Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

The influence of inner electric field on the performance of three types of Zn-porphyrin sensitizers in dye sensitized solar cells: A theoretical study

Miao Xie[a,b], **Fu-Quan Bai**[a,*], **Hong-Xing Zhang**[a], **Yue-Qing Zheng**[b,*]

a *Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China.*

*E-mail: baifq@jlu.edu.cn (Fu-Quan Bai).

b *Research Center of Applied Solid State Chemistry, Chemistry Institute for Synthesis and Green Application, Ningbo University, Ningbo 315211, P.R. China*

*E-mail: zhengcm@nbu.edu.cn (Yue-Qing Zheng)

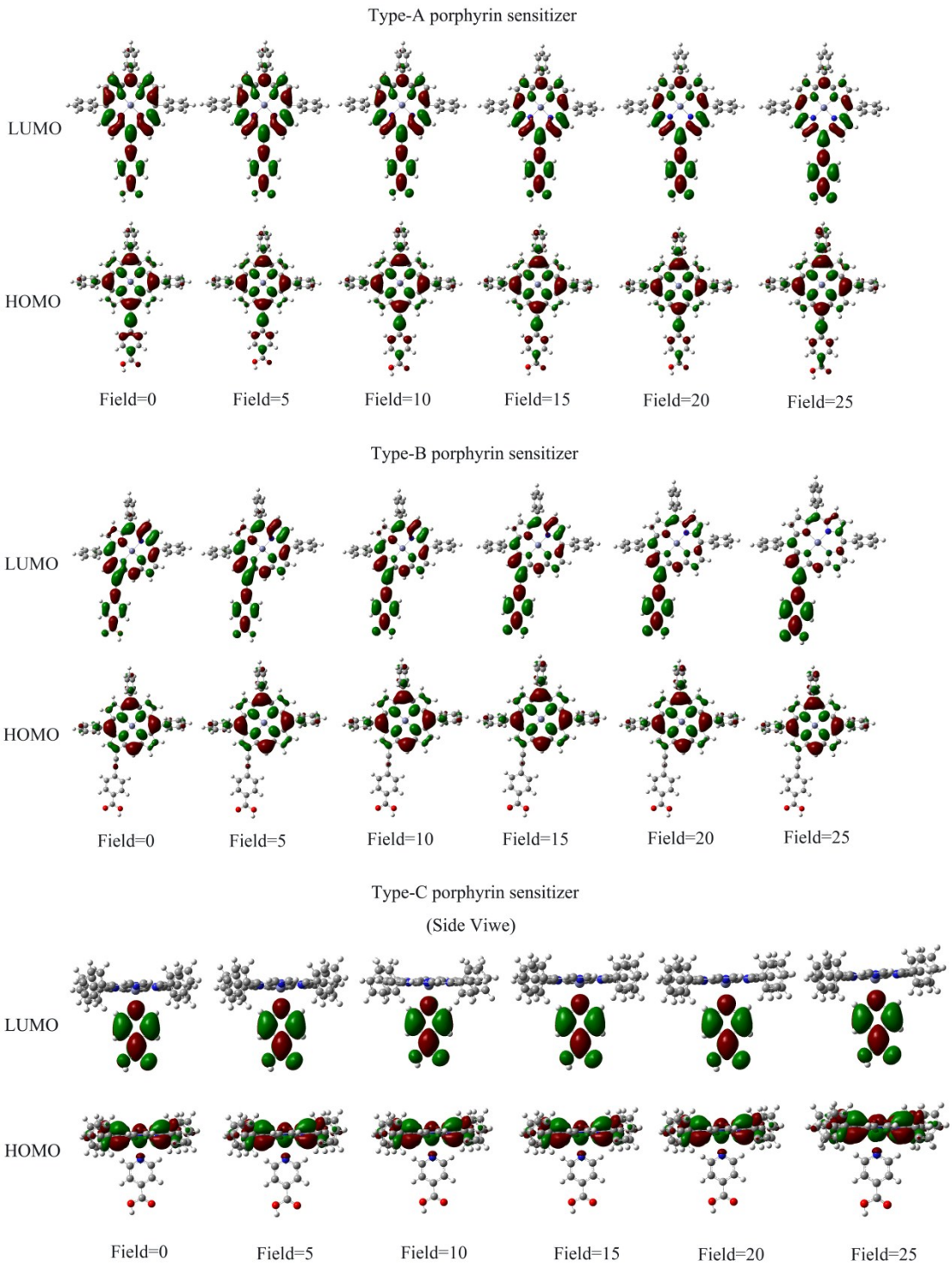

Fig. S1. Profiles of HOMO and LUMO of dye A, B and C system in THF solution with different electric field strengths.

Table S1 Partial Molecular Orbital Compositions (%) of dye B system in THF solution with different electric field strengths. (The abbreviations: the Zn-Por is Zn-porphyrin, the PH is phenyl group)

Field (10^{-4} a.u.)	MO	Energy(eV)	Main Component (%)				Assignment
			Zn-Por	PH	π-bridge	COOH	
Field=0	LUMO+2	-1.847	29	3	48	20	**π***(Zn-phy)+**π***(π)+ **π***(COOH)
	LUMO+1	-2.386	90	10	0	0	**π***(Zn-phy)
	LUMO	-2.604	74	7	16	4	**π***(Zn-phy)
	HOMO	-5.213	84	14	1	0	**π**(Zn-phy)
	HOMO-1	-5.370	88	4	8	0	**π**(Zn-phy)
	HOMO-2	-6.069	53	2	43	3	**π** (Zn-phy)+**π**(π)
Field+5	LUMO+2	-1.948	33	3	43	20	**π***(Zn-phy)+**π***(π)+ **π***(COOH)
	LUMO+1	-2.345	90	10	0	0	**π***(Zn-phy)
	LUMO	-2.619	66	6	22	6	**π***(Zn-phy)+**π***(π)
	HOMO	-5.171	85	14	1	0	**π**(Zn-phy)
	HOMO-1	-5.344	90	4	6	0	**π**(Zn-phy)
	HOMO-2	-6.126	53	2	42	3	**π**(Zn-phy) +**π**(π)
Field+10	LUMO+2	-2.035	41	4	31	10	**π***(Zn-phy)+**π***(π)

	LUMO+1	-2.306	90	10	0	0	**π***(Zn-phy)
	LUMO	-2.656	55	4	31	10	**π***(Zn-phy)+**π***(π)
	HOMO	-5.129	85	14	1	0	**π**(Zn-phy)
	HOMO-1	-5.317	90	4	5	0	**π**(Zn-phy)
	HOMO-2	-6.179	55	2	40	3	**π**(Zn-phy) +**π**(π)
Field+15	LUMO+2	-2.101	51	5	27	17	**π***(Zn-phy)+**π***(π)
	LUMO+1	-2.267	90	10	0	0	**π***(Zn-phy)
	LUMO	-2.720	43	3	40	14	**π***(Zn-phy)+**π***(π)
	HOMO	-5.087	84	15	1	0	**π**(Zn-phy)
	HOMO-1	-5.288	91	4	5	0	**π**(Zn-phy)
	HOMO-2	-6.224	57	6	35	2	**π**(Zn-phy)+**π**(π)
	HOMO-3	-6.321	24	74	2	0	**π**(Zn-phy)+**π**(PH)
Field+20	LUMO+2	-2.145	61	5	20	14	**π***(Zn-phy)+**π***(π)
	LUMO+1	-2.229	89	10	1	0	**π***(Zn-phy)
	LUMO	-2.811	32	2	47	19	**π***(Zn-phy)+**π***(π)
	HOMO	-5.044	84	15	1	0	**π**(Zn-phy)
	HOMO-1	-5.259	91	4	4	0	**π**(Zn-phy)

	HOMO-2	-6.151	22	77	1	0	**π**(Zn-phy)+**π**(PH)
	HOMO-4	-6.274	59	7	31	2	**π**(Zn-phy)+**π**(π)
Field+25	LUMO+2	-2.165	74	6	11	9	**π***(Zn-phy)
	LUMO+1	-2.197	83	10	4	3	**π***(Zn-phy)
	LUMO	-2.924	23	1	52	24	**π***(Zn-phy)+**π***(π)
	HOMO	-5.002	84	16	1	0	**π**(Zn-phy)
	HOMO-1	-5.229	91	4	4	0	**π**(Zn-phy)
	HOMO-2	-5.994	21	79	0	0	**π**(Zn-phy)+**π**(PH)
	HOMO-4	-6.274	80	8	11	1	**π**(Zn-phy)

Table S2 Partial Molecular Orbital Compositions (%) of dye C system in THF solution with different electric field strengths. (The abbreviations: the Zn-Por is Zn-porphyrin, the PH is phenyl group)

Field (10^{-4} a.u.)	MO	Energy(eV)	Main Component (%)				Assignment
			Zn-Phy	PH	π-bridge	COOH	
Field=0	LUMO+2	-2.232	79	11	7	3	π*(Zn-phy)
	LUMO+1	-2.239	87	12	1	0	π*(Zn-phy)
	LUMO	-2.371	10	1	63	26	π*(π)+ π*(COOH)
	HOMO	-4.958	81	17	2	0	π(Zn-phy)
	HOMO-1	-5.235	95	5	0	0	π(Zn-phy)
Field+5	LUMO+2	-2.241	85	12	2	1	π*(Zn-phy)
	LUMO+1	-2.242	86	12	1	0	π*(Zn-phy)
	LUMO	-2.487	4	1	67	29	π*(π)+ π*(COOH)
	HOMO	-4.961	81	17	2	0	π(Zn-phy)
	HOMO-1	-5.238	95	5	0	0	π(Zn-phy)
Field+10	LUMO+2	-2.245	87	12	1	0	π*(Zn-phy)
	LUMO+1	-2.247	86	12	1	1	π*(Zn-phy)
	LUMO	-2.608	2	0	67	31	π*(π)+ π*(COOH)

	HOMO	-4.966	81	17	2	0	π(Zn-phy)
	HOMO-1	-5.241	95	5	0	0	π(Zn-phy)
Field+15	LUMO+2	-2.248	87	12	1	0	π*(Zn-phy)
	LUMO+1	-2.251	87	12	0	0	π*(Zn-phy)
	LUMO	-2.731	2	0	66	32	π*(π)+ π*(COOH)
	HOMO	-4.970	81	17	1	0	π(Zn-phy)
	HOMO-1	-5.245	95	5	0	0	π(Zn-phy)
Field+20	LUMO+2	-2.251	87	12	1	0	π*(Zn-phy)
	LUMO+1	-2.256	87	12	0	0	π*(Zn-phy)
	LUMO	-2.855	1	0	66	33	π*(π)+ π*(COOH)
	HOMO	-4.974	81	17	1	0	π(Zn-phy)
	HOMO-1	-5.248	95	5	0	0	π(Zn-phy)
Field+25	LUMO+2	-2.255	87	12	1	0	π*(Zn-phy)
	LUMO+1	-2.259	87	12	0	0	π*(Zn-phy)
	LUMO	-2.979	1	0	65	33	π*(π)+ π*(COOH)
	HOMO	-4.978	81	17	1	0	π(Zn-phy)

	HOMO-1	-5.252	95	5	0	0	π(Zn-phy)

Table S3 Calculated absorptions (λ > 350 nm) of the dye A system in THF solution with different electric field strengths.

Field (10^{-4} a.u.)	**Main transitions**	**ΔEcal(eV)**	**λcal(nm)**	***f***	**Character**
Field=0	HOMO → LUMO (82%)	2.0695	599	0.5044	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (59%)	2.8096	441	1.7659	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (24%)				π (Zn-phy) → π* (Zn-phy) + π* (COOH)
	H-1 → LUMO (53%)	2.8382	436	1.0628	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (42%				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (63%)	3.3902	365	0.2285	π (Zn-phy) → π* (Zn-phy) + π* (COOH)
	H-3 → LUMO (20%)				π (Zn-phy) → π* (Zn-phy)
Field+5	HOMO → LUMO (83%)	2.0575	602	0.5514	π (Zn-phy) → π* (Zn-phy) +π* (π)
	H-1 → L+1 (50%)	2.7555	449	1.4532	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (37%)				π (Zn-phy) → π* (Zn-phy) + *(π) + π* (COOH)
	H-1 → LUMO (47%)	2.7928	443	0.8840	π (Zn-phy) → π* (Zn-phy) +π* (π)
	HOMO → L+1 (43%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (49%)	3.0951	400	0.4230	π (Zn-phy) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-2 → LUMO (24%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+1 (21%)				π (Zn-phy) → π* (Zn-phy)

	H-1 → L+2 (82%)	3.2740	378	0.4853	π (Zn-phy) → π* (Zn-phy) +π* (π) + π* (COOH)
Field+10	HOMO → LUMO (85%)	2.0372	608	0.6201	π (Zn-phy) → π* (Zn-phy) +π* (π)
	HOMO → L+2 (47%)	2.6836	462	1.0944	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+1 (42%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (42%)	2.7226	455	0.6413	π (Zn-phy) → π* (Zn-phy)
	H-1 → LUMO (40%)				π (Zn-phy) → π* (Zn-phy) +π* (π)
	HOMO → L+2 (41%)	3.0674	404	0.7339	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+1 (31%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (79%)	3.1925	388	0.7858	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
Field+15	HOMO → LUMO (87%)	2.0063	617	0.7107	π (Zn-phy) → π* (Zn-phy) +π* (π)
	HOMO → L+2 (54%)	2.6043	476	0.7727	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+1 (37%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (43%)	2.6331	470	0.4155	π (Zn-phy) → π* (Zn-phy)
	H-1 → LUMO (32%)				π (Zn-phy) → π* (Zn-phy) +π* (π)
	H-1 → L+2 (25%)				π (Zn-phy) → π* (Zn-phy) +π* (π)
	H-1 → L+1 (38%)	3.0435	407	0.9717	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (33%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)

	H-1 → L+2 (66%)	3.1267	396	0.8680	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
Field+20	HOMO → LUMO (90%)	1.9622	631	0.8157	π (Zn-phy) → π* (Zn-phy) +π* (π)
	HOMO → L+2 (58%)	2.5278	490	0.5082	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+1 (34%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (46%)	2.5390	488	0.2509	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (30%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → LUMO (23%)				π (Zn-phy) → π* (Zn-phy) +π* (π)
	H-1 → L+1 (45%)	3.0234	410	1.1654	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (32%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+2 (56%)	3.0887	401	1.0457	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	HOMO → L+1 (24%)				π (Zn-phy) → π* (Zn-phy)
Field+25	HOMO → LUMO (93%)	1.9031	651	0.9172	π (Zn-phy) → π* (Zn-phy) +π* (π)
	HOMO → L+2 (61%)	503	503	0.3023	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+1 (33%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (45%)	2.9932	414	1.282	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (26%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-4 → LUMO (70%)	3.0298	409	0.3229	π (Zn-phy) → π* (Zn-phy) +π* (π)

	H-1 → L+2 (47%) H-4 → LUMO (24%)	3.0567	405	0.8499	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH) π (Zn-phy) → π* (Zn-phy) +π* (π)

Table S4 Calculated absorptions (λ > 350 nm) of the dye B system in THF solution with different electric field strengths.

B	Main transitions	ΔEcal(eV)	λcal(nm)	*f*	Character
Field=0	HOMO → LUMO (68%)	2.1736	570	0.0515	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (27%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → LUMO (53%)	2.2161	559	0.0762	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (42%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (38%)	2.7341	453	1.8339	π (Zn-phy) → π* (Zn-phy)
	H-1 → LUMO (36%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (40%)	2.8254	438	0.3765	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+1 (39%)				π (Zn-phy) → π* (Zn-phy)
	H-2 → L+1 (39%)	3.1394	394	0.3304	π (Zn-phy)+π (π) → π* (Zn-phy)
	HOMO → L+2 (33%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-2 → L+1 (50%)	3.2885	377	0.5379	π (Zn-phy)+π (π) → π* (Zn-phy)
	HOMO → L+2 (22%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-1 → L+2 (56%)	3.3751	367	0.6301	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
Field+5	HOMO → LUMO (75%)	2.1432	578	0.0698	π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → L+1 (23%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (36%)	2.6914	460	1.6411	π (Zn-phy) → π* (Zn-phy)

	H-1 → LUMO (32%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	HOMO → L+2 (38%)	3.1441	394	0.9262	π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → L+1 (37%)				π (Zn-phy) → π* (Zn-phy)
	H-2 → L+1 (30%)	3.3013	375	0.3091	π(Zn-phy) +π(π) → π* (Zn-phy)
	H-1 → L+2 (23%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π) + π* (COOH)
	H-2 → L+1 (56%)	3.3615	368	0.5434	π(Zn-phy) +π(π) → π* (Zn-phy)
Field+10	HOMO → LUMO (81%)	2.0933	592	0.0887	π (Zn-phy) → π* (Zn-phy) +π*(π)
	HOMO → L+2 (56%)	2.5931	478	0.2267	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)
	H-1 → L+1 (30%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (39%)	2.6200	473	1.1096	π (Zn-phy) → π* (Zn-phy)
	H-1 → LUMO (33%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → L+2 (21%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-2 → LUMO (53%)	3.0173	410	0.5753	π (Zn-phy) + π (π) → π* (Zn-phy) +π*(π)
	H-1 → L+2 (41%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)
	H-1 → L+1 (46%)	3.1301	396	1.1620	π (Zn-phy) → π* (Zn-phy)
.	HOMO → L+2 (36%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)
	H-2 → LUMO (36%)	3.2938	376	0.3866	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)
	H-1 → L+2 (27%)				π (Zn-phy) → π* (Zn-phy) +π*(π)

Field+15	HOMO → LUMO (88%)	2.0141	615	0.1013	π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → LUMO (69%)	2.1454	577	0.1859	π (Zn-phy) → π* (Zn-phy) +π*(π)
	HOMO → L+1 (28%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (44%)	2.5266	490	0.8322	π (Zn-phy) → π* (Zn-phy)
	H-1 → LUMO (28%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → L+2 (26%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-2 → LUMO (47%)	2.9812	415	1.0053	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)
	H-1 → L+2 (40%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → L+1 (45%)	3.1028	399	1.1051	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (31%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-3 → LUMO (28%)	3.2837	377	0.3729	π (Zn-phy)+ π (PH) → π* (Zn-phy) +π* (π)
	H-2 → LUMO (23%)				π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)
Field+20	HOMO → LUMO (94%)	1.8997	652	0.1003	π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → LUMO (80%)	2.0820	595	0.2836	π (Zn-phy) → π* (Zn-phy) +π*(π)
	HOMO → L+1 (50%)	2.4390	508	0.5186	π (Zn-phy) → π*(π)
	H-1 → L+2 (29%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-4 → LUMO (33%)	2.9340	422	1.2492	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)

	H-1 → L+2 (31%)				π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-2 → LUMO (57%)	3.0078	412	0.2459	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)
	H-1 → L+1 (45%)	3.1191	397	0.9800	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (28%)				π (Zn-phy) → π* (Zn-phy)
	H-4 → LUMO (35%)	3.2297	383	0.2236	π (Zn-phy)+ π (π) → π* (Zn-phy) +π* (π)
Field+25	HOMO → LUMO (97%)	1.7551	706	0.0895	π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → LUMO (90%)	1.9841	624	0.3698	π (Zn-phy) → π* (Zn-phy) +π*(π)
	HOMO → L+1 (39%)	2.3738	522	0.2761	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (23%)				π (Zn-phy) → π* (Zn-phy)
	H-4 → LUMO (26%)	2.8978	427	1.3003	π (Zn-phy) → π* (Zn-phy) +π*(π)
	H-1 → L+2 (25%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (37%)	3.0719	403	1.1636	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (22%)				π (Zn-phy) → π* (Zn-phy)

Table S5 Calculated absorptions (λ > 350 nm) of the dye C system in THF solution with different electric field strengths.

C	Main transitions	ΔEcal(eV)	λcal(nm)	*f*	Character
Field=0	HOMO → LUMO (98%)	2.0814	595	0.0058	π(Zn-phy) →π*(π)+ π*(COOH)
	HOMO → L+1 (64%)	2.2096	561	0.0315	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (26%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (67%)	2.2307	555	0.0318	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (32%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (60%)	3.0592	405	1.4093	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (33%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (64%)	3.0685	404	1.4725	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (31%)				π (Zn-phy) → π* (Zn-phy)
Field+5	HOMO → LUMO (99%)	1.9696	629	0.0024	π(Zn-phy) →π*(π)+ π*(COOH)
	HOMO → L+1 (45%)		562	0.0255	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (19%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → LUMO (19%)				π(Zn-phy) →π*(π)+ π*(COOH)
	HOMO → L+2 (53%)	2.2045	556	0.0350	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (27%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (54%)	3.0598	405	1.4120	π (Zn-phy) → π* (Zn-phy)

	HOMO → L+1 (28%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (55%)	3.0684	404	1.4693	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (28%)				π (Zn-phy) → π* (Zn-phy)
Field+10	HOMO → LUMO (100%)	1.8541	668	0.0013	π(Zn-phy) →π*(π)+ π*(COOH)
	HOMO → L+2 (58%)	2.2223	558	0.0346	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (33%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (64%)	2.2223	557	0.0359	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (34%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (63%)	3.0603	405	1.4145	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (33%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (63%)	3.0679	404	1.4612	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (33%)				π (Zn-phy) → π* (Zn-phy)
Field+15	HOMO → LUMO (100%)	1.7372	713	0.0008	π(Zn-phy) →π*(π)+ π*(COOH)
	HOMO → L+2 (64%)	2.2177	559	0.0348	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (34%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (65%)	2.2242	557	0.0363	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (34%)				π (Zn-phy) → π* (Zn-phy)

	H-1 → L+1 (63%)	3.0608	405	1.4167	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (33%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (62%)	3.0664	404	1.4364	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (32%)				π (Zn-phy) → π* (Zn-phy)
Field+20	HOMO → LUMO (100%)	1.6194	765	0.0005	π(Zn-phy) →π*(π)+ π*(COOH)
	HOMO → L+2 (65%)	2.2169	559	0.0344	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (34%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (65%)	2.2242	557	0.0365	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (34%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+2 (51%)	3.0594	405	1.2455	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (27%)				π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (60%)	3.0616	404	1.4017	π (Zn-phy) → π* (Zn-phy)
	HOMO → L+2 (31%)				π (Zn-phy) → π* (Zn-phy)
Field+25	HOMO → LUMO (100%)	1.5008	826	0.0003	π(Zn-phy) →π*(π)+ π*(COOH)
	HOMO → L+2 (65%)	2.2169	559	0.0341	π (Zn-phy) → π* (Zn-phy)
	H-1 → L+1 (34%)				π (Zn-phy) → π* (Zn-phy)
	HOMO → L+1 (65%)	2.2243	557	0.0366	π (Zn-phy) → π* (Zn-phy)

H-1 → L+2 (34%)				π (Zn-phy) → π* (Zn-phy)
H-2 → LUMO (92%)	2.9873	415	0.0868	π(Zn-phy) →π*(π)+ π*(COOH)
H-1 → L+1 (64%)	3.0619	404	1.4191	π (Zn-phy) → π* (Zn-phy)
HOMO → L+2 (34%)				π (Zn-phy) → π* (Zn-phy)
H-1 → L+2 (58%)	3.0721	403	1.3330	π (Zn-phy) → π* (Zn-phy)
HOMO → L+1 (30%)				π (Zn-phy) → π* (Zn-phy)

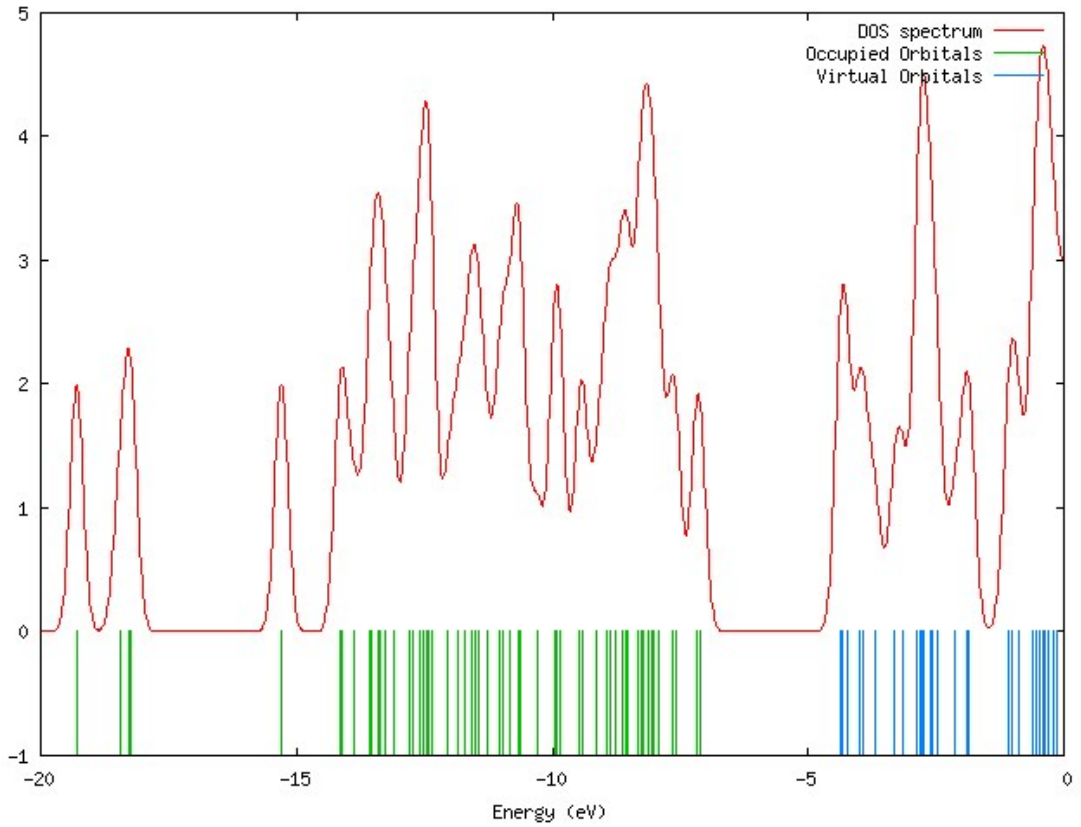

Fig.S2. The density of states (DOS) plot for the bare $(TiO_2)_5$ model

Table S6 Partial molecular orbital compositions (%) of the bare $(TiO_2)_5$ model.

Complex	Orbital	Energy(eV)	Main Component (%)			Assignment
			Ti	O	H	
$(TiO_2)_5$	LUMO+9	-2.804	82	17	1	3d (Ti)
	LUMO+8	-2.868	86	11	3	3d (Ti)
	LUMO+7	-3.150	85	11	4	3d (Ti)
	LUMO+6	-3.314	88	10	2	3d (Ti)
	LUMO+5	-3.696	85	14	1	3d (Ti)
	LUMO+4	-3.925	86	12	1	3d (Ti)
	LUMO+3	-3.999	89	10	1	3d (Ti)
	LUMO+2	-4.243	86	14	0	3d (Ti)
	LUMO+1	-4.337	84	14	2	3d (Ti)
	LUMO	-4.369	84	14	1	3d (Ti)
	HOMO–LUMO Energy Gap (2.744 eV)					
	HOMO	-7.113	2	98	0	2p (O)
	HOMO-1	-7.187	2	98	0	2p (O)
	HOMO-2	-7.595	5	94	1	2p (O)
	HOMO-3	-7.651	5	95	0	2p (O)
	HOMO-4	-7.902	6	93	1	2p (O)
	HOMO-5	-8.018	6	93	1	2p (O)
	HOMO-6	-8.040	5	94	1	2p (O)
	HOMO-7	-8.130	5	93	1	2p (O)
	HOMO-8	-8.233	5	95	0	2p (O)
	HOMO-9	-8.247	6	94	0	2p (O)

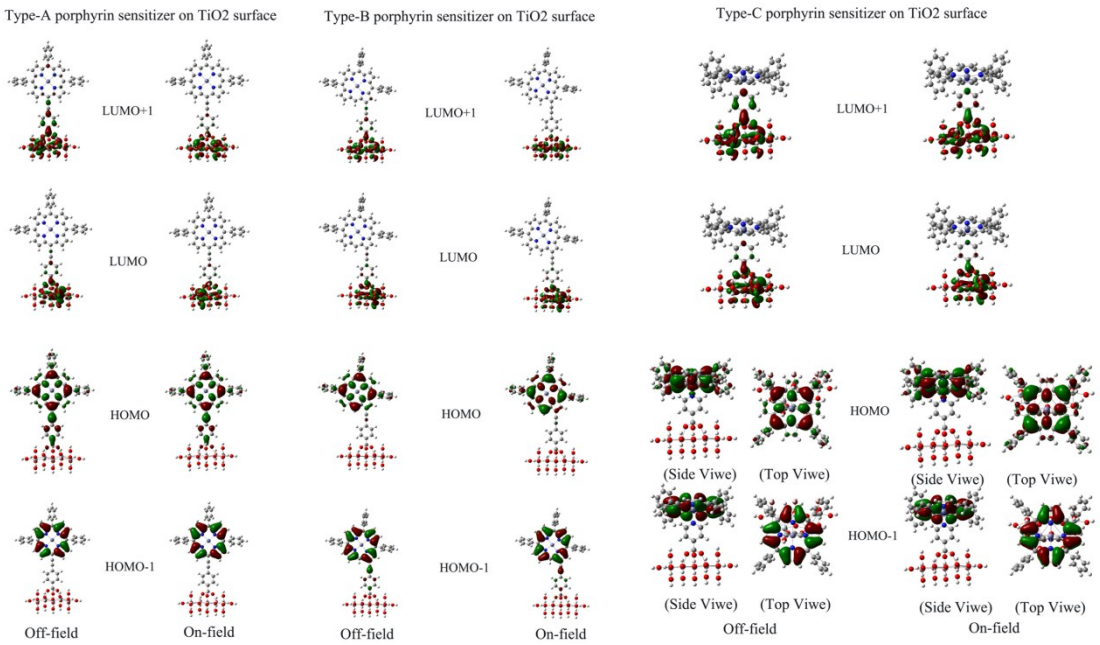

Fig. S3. Profiles of the HOMO and LUMO of the dye A, B and C absorbed on TiO_2 model in THF solution

Table S7 Partial Molecular Orbital Compositions (%) of dye A absorb on TiO_2 in THF solution with different electric field strengths.

Dye	Field (10^{-4} au)	MO	Energy (eV)	MainComponent (%)		Assignment
				dye	TiO_2	
B	0	LUMO+16	-2.003	0	100	d (TiO_2)
		LUMO+13	-2.484	85	15	d (TiO_2)+ π* (dye)
		LUMO+11	-2.549	98	2	π* (dye)
		LUMO+7	-2.868	1	99	d (TiO_2)
		LUMO+6	-2.982	52	48	π* (dye)+d (TiO_2)
		LUMO+4	-3.147	12	88	d (TiO_2)
		LUMO+2	-3.364	10	90	d (TiO_2)
		LUMO+1	-3.390	9	91	d (TiO_2)
		LUMO	-3.646	7	93	d (TiO_2)
		HOMO	-5.392	100		π (dye)
		HOMO-1	-5.570	100		π (dye)
		HOMO-2	-6.362	100		π (dye)
		HOMO-4	-6.823	100		π (dye)
	5	LUMO+15	-2.462	99	1	π* (dye)
		LUMO+14	-2.506	91	9	π* (dye)
		LUMO+10	-2.897	3	97	d (TiO_2)
		LUMO+7	-3.118	53	47	π* (dye)+d (TiO_2)
		LUMO+6	-3.148	12	88	d (TiO_2)
		LUMO	-3.906	5	95	d (TiO_2)
		HOMO	-5.311	100		π (dye)
		HOMO-1	-5.505	100		π (dye)
		HOMO-2	-6.377	100		π (dye)

Table S8 Partial Molecular Orbital Compositions (%) of dye C absorb on TiO_2 in THF solution with different electric field strengths.

Dye	Field (10^{-4} au)	MO	Energy (eV)	Main Component (%)		Assignment
				dye	TiO_2	
C	0	LUMO+15	-2.467	100		π* (dye)
		LUMO+14	-2.471	100		π* (dye)
		LUMO+1	-3.585	14	86	d (TiO_2)
		LUMO	-3.841	7	93	d (TiO_2)
		HOMO	-5.179	100		π (dye)
		HOMO-1	-5.464	100		π (dye)
		HOMO-7	-6.949	100		π (dye)
		HOMO-8	-6.958	100		π (dye)
	5	LUMO+17	-2.038	13	87	d (TiO2)
		LUMO+15	-2.404	100		π* (dye)
		LUMO+14	-2.408	100		π* (dye)
		LUMO+10	-2.907	2	98	d (TiO_2)
		LUMO	-4.005	6	94	d (TiO_2))
		HOMO	-5.116	100		π (dye)
		HOMO-1	-5.400	100		π (dye)

Table S9 Calculated absorptions (λ > 350 nm) of the dye A on TiO_2 model in THF solution with different electric field strengths.

Dye	Field (10^{-4} au)	Main transitions	ΔEcal(eV)	λcal(nm)	*f*	Character
A	0	HOMO → LUMO (99%)	1.4920	830	0.1409	π (dye) → d (TiO_2)
		HOMO → L+1 (99%)	1.7328	715	0.3556	π (dye) → d (TiO_2) +π* (dye)
		HOMO → L+4 (94%)	1.9667	630	0.2186	π (dye) → d (TiO_2) +π* (dye)
		HOMO → L+10 (61%)	2.4896	498	0.2008	π (dye) → d (TiO_2)
		HOMO → L+13 (44%)	2.5475	486	0.2957	π (dye) → π* (dye) + d (TiO_2)
		HOMO → L+10 (36%)				π (dye) → d (TiO_2)
		H-2 → LUMO (86%)	2.7430	451	0.1854	π (dye) → d (TiO_2)
		H-2 → L+1 (38%)	2.9135	425	0.6899	π (dye) → d (TiO_2) +π* (dye)
		H-1 → L+11 (19%)				π (dye) → d (TiO_2)
		H-1 → L+13 (53%)	3.0637	405	0.6836	π (dye) → π* (dye) + d (TiO_2)
		H-1 → L+14 (23%)				π (dye) → d (TiO_2)
		H-2 → L+1 (20%)	3.0713	404	0.2668	π (dye) → d (TiO_2) +π* (dye)
		H-2 → L+2 (17%)				π (dye) → d (TiO_2)
		H-6 → LUMO (15%)				π (dye) → d (TiO_2)
		H-1 → L+14 (76%)	3.0734	403	0.3097	π (dye) → d (TiO_2)

5	HOMO → LUMO (99%)	1.1999	1033	0.0886	π (dye) → d (TiO_2)
	HOMO → L+2 (94%)	1.4749	840	0.1850	π (dye) → d (TiO_2)
	HOMO → L+6 (75%)	1.9249	644	0.6857	π (dye) → d (TiO_2) +π* (dye)
	HOMO → L+15 (54%)	2.4195	512	0.1878	π (dye) → π* (dye) + d (TiO_2)
	H-1 → L+14 (22%)				π (dye) → π* (dye)
	H-2 → L+3 (77%)	2.8853	429	0.1843	π (dye) → d (TiO_2)
	H-2 → L+4 (39%)	2.9463	420	0.4732	π (dye) → d (TiO_2)
	H-1 → L+14 (16%)				π (dye) → π* (dye)
	H-4 → L+1 (32%)	2.9984	413	0.2328	π (dye) → d (TiO_2)
	H-2 → L+4 (24%)				π (dye) → d (TiO_2)
	H-1 → L+15 (61%)	3.0232	410	1.1117	π (dye) → π* (dye) + d (TiO_2)
	HOMO → L+14 (29%)				π (dye) → π* (dye)

Table S10 Calculated absorptions (**λ** > 350 nm) of the dye B on TiO_2 model in THF solution with different electric field strengths.

Dye	Field (10^{-4} au)	Main transitions	ΔEcal(eV)	λcal(nm)	*f*	Character
B	0	HOMO → LUMO (99%)	1.5453	802	0.0160	π (dye) → d (TiO_2)
		H-1 → L+1 (78%)	1.9448	637	0.1647	π (dye) → d (TiO_2)
		H-1 → L+2 (16%)				π (dye) → d (TiO_2)
		H-1 → L+7 (28%)	2.4759	500	0.4071	π (dye) → d (TiO_2)
		H-1 → L+6 (25%)				π (dye) → π* (dye) + d (TiO_2)
		HOMO → L+11 (23%)				π (dye) → π* (dye)
		H-1 → L+7 (67%)	2.4960	496	0.2097	π (dye) → d (TiO_2)
		H-2 → L+1 (63%)	2.6327	470	0.2805	π (dye) → d (TiO_2)
		H-2 → L+4 (66%)	2.857	433	0.3113	π (dye) → d (TiO_2)
		H-1 → L+11 (40%)	3.0864	401	1.0060	π (dye) → π* (dye)
		HOMO → L+13 (23%)				π (dye) → d (TiO_2) +π* (dye)
		HOMO → L+16 (24%)	3.1997	387	0.1693	π (dye) → d (TiO_2)
		H-4 → L+1 (19%)				π (dye) → d (TiO_2)
		H-4 → L+1 (23%)	3.2173	385	0.2196	π (dye) → d (TiO_2)
	5	HOMO → LUMO (100%)	1.2087	1025	0.0085	π (dye) →d (TiO_2)

	H-1 → L+7 (59%)	2.0748	597	0.2876	π (dye) → π* (dye) + d (TiO_2)
	H-1 → L+6 (24%)				π (dye) →d (TiO_2)
	H-1 → L+10 (50%)	2.4210	512	0.2641	π (dye) → d (TiO_2)
	HOMO → L+15 (16%)				π (dye) → π* (dye)
	H-2 → L+7 (47%)	2.8289	438	0.9047	π (dye) → π* (dye) + d (TiO_2)
	H-2 → L+6 (17%)				π (dye) → d (TiO_2)
	H-1 → L+14 (16%)				π (dye) → π* (dye)

Table S11 Calculated absorptions (**λ** > 350 nm) of the dye C on TiO_2 model in THF solution with different electric field strengths.

Dye	Field (10^{-4} au)	Main transitions	ΔEcal(eV)	λcal(nm)	*f*	Character
C	0	HOMO → L+15 (58%)	2.2107	560	0.0371	π (dye) → π* (dye)
		H-1 → L+14 (30%)				π (dye) → π* (dye)
		HOMO → L+14 (58%)	2.2182	558	0.0391	π (dye) → π* (dye)
		H-1 → L+15 (30%)				π (dye) → π* (dye)
		H-7 → L+1 (23%)	3.0478	407	0.4441	π (dye) → d (TiO_2)
		H-1 → L+15 (20%)				π (dye) → π* (dye)
		H-8 → L+1 (17%)				π (dye) → d (TiO_2)
		H-1 → L+14 (52%)	3.0544	406	1.1909	π (dye) → π* (dye)
		HOMO → L+15 (26%)				π (dye) → π* (dye)
		H-1 → L+15 (24%)	3.0787	402	0.6336	π (dye) → π* (dye)
		H-8 → L+1 (19%)				π (dye) → d (TiO_2)
	5	HOMO → L+15 (46%)	2.2096	561	0.0280	π (dye) → π* (dye)
		H-1 → L+14 (23%)				π (dye) → π* (dye)
		H-1 → L+10 (23%)				π (dye) → d (TiO_2)
		H-1 → L+17 (41%)	3.0478	406	0.7352	π (dye) → d (TiO_2)

H-1 → L+14 (35%)	π (dye) → π* (dye)
HOMO → L+15 (17%)	π (dye) → π* (dye)

Table S12 The main parameters r of the dye B in THF with different electric field strengths for the charge transfer analysis under B3LYP/6-31G(d) level.

Field (10^{-4} a.u.)	NO.	D_{CT} (Å)	q_{CT} (e)	μ_{CT} (Debye)	H(Å)	t(Å)	$Overlap_{C+-C-}$
0	1	2.435	0.203	2.379	5.291	-2.856	0.910
	2	1.511	0.160	1.160	4.837	-3.326	0.961
	3	0.497	0.280	0.669	4.901	-4.404	0.977
	4	4.874	0.632	14.786	5.523	-0.649	0.818
	6	2.832	0.588	8.000	4.958	-2.126	0.895
	7	2.966	0.283	4.028	5.883	-2.917	0.917
	8	3.315	0.439	6.988	5.568	-2.253	0.899
5	1	3.163	0.246	3.733	5.444	-2.281	0.886
	3	4.126	0.365	7.228	5.466	-1.340	0.877
	6	3.245	0.587	9.155	5.027	-1.782	0.870
	7	1.649	0.267	2.113	5.491	-3.842	0.968
	8	2.914	0.503	7.045	5.104	-2.190	0.897
10	1	1.928	0.246	2.279	5.233	-3.305	0.914
	3	5.185	0.782	19.463	5.561	-0.376	0.799
	4	4.980	0.547	13.084	5.505	-0.525	0.821
	5	0.487	0.453	1.061	5.096	-4.609	0.981
	6	2.568	0.428	5.284	5.152	-2.584	0.909
	7	0.497	0.326	0.780	4.950	-4.453	0.988
15	1	4.336	0.409	8.510	5.608	-1.272	0.844
	2	3.313	0.235	3.733	5.274	-1.961	0.898
	4	5.138	0.651	16.059	5.509	-0.371	0.811
	5	0.647	0.416	1.292	5.043	-4.396	0.981
	6	0.596	0.312	0.892	5.654	-5.058	0.981
	9	1.645	0.479	3.784	5.533	-3.888	0.960
20	1	4.721	0.545	12.360	5.638	-0.917	0.828

	2	3.957	0.300	5.711	5.377	-1.420	0.868
	4	5.187	0.662	16.491	5.530	-0.343	0.808
	5	1.414	0.386	2.622	5.189	-3.775	0.980
	6	3.958	0.450	8.549	5.626	-1.668	0.890
	8	5.331	0.678	17.367	6.084	-0.753	0.858
	10	4.939	1.000	23.720	5.710	-0.771	0.819
25	1	4.950	0.701	16.654	5.654	-0.704	0.817
	2	4.452	0.409	8.748	5.452	-1.000	0.843
	4	5.179	0.596	14.873	5.571	-0.392	0.813
	7	5.341	0.935	23.977	6.015	-0.674	0.849
	9	5.411	0.832	21.622	6.128	-0.674	0.848

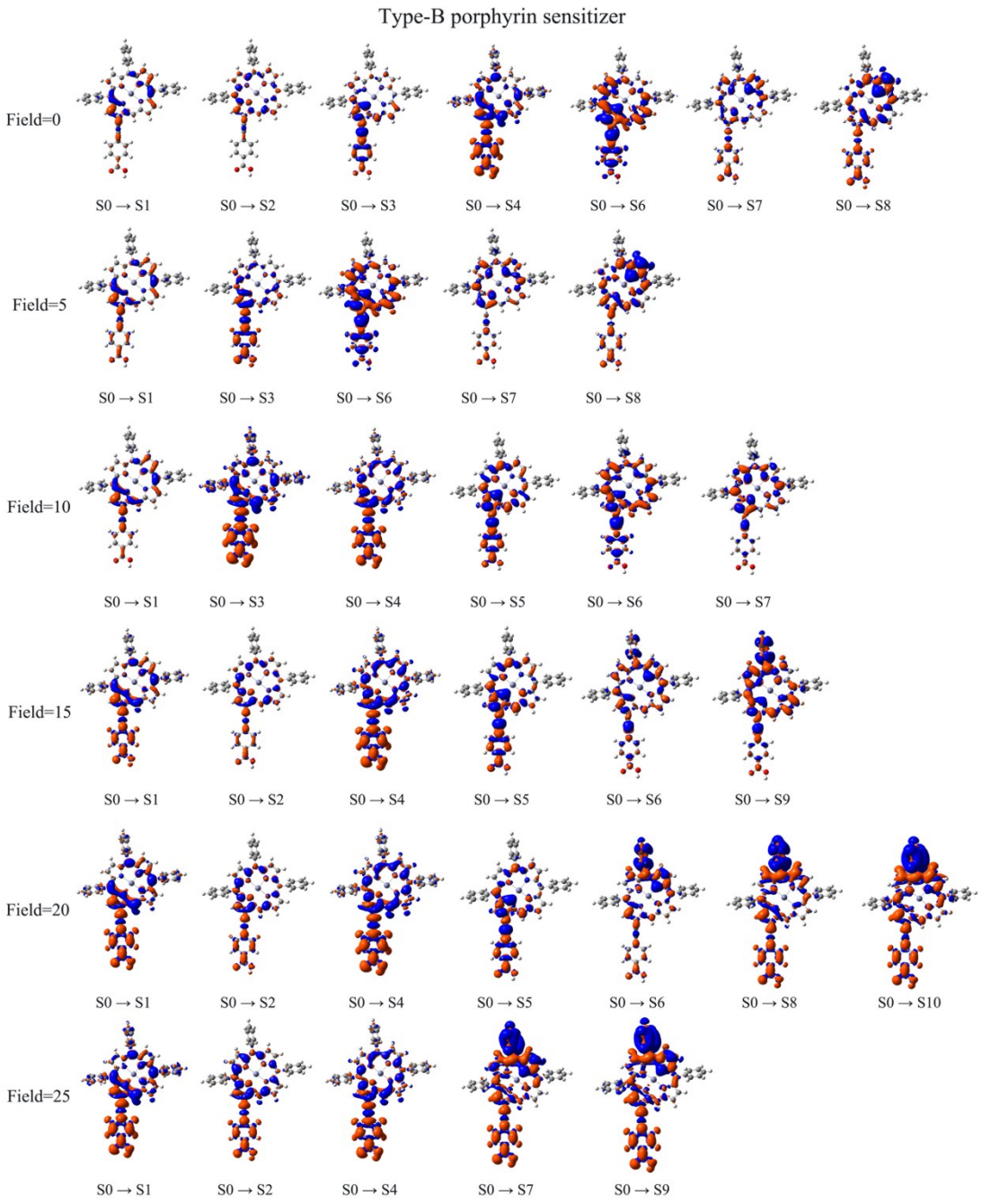

Fig. S4. Computed electronic density variation $\Delta\rho$ for selected transitions of dye B system with different electric field strengths. The blue and orange lobes represent a density increase and depletion upon excitation, respectively.

Table S13 The main parameters of the dye C in THF with different electric field strengths for the charge transfer analysis under B3LYP/6-31G(d) level.

Field (10^{-4} a.u.)	NO.	D_{CT} (Å)	q_{CT} (e)	μ_{CT} (Debye)	H(Å)	t(Å)	$Overlap_{C+-C-}$
0	1	2.786	1.402	18.759	4.187	-1.401	0.702
	2	2.781	1.401	18.718	4.155	-1.374	0.712
	3	0.334	0.160	0.257	4.108	-3.774	0.963
	5	0.140	0.197	0.133	3.980	-3.84	0.975
	6	1.993	0.301	2.886	4.128	-2.135	0.813
5	1	2.795	1.405	18.868	4.191	-1.396	0.702
	2	2.789	1.418	18.996	4.159	-1.37	0.712
	3	0.087	0.154	0.065	4.132	-4.045	0.994
	5	2.319	1.4713	15.740	4.003	-1.684	0.736
	6	2.780	1.200	16.025	4.145	-1.365	0.711
10	1	2.804	1.408	18.957	4.196	-1.392	0.701
	3	0.013	0.153	0.009	4.113	-4.100	0.997
	4	0.046	0.153	0.034	4.151	-4.105	0.993
	5	2.320	1.413	15.740	4.003	-1.683	0.736
	6	5.253	1.387	18.512	4.157	1.096	0.712
15	1	2.813	1.409	19.035	4.200	-1.387	0.701
	3	0.048	0.153	0.036	4.112	-4.064	0.990
	4	0.066	0.153	0.019	4.151	-4.085	0.988
	5	2.324	1.411	15.752	4.004	-1.68	0.736
	6	2.788	1.412	18.905	4.161	-1.373	0.711
20	1	2.821	1.410	19.106	4.204	-1.383	0.701
	3	0.068	0.153	0.050	4.115	-4.047	0.984
	4	0.078	0.153	0.057	4.153	-4.075	0.985
	5	2.796	1.421	19.091	4.166	-1.37	0.711
	6	2.321	1.412	15.736	4.004	-1.683	0.736

25	1	2.830	1.410	19.171	4.208	-1.378	0.701
	3	0.079	0.153	0.058	4.118	-4.039	0.981
	4	0.086	0.153	0.063	4.155	-4.069	0.983
	5	2.805	1.425	19.202	4.170	-1.365	0.711
	9	2.312	1.429	15.865	3.973	-1.661	0.748
	10	2.798	1.282	17.230	4.126	-1.328	0.702

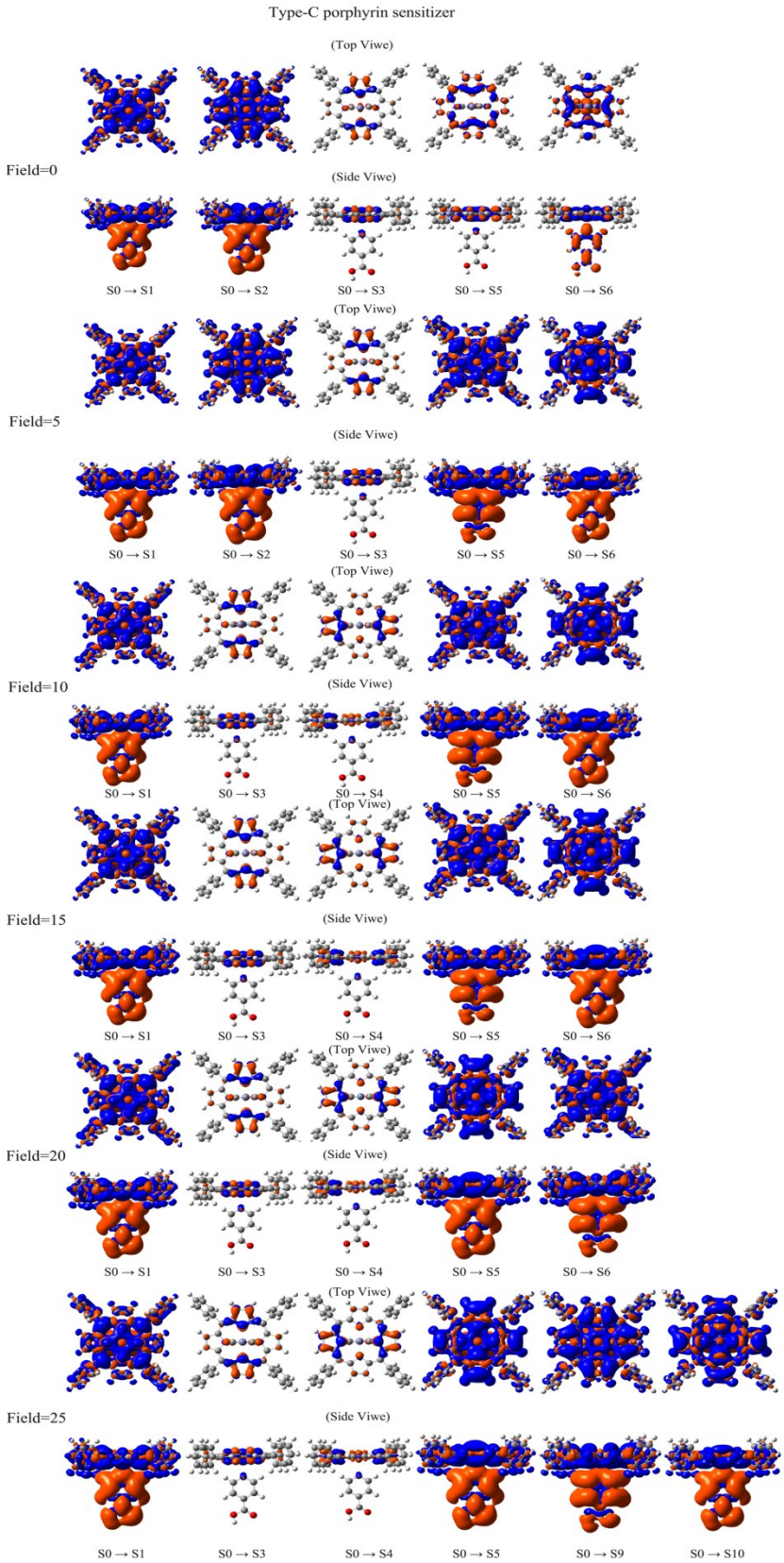

Fig. S5. Computed electronic density variation $\Delta\rho$ for selected transitions of dye C system with different electric field strengths. The blue and orange lobes represent a density increase and depletion upon excitation, respectively.

Table S14 Effects of electric field on the natural bond orbitals (NBOs) charge for the dye B with different electric field strengths.

Field (10^{-4} a.u.)	Natural bond orbital (NBO) charge (e)						$\mu_{x\text{-bare}}$ (Debye)
	C_1	C_2	C_3	C_4	C_5	C_6	
Field=0	0.764	-0.172	-0.092	0.004	0.024	-0.135	-4.4161
Field=5	0.765	-0.175	-0.089	-0.002	0.030	-0.138	-6.3995
Field=10	0.765	-0.179	-0.086	-0.008	0.036	-0.142	-8.4091
Field=15	0.765	-0.182	-0.083	-0.015	0.042	-0.145	-10.4537
Field=20	0.765	-0.185	-0.080	-0.021	0.047	-0.149	-12.5443
Field=25	0.764	-0.188	-0.078	-0.027	0.053	-0.152	-14.6952

Table S15 Effects of electric field on the natural bond orbitals (NBOs) charge for the dye C with different electric field strengths.

Field (10^{-4} **a.u.**)	**Natural bond orbital (NBO) charge (e)**			$\mu_{x\text{-bare}}$ **(Debye)**
	C_1	C_2	N_3	
Field=0	0.770	-0.135	-0.484	4.1342
Field=5	0.769	-0.135	-0.484	3.4434
Field=10	0.769	-0.135	-0.484	2.7523
Field=15	0.769	-0.135	-0.483	2.0607
Field=20	0.768	-0.135	-0.483	1.3686
Field=25	0.768	-0.135	-0.483	0.6760

Table S16 The electronic injection free enthalpy ΔG^{inject} (eV), ground E^{dye} (eV) and excited E^{dye*} (eV) state oxidation potentials, the calculated transition energy $E_{0\text{-}0}$ (eV) and dye regeneration ΔG^{reg} of dye B system.

Field (10^{-4} a.u.)	$\boldsymbol{E^{dye}}$ **(eV)**	$\boldsymbol{E_{0\text{-}0}}$ **(eV)**	$\boldsymbol{E^{dye*}}$ **(eV)**	$\boldsymbol{\Delta G^{inject}}$ **(eV)**	$\boldsymbol{\Delta G^{reg}}$ **(eV)**
Field=0	-4.97	2.17	-2.80	1.20	0.17
Field=5	-4.99	2.14	-2.85	1.15	0.19
Field=10	-5.02	2.09	-2.93	1.07	0.22
Field=15	-5.04	2.01	-3.03	0.97	0.24
Field=20	-5.13	1.90	-3.23	0.77	0.33
Field=25	-5.15	1.76	-3.39	0.61	0.35

Table S17 The electronic injection free enthalpy ΔG^{inject} (eV), ground E^{dye} (eV) and excited E^{dye*} (eV) state oxidation potentials, the calculated transition energy $E_{0\text{-}0}$ (eV) and dye regeneration ΔG^{reg} of dye C system.

Field (10^{-4} a.u.)	$\boldsymbol{E^{dye}}$ **(eV)**	$\boldsymbol{E_{0\text{-}0}}$ **(eV)**	$\boldsymbol{E^{dye*}}$ **(eV)**	$\boldsymbol{\Delta G^{inject}}$ **(eV)**	$\boldsymbol{\Delta G^{reg}}$ **(eV)**
Field=0	-5.16	2.08	-3.08	0.92	0.36
Field=5	-5.16	1.97	-3.19	0.81	0.36
Field=10	-5.16	1.85	-3.31	0.69	0.36
Field=15	-5.16	1.74	-3.42	0.58	0.36
Field=20	-5.16	1.62	-3.54	0.46	0.36
Field=25	-5.16	1.50	-3.66	0.34	0.36