L+1(89%)
673.9	0.715	H→L(64%) H→L+1(27%)	365.0	0.012	H-6→L+1(90%)
575.5	0.033	H→L+1(61%) H→L(27%)	358.6	0.019	H-12→L+1(60%) H-8→L+1(11%)
555.4	0.110	H-1→L(53%) H-1→L+1(26%)	356.1	0.032	H-3→L+2(94%)
		H-2→L+2(12%)	348.4	0.010	H-16→L(72%)
508.6	0.126	H-2→L(40%) H→L+2(36%)	348.0	0.043	H-11→L(42%) H-17→L(24%)
		H-1→L+2(21%)			H-13→L(11%)
491.5	0.349	H-1→L+1(40%) H-1→L(34%)	342.8	0.032	H-14→L(72%)
		H-2→L+2(14%)			**H-1BTD**
442.7	0.018	H-3→L(79%) H-3→L+1(15%)	727.3	0.691	H→L(89%)
432.2	1.859	H-2→L+2(47%) H-1→L+1(27%)	588.0	0.232	H-1→L(76%) H-2→L(10%)
417.8	0.952	H-1→L+2(45%) H-2→L+1(38%)	550.1	0.017	H→L+1(74%) H-2→L+2(11%)
402.2	0.126	H-3→L+1(82%) H-3→L(13%)	529.9	0.134	H→L+2(59%) H-2→L(30%)
396.4	0.011	H-4→L(41%) H-7→L(22%)	479.3	0.033	H-3→L(33%) H-1→L+2(24%)
		H-2→L+2(10%)			H-2→L+1(15%)
387.1	0.010	H-3→L+2(93%)`	478.7	0.453	H-1→L+1(36%) H-2→L+2(23%)
364.4	0.019	H→L+3(58%) H-6→L+2(11%)			H→L+1(12%)
357.8	0.047	H-4→L+1(31%) H-4→L(10%)	477.1	0.024	H-3→L(55%) H-2→L+1(25%)
349.3	0.043	H-4→L+2(32%) H-15→L(21%)			H-1→L+2(15%)
		H-15→L+1(21%)	425.3	0.017	H-5→L(86%) H-4→L(10%)
346.8	0.055	H-7→L+1(32%) H-4→L+1(20%)	422.6	0.457	H-6→L(38%) H-4→L(18%)
		P-Th(BTD)			H-1→L+1(11%) H-2→L+2(10%)
725.4	1.018	H→L(82%) H→L+1(11%)	421.8	0.458	H-6→L(55%) H-2→L+2(12%)
598.5	0.243	H-1→L(66%) H→L+1(26%)			H-1→L+1(12%)
582.6	0.067	H→L+1(50%) H→L(15%)	408.5	0.805	H-1→L+2(25%) H-2→L+1(24%)

		H-1→L(15%) H-2→L+2(11%)			H-1→L+1(13%) H-4→L(13%)
526.6	0.120	H-2→L(53%) H→L+2(39%)			H-2→L+2(12%)
505.4	0.281	H-1→L+1(55%) H-2→L+2(20%)	408.2	0.369	H-4→L(41%) H-2→L+1(17%)
		H-1→L(10%)			H-1→L+2(15%)
466.5	0.011	H-3→L(92%)	403.4	0.032	H-7→L(80%)
455.3	0.903	H-4→L(40%) H-1→L+1(20%)	388.0	0.129	H-3→L+1(93%)
		H-2→L+2(19%) H-7→L(12%)	375.5	0.153	H-9→L(61%)
424.2	0.813	H-2→L+1(44%) H-1→L+2(41%)	365.5	0.024	H-15→L(70%) H-6→L+2(10%)
419.4	0.519	H-4→L(36%) H-2→L+2(32%)			**H-3BTD**
404.5	0.104	H-3→L+1(90%)	739.4	1.062	H→L(78%) H→L+1(12%)
378.4	0.041	H→L+3(69%) H-4→L+1(12%)	610.9	0.094	H→L+1(41%) H-1→L(32%)
369.2	0.173	H-4→L+1(58%)			H→L+2(11%)
361.5	0.027	H-8→L+2(41%) H-12→L+2(20%)	601.5	0.314	H-1→L(44%) H→L+1(19%)
		H-9→L+2(12%)			H→L(16%) H-1→L+1(11%)
359.3	0.022	H-12→L+2(38%) H-8→L+2(19%)	538.1	0.082	H-2→L(52%) H→L+3(40%)
		H-4→L+2(19%) H-9→L+2(15%)	534.3	0.039	H→L+2(38%) H→L+1(21%)
355.7	0.034	H-16→L(51%) H-16→L+1(19%)			H→L+4(19%) H-2→L+3(12%)
354.4	0.055	H-4→L+2(31%) H-12→L+2(28%)	518.5	0.148	H-1→L+1(52%) H-1→L(12%)
		H-14→L(17%) H-14→L+1(10%)			H-2→L+3(10%)
		SM371	495.3	0.043	H-1→L+3(37%) H-2→L+1(29%)
659.5	0.487	H→L(91%)			H→L+3(17%)
546.3	0.029	H-1→L(75%) H-2→L+1(19%)	488.8	0.048	H→L+4(46%) H→L+2(36%)
504.2	0.129	H→L+1(40%) H-1→L+1(31%)			H-1→L+4(10%)
		H-2→L(28%)	475.0	0.028	H-3→L(90%)
437.2	0.064	H-3→L(83%)	474.3	0.720	H-4→L(44%) H-1→L+1(16%)
435.8	2.135	H-2→L+1(61%) H-1→L(18%)			H→L+4(10%)
418.1	0.985	H-1→L+1(52%) H-2→L(26%)	458.6	0.016	H-1→L+2(30%) H-4→L(25%)
		H-3→L(15%)			H-1→L+1(12%) H-1→L+4(10%)
393.6	0.041	H→L+2(74%)	455.9	0.061	H-2→L+1(50%) H-1→L+3(18%)
388.3	0.013	H-3→L+1(97%)			H-2→L+2(16%) H-2→L+4(13%)
385.6	0.016	H-11→L(61%) H-12→L(21%)	428.8	0.102	H-1→L+2(40%) H-1→L+4(28%)
		H-9→L(12%)	422.4	0.076	H-3→L+1(68%)
349.9	0.045	H-9→L(49%) H-16→L(11%)	420.7	0.372	H-1→L+4(36%) H-2→L+3(24%)
		H-2→L+2(11%)			H-4→L+1(15%)
349.9	0.076	H-2→L+2(63%) H-15→L(11%)	420.1	0.013	H-5→L(84%) H-5→L+1(11%)
348.2	0.093	H-15→L(48%) H-2→L+2(20%)	413.9	0.667	H-2→L+2(49%) H-1→L+3(27%)
		H-6→L+1(10%)			H-3→L+1(14%)
343.9	0.015	H-13→L(67%) H-15→L(12%)	407.9	0.161	H-2→L+4(78%) H-2→L+2(10%)
338.2	0.984	H→L+4(88%)	405.4	0.149	H-7→L(50%) H-4→L+1(18%)
325.0	0.015	H→L+3(83%)			H-4→L(13%)
324.5	0.030	H-10→L(90%)	401.9	0.221	H-4→L+1(35%) H-7→L(19%)
		L-3Ph			H-7→L+1(12%)
651.2	0.593	H→L(90%)	393.4	0.016	H-12→L(29%) H-12→L+1(20%)
543.5	0.042	H-1→L(78%) H-2→L+1(16%)			H-11→L(11%)
501.1	0.104	H-1→L+1(41%) H→L+1(32%)	387.5	0.011	H-3→L+3(95%)
		H-2→L(25%)	379.9	0.025	H-3→L+2(77%) H-3→L+4(12%)
443.8	2.540	H-2→L+1(58%) H-1→L(15%)			**C-3A**
430.5	0.334	H-3→L(49%) H-1→L+1(24%)	677.0	0.657	H→L(90%)
		H-2→L(22%)	565.5	0.132	H-1→L(86%)
418.9	0.704	H-3→L(49%) H-1→L+1(28%)	508.1	0.125	H→L+1(37%) H-1→L+1(32%)
		H-2→L(17%)			H-2→L(28%)
377.3	0.038	H-4→L(59%) H-11→L(13%)	500.2	0.544	H→L+2(43%) H-2→L+1(30%)
361.9	0.032	H-7→L(58%) H-8→L(10%)			H-1→L+2(10%) H-4→L(10%)
355.3	0.067	H-1→L+2(82%)	473.3	0.160	H-4→L(49%) H→L+2(36%)
351.9	0.025	H-4→L+1(46%) H-2→L+2(29%)	449.9	0.277	H-1→L+1(45%) H-2→L(28%)
347.8	0.120	H-2→L+2(62%) H-4→L+1(18%)			H-3→L(14%)
339.4	0.046	H-13→L(35%) H-17→L(30%)	438.9	0.114	H-3→L(82%)
		H-16→L+1(12%)	427.6	0.225	H-1→L+2(54%) H-4→L(19%)

339.1	0.957	H→L+4(83%) H-1→L+4(10%)			H→L+2(13%)
338.6	0.029	H-14→L(47%) H-4→L+1(14%)	410.1	0.138	H-2→L+2(67%) H-4→L+1(20%)
		H-7→L+1(14%) H-16→L(13%)	405.1	0.553	H-2→L+1(34%) H-1→L+2(24%)
332.1	0.228	H-7→L+1(72%) H-14→L(15%)			H-4→L(16%) H-4→L+2(14%)
		H-1Th	382.2	0.015	H-7→L(55%) H-8→L(34%)
671.2	0.541	H→L(91%)	378.6	0.684	H-4→L+1(71%) H-2→L+2(17%)
554.9	0.067	H-1→L(79%) H-2→L+1(15%)	378.4	0.011	H-8→L(54%) H-7→L(32%)
507.3	0.135	H→L+1(42%) H-1→L+1(29%)	371.2	0.394	H-4→L+2(72%)
		H-2→L(28%)	357.9	0.017	H-12→L+1(70%) H-11→L+1(18%)
448.1	1.786	H-2→L+1(54%) H→L+2(18%)	351.8	0.034	H-3→L+2(95%)
		H-1→L(13%)	349.3	0.011	H-17→L(79%)
444.1	0.053	H-3→L(83%)	343.8	0.024	H-14→L(78%)
425.1	0.834	H-1→L+1(52%) H-2→L(25%)	343.6	0.035	H-16→L(49%) H-16→L+2(16%)
		H-3→L(14%)			H-1→L+5(14%) H-4→L+5(10%)

[a] Only oscillator strength $f > 0.01$ and orbital percentage > 10% are reported, where H = HOMO and L = LUMO.

Table S3. The values of HOMO and LUMO energies, the HOMO-LUMO gaps, the lowest vertical excitation energies (EA), oscillator strengths, and relative LHE (RLHE) of all porphyrin sensitizers calculated in THF solution.

Sensitizers	H	L	ΔH-L	E_A	f	RLHE
SM315	-2.853	-4.775	1.922	1.771	0.801	1.249
P-Ph(BTD)	-2.765	-5.071	2.306	1.840	0.715	1.197
P-(BTD)Th	-2.988	-4.778	1.790	1.686	0.961	1.321
P-Th(BTD)	-2.949	-4.775	1.826	1.709	1.018	1.341
SM371	-2.611	-4.777	2.166	1.880	0.487	1.000
L-2Ph	-2.548	-4.754	2.206	1.899	0.559	1.074
L-3Ph	-2.526	-4.745	2.219	1.904	0.593	1.105
H-1Th	-2.675	-4.784	2.109	1.847	0.541	1.057
H-2Th	-2.674	-4.755	2.081	1.827	0.835	1.266
H-3Th	-2.671	-4.742	2.071	1.819	1.106	1.367
C-2A	-2.642	-4.789	2.147	1.871	0.527	1.043
C-3A	-2.681	-4.768	2.087	1.831	0.657	1.157
H-1BTD	-3.008	-4.813	1.805	1.705	0.691	1.181
H-2BTD	-3.067	-4.788	1.721	1.673	0.913	1.302
H-3BTD	-3.083	-4.777	1.694	1.677	1.062	1.355

Note: All energies are in eV, where H = HOMO and L = LUMO.