Influence of the Nature of the Anchoring Group on Electron Injection Processes at Dye-Titania Interfaces

SUPPORTING INFORMATION

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gure S1. (Left): Charge transfer vs Mulliken Electronegativity for free catechol dyes. (right): Charge transfer vs Mulliken Electronegativity for free carboxylic dyes.

Table S1 describes the lowest excitation energy and the excitations with a significant intensity around the main peak for each absorption band for both the isolated and grafted T2-carboxylic and T5-carboxylic dyes. The most intense contribution to the lowest energy band for the isolated dyes arises from an excitation from the HOMO to LUMO orbital. For the grafted T2-carboxylic dye, the four dominant transitions in the lowest absorption band occur from HOMO to LUMO+9, LUMO+10, LUMO+11 and LUMO+27; these unoccupied levels all feature the signature of the

LUMO shape characteristic of the isolated molecule (see **Figure S2** left for the LUMO+10 level). Similarly, the four excitations contributing to the lowest absorption band for the grafted T5-carboxylic have also a dye-to-dye character. The excitation at 2.03 eV (610 nm) has the largest intensity and is described at 78% by a HOMO to LUMO+6 transition; the LUMO+6 of the complex is the unoccupied level with the largest weight on the dye, thus rationalizing the large transition dipole moment due to the large spatial overlap between the two levels (see **Figure S2**, right).

Table S1. Main contributions for each dominant optical transition for both the isolated and grafted ^a T2-carboxylic and T5-carboxylic dyes, as obtained at the TD-DFT level.

	Energy, eV	Oscillator	Main contribution
	(excitation number)	strength	
T2-carb isolated	3.72	0.5211	HOMO->LUMO (99%)
T2-carb grafted	2.67 (1)	0.0016	HOMO->L+1 (58%), HOMO->L+2 (36%) HOMO->L+4 (4%)
	2.87 (8)	0.1374	HOMO->L+9 (71%), HOMO->L+7 (17%)
	2.94 (11)	0.1825	HOMO->L+10 (84%), HOMO->L+12 (5%) HOMO->L+11 (3%)
	2.98 (13)	0.1793	HOMO->L+11 (40%), HOMO->L+13 (35%) HOMO->L+12 (13%)
	3.25 (28)	0.1258	HOMO->L+27 (66%), HOMO->L+26 (11%)
T5-carb isolated	2.57	1.44	HOMO->LUMO (100%)
T5-carb grafted	1.94 (1)	0.0017	HOMO->LUMO (51%), HOMO->L+1 (25%), HOMO->L+2 (22%)
	1.96 (3)	0.2384	HOMO->L+2 (63%), HOMO->L+3 (14%), HOMO->L+1 (10%)
	1.97 (4)	0.2635	HOMO->L+3 (77%), HOMO->L+2 (10%), HOMO->L+1 (9%)
	2.03 (7)	0.6403	HOMO->L+6 (78%), HOMO->L+5 (14%)
	2.06 (8)	0.3356	HOMO->L+7 (80%), HOMO->L+8 (14%)

^aOnly the lowest excitation and four selected transitions with a significant oscillator strength around the main peak are included





Figure S2. (left): Shape of the HOMO and LUMO+10 levels of the grafted T2-carboxylic system. (right): shape of the HOMO and LUMO+6 levels of the grafted T5-carboxylic system.

Table S2 describes the lowest excitation energy and the excitations with a significant intensity around the main peak for each band of the isolated and grafted T2-catechol and T5-catechol dyes. As it is the case for the Tn-carboxylic dyes, the most intense contribution to the lowest energy band for the isolated dyes originates from an excitation from the HOMO to the LUMO orbitals. In contrast, for the grafted T2-catechol dye, the behavior is quite different compared to T2-carboxylic dye since a new low-energy shoulder appears upon grafting around 2.48 eV (500 nm). The main contributions to this shoulder are excitations from the HOMO orbital strongly localized on the dye to LUMO+30, LUMO+26 and LUMO+27 orbitals strongly localized on the cluster (Figure S3). These orbitals are formed by interaction of d orbitals of Ti atoms and p orbitals of the oxygen atoms in the dye. These optical transitions are thus associated with a direct photoexcitation from the HOMO of the dye to the titania conduction band. The spectrum of the grafted T2-catechol dye shows a second band with a maximum peak at 3.31 eV (374 nm). This band is made of numerous excitations that all have a dominant charge transfer character from the dye to titania cluster. Due to the high energetic position of the dye LUMO within the titania conduction band for the T2catechol dye, many excited states have to be calculated to reach a state with a strong intra-dye character. For instance, the LUMO+84, which is delocalized over the whole system with a significant contribution from the dye, weakly participates in the excitation state number 120. Thus, the T2-catechol dye present a prevalent direct injection mechanism from the highest occupied molecular orbital to the titania conduction band.

	Energy, eV	Oscillator	Main contribution
	(excitation number)	strength	
T2-cat isolated	3.53	0.74	HOMO->LUMO (99%)
T2-cat grafted	1.78 (1)	0.0002	HOMO->LUMO (86%), HOMO->L+1 (8%), HOMO->L+2 (4%)
	2.48 (27)	0.0697	HOMO->L+30 (41%), HOMO->L+26 (16%), HOMO->L+27 (13%), HOMO->L+28 (8%)
	3.27 (96)	0.0603	HOMO->L+72 (29%), HOMO->L+70 (23%), H-1->L+19 (8%)
	3.31(103)	0.0785	H-1->L+21 (24%), H-1->L+19 (17%), H-1->L+18 (10%), HOMO->L+75 (6%)
	3.43 (120)	0.0558	H-1->L+29 (11%), HOMO->L+80 (11%), HOMO->L+83 (7%), HOMO->L+84 (3%)
T5-cat isolated	2.59	1.8543	HOMO->LUMO (99%)
T5-cat grafted	1.43 (1)	0.0002	HOMO->LUMO (98%)

Table S2. Main contributions of each dominant transition for both the isolated and grafted ^a T2-catechol and T5-catechol dyes, as calculated at the TD-DFT level.

2.37 (49)	0.5627	HOMO->L+41 (39%), HOMO->L+42 (13%), HOMO->L+40 (9%),
2.42 (54)	0.1254	HOMO->L+45 (48%), HOMO->L+43 (27%), HOMO->L+42 (7%),
2.45 (58)	0.2628	HOMO->L+46 (27%), H-1->L+9 (14%), HOMO->L+49 (13%), HOMO->L+47 (7%)
2.47(59)	0.1835	HOMO->L+46 (46%), HOMO->L+47 (26%), HOMO->L+50 (8%)

^aOnly the lowest excitation and four selected transitions with a significant oscillator strength around the main peak are included



Figure S3. Shape of the HOMO, HOMO-1, LUMO+21 and LUMO+30 levels of the grafted T2-catechol system.

Finally, the absorption spectrum of the T5-catechol dye shows one intense band centered at 2.37 eV (523 nm). The occupied orbital that contributes the most to the excitations in this band is the HOMO whilst the virtual orbitals with a significant contribution are LUMO+41, LUMO+43, LUMO+45, LUMO+46 and LUMO+47 (see Table S2). LUMO+47 is an orbital delocalized over the whole system and features over the dye backbone the fingerprint of the LUMO level, while the rest of the orbitals are localized on the cluster with negligible contributions from the dye (**Figure S4**).



Figure S4: Shape of the HOMO, LUMO+41 and LUMO+41 levels of the grafted T5-catechol system.