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Supporting Information: Interfacial charge separation and photovoltaic efficiency in Fe(II)-carbene sensitized solar cells

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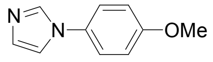
Synthesis of heteroleptic complexes

The access to complexes **C5**, **C6** and **C7** required the synthesis of precursors **L1**, **L2**, **L3** and **L4**. L1[1] and L2[2] were prepared following reported procedures. The first step towards **L3** and **L4** was the Ullmann synthesis of arylimidazoles 1[3] and 2.[4]

Synthesis of ligands



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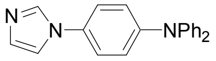

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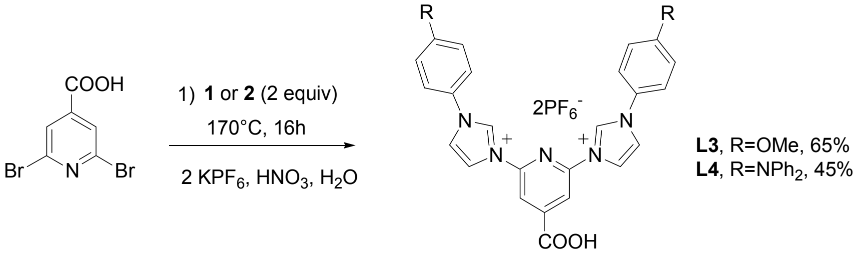


Synthesis of ligand L3

A mixture of 2,6-dibromopyridine-4-carboxylic acid (0.5 g, 1.7 mmol) and **1** (1 mL, 12.4 mmol) was stirred at 150 °C under Argon overnight. After cooling, Et_2O (5 mL) was added and the resultant precipitate was filtered. The crude product was dissolved in a minimum amount of water and a saturated solution of KPF_6 in water (10 mL) was added. The solution was finally acidified to pH=2 using diluted HNO_3. Filtered, washing with water and drying under vacuum afforded **L2** (0.95g, 65%) as an off-white solid. ^{1}H NMR (200 MHz, CD_3CN): δ = 9.95 (s, 2 H), 8.62 (s, 2H), 8.56 (s, 2H), 8.02 (s, 2H), 7.74 (d, J = 9.2 Hz, 4H), 7.23 (d, J = 9.2 Hz, 4H), 3.92 (s, 6H) ppm. HRMS (ESI) calcd for $C_{26}H_{23}N_5O_4P_2F_{12}$ m/z = 234.5870 [M – 2 PF6]$^{2+}$. Found: 234.5910.

Synthesis of ligand L4

The procedure used for **L3** was repeated using 2,6-dibromopyridine-4-carboxylic acid (0.25 g, 0.85 mmol) and **2** (0.53 g, 1.7 mmol) affording **L4** as a white powder (0.61 g, 45%). ^{1}H NMR (200 MHz, CD_3CN): δ = 10.8 (s, 2 H), 9.1 (s, 2H), 8.8 (s, 2H), 8.5 (s, 2H), 7.84 (d, J = 8.8 Hz, 4H), 7.4 (m, 8H), 7.19 (m, 16H) ppm. HRMS (ESI) calcd pour $C_{48}H_{37}N_7O_2P_2F_{12}$ m/z = 371,6499 [M – 2 PF6]$^{2+}$. Found: 371,6526.

Synthesis of heteroleptic complexes C5, C6 and C7

Synthesis of C5

L1 (92 mg, 0.17 mmol), **L2** (100 mg, 0.17 mmol) and anhydrous $FeCl_2$ (22 mg, 0.17 mmol) were dissolved in anhydrous DMF (3 mL), *t*BuOK (130 mg, 1 mmol) was then added and the mixture was stirred for 10 min at 20°C. A saturated solution of KPF_6 in water (10 mL) was then added. The solution was finally acidified to pH=2 using diluted HNO_3. The dark red precipitate was collected by filtration and purified by column chromatography on silicagel using a mixture of Acetone/water/ $KNO_{3\ (sat)}$ = 10/3/1. The dark orange fraction was collected and acidified to pH=2 using diluted HNO_3 leading to a dark red solution. A saturated solution of KPF_6 in water (10 mL) was then added. The acetone was evaporated and after filtration, washing with water and drying under vacuum C5 was obtained as a dark red solid (31 mg, 20 %). ^{1}H NMR (200 MHz, CD_3CN): δ = 8.29 (s, 2H), 8.26 (t, *J* = 8.2 Hz, 1H), 8.18 (d, *J* = 2.2 Hz, 2H), 8,04 (d, *J* = 2,4 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 2.2 Hz, 2H), 7.01 (d, *J* = 2.2 Hz, 2H), 2.55 (s, 6H), 2.50 (s, 6H) ppm. ^{13}C RMN (100 MHz, CD_3CN): δ = 199.5, 199.3, 164.5, 154.7, 153.6, 139.2, 138.8, 126.7, 126.6, 116.7, 116.4, 105.6, 104.5, 34.6, 34.5 ppm. HRMS (ESI) Calcd for $C_{27}H_{26}FeN_{10}O_2P_2F_{12}$ m/z = 289.0789 [M – 2 PF6]$^{2+}$. Found: 289.0793.

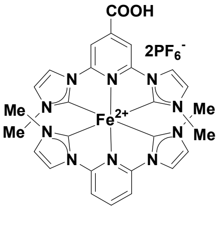
Synthesis of C6

The procedure used for **C5** was repeated using **L1** (60 mg, 0.13 mmol), **L3** (100 mg, 0.13 mmol), $FeCl_2$ (17 mg, 0.13 mmol) and *t*BuOK (130 mg, 1 mmol) affording **C6** as a dark red solid (25 mg, 15 %). ^{1}H NMR (400Mz, CD_3CN): δ = 8.44 (s, 2H), 8.31 (d, *J* = 2.4 Hz, 2H), 7.84 (d, *J* = 2.1 Hz, 2H), 7.52 (t, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 2H), 7.05 (d, *J* = 2.1 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.47 (d, *J* = 8.7 Hz, 4H), 6.25 (d, *J* = 8.9 Hz, 4H), 3.76 (s, 6H), 2.6 (s, 6H) ppm. HRMS (ESI) Calcd for $C_{39}H_{34}FeN_{10}O_4P_2F_{12}$ m/z = 381.1052 [M – 2 PF6]$^{2+}$ Found: 381.1069.

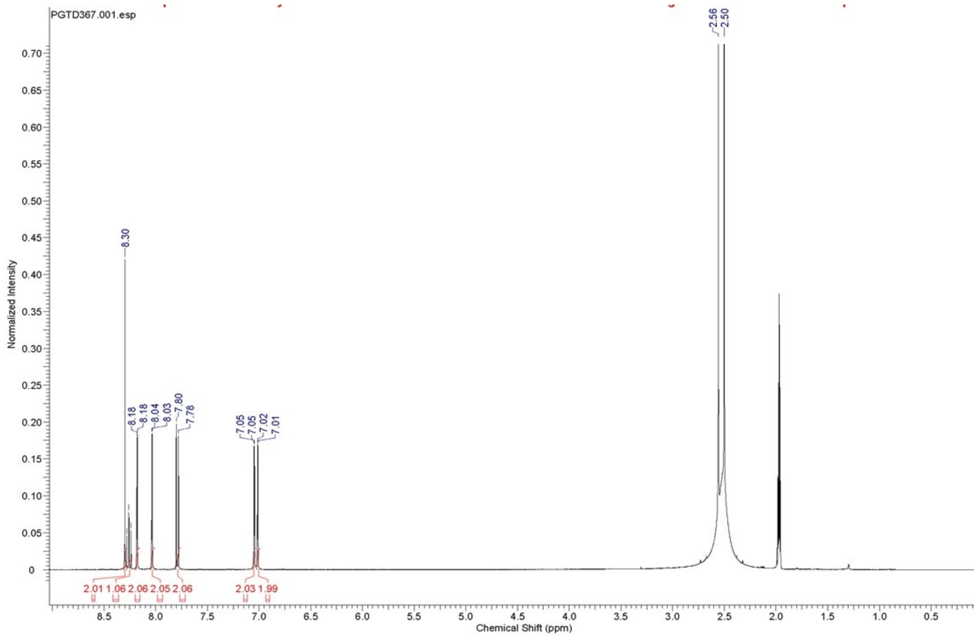
Synthesis of C7

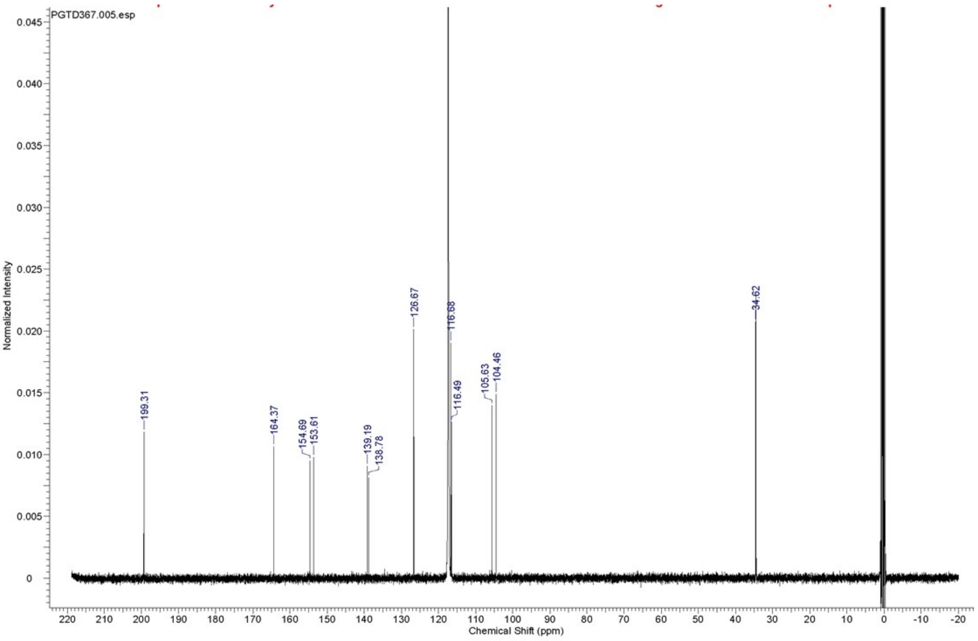
The procedure used for **C5** was repeated using **L1** (81 mg, 0.15 mmol), **L4** (150 mg, 0.15 mmol) $FeCl_2$ (20 mg, 0.15 mmol) and *t*BuOK (130 mg, 1 mmol) affording **C6** as a dark red solid (37 mg, 16 %). ^{1}H NMR (400Mz, CD_3CN): 8.40 (s, 2H), 8.30 (d, *J* = 2.3 Hz, 2H), 7.77 (d, *J* = 2.2 Hz, 2H), 7.65 (t, *J* = 8 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 8H), 7.22 (t, *J* = 7.5 Hz, 4H), 7.11 (d, *J* = 8.3 Hz, 8H), 7.06 (d, *J* = 8 Hz, 2H), 7.04 (d, *J* = 2.4 Hz, 2H), 6.98 (d, *J* = 2.2 Hz, 2H), 6.47 (d, *J* = 8.8 Hz, 4H), 6.15 (d, *J* = 8.8 Hz, 4H), 2.57 (s, 6H) ppm. ^{13}C RMN (100 MHz, CD_3CN): δ = 199.5, 199.3, 164.5, 154.7, 153.6, 139.2, 138.8, 126.7, 126.6, 116.7, 116.4, 105.6, 104.5, 34.6, 34.5 ppm. HRMS (ESI) Calcd for $C_{61}H_{48}FeN_{12}O_2P_2F_{12}$ m/z = 518.1682 [M – 2 PF6]$^{2+}$. Found: 518.1727.

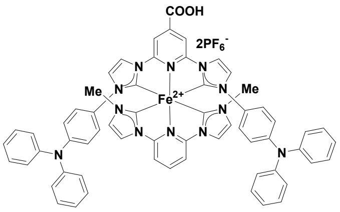
NMR spectra of complexes



C5



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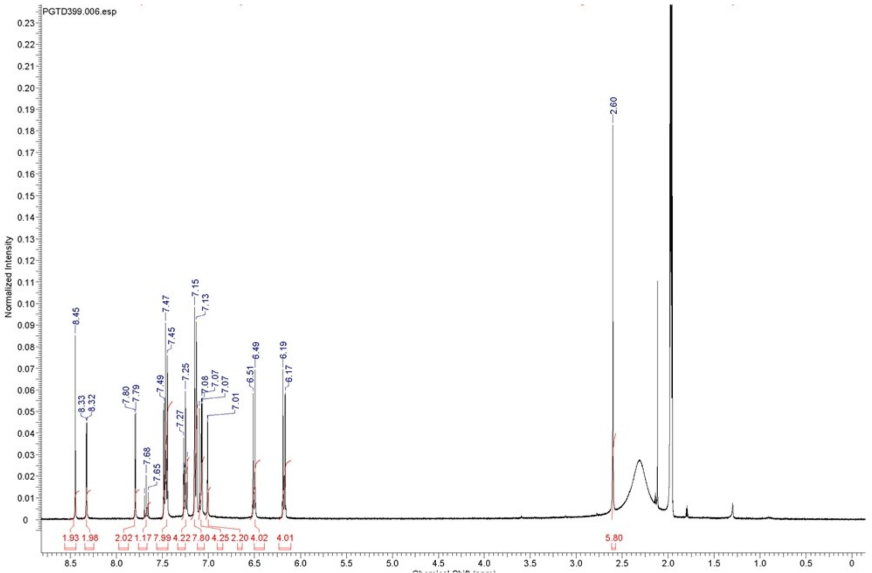
Me
Fe2+
Me
N
N

C7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Normalized Intensity
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8.32
7.80
7.79
7.68
7.65
7.49
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7.45
7.27
7.25
7.15
7.13
7.08
7.07
7.07
7.01
6.51
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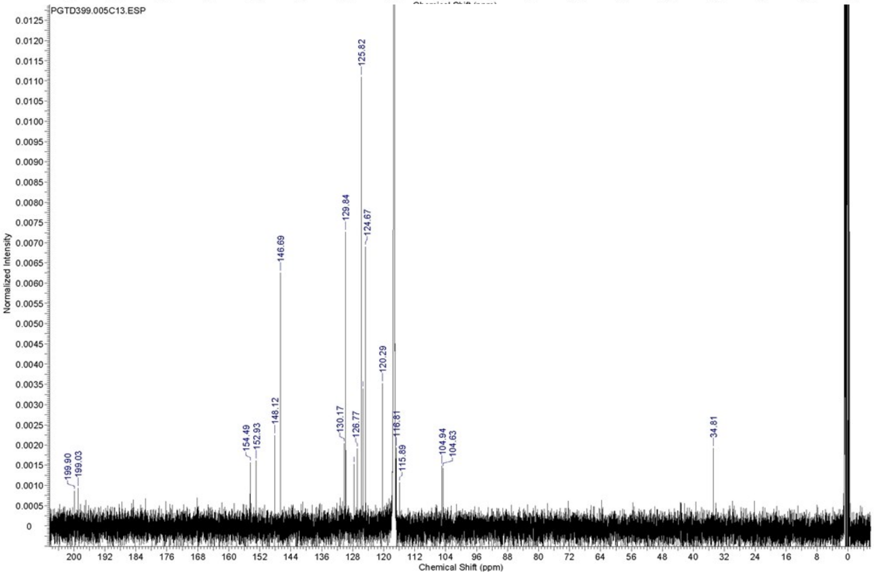
5.80


PGTD399.005C13.ESP
Normalized Intensity
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146.69
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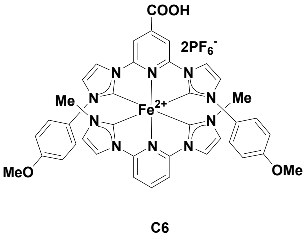
125.82
124.67
120.29
116.81
115.89
104.94
104.63
34.81
Chemical Shift (ppm)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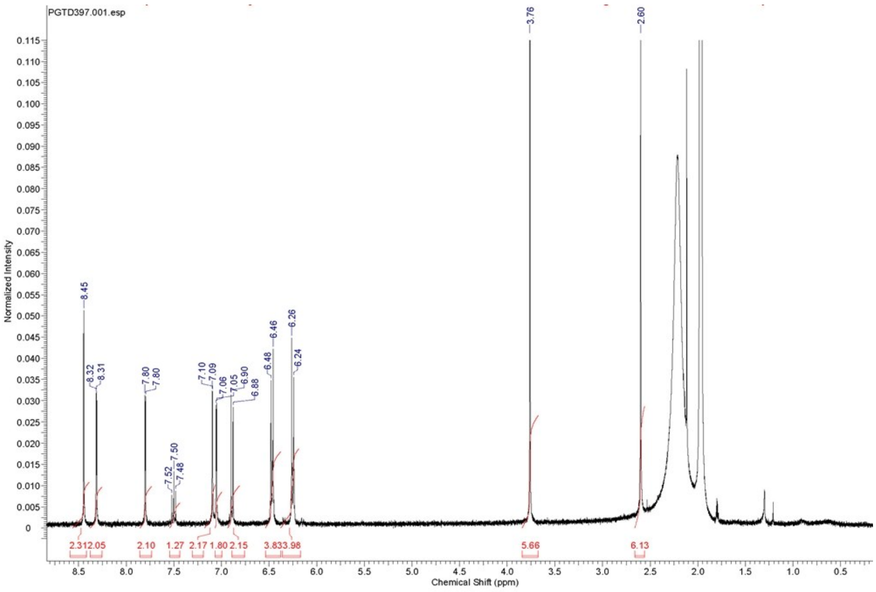
2PF6-
Me
Fe2+
Me
N
MeO
OMe

C6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Normalized Intensity
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7.80
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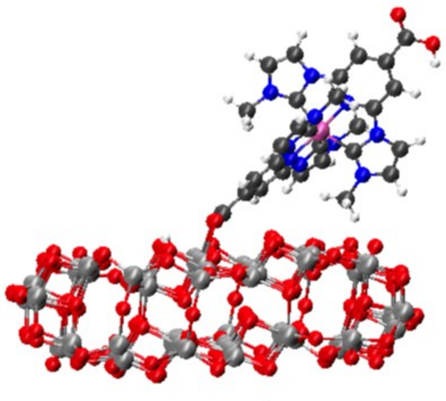
7.09
7.06
7.05
6.90
6.88
6.48
6.46
6.26
6.24
3.76
2.60
2.31 2.05 2.10 1.27 2.17 1.80 2.15 3.83 3.98
5.66
6.13
Chemical Shift (ppm)

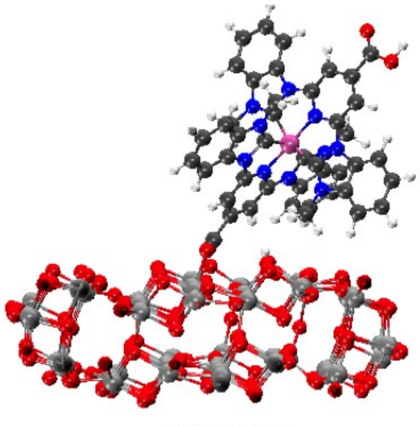
TABLE S1. Optical and electrochemical properties

	In acetonitrile solution					Sensitized TiO_2	
Dye	$\lambda_{abs\text{-}max}$ (nm)[a]	ε ($M^{-1}.cm^{-1}$) [a]	E_{ox} (Fe^{III}/Fe^{II}) [b] (V)	E_{red1} (V)	ΔE (eV) [c]	$\lambda_{abs\text{-}max}$ (nm)	Absorbance (a.u.)
C2	302	19000	0.85 (rev)	-1.35 (irrev)	2.20	509	1.40
	394	7000					
	520	16200					
C4	325	42200	1.13 (rev)	-1.23 (irrev)	2.36	494	0.67
	370	5000					
	501	12800					
C5	285	18673	0.82	-1.35 (irrev)	2.17	484	1.30
	394	7625					
	433	7050					
	506	12650					
C6	298	25700	0.81	-1.33 (irrev)	2.14	481	1.59
	396	10100					
	428	8540					
	509	17700					
C7	296	40600	0.82	-1.34	2.16	478	0.77
	395	6115					
	431	5075					
	509	9500					

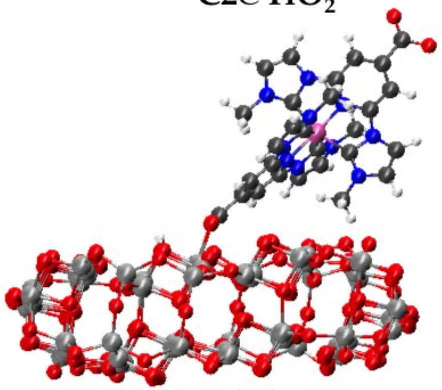
[a] Measured at 25 °C. [b] First oxidation potential. Potentials are quoted *vs* SCE. Under these conditions, $E_{1/2\ (Fc+/Fc)}$ = 0.39V/S.C.E. Recorded in using $Bu_4N^+PF_6^-$ (0.1M) as supporting electrolyte at 100 mV. s^{-1}. [c] Electrochemical band gap (ΔE $=E_{ox} - E_{red1}$)



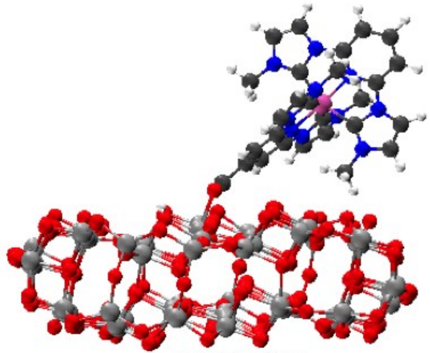
C2@TiO_2



C4@TiO_2



C2(D)@TiO_2



C5@TiO_2

Figure S1. GGA optimized ground state molecular structures of the C2, C4, C2(D) and C5 grafted on the anatase $(TiO_2)_{82}$ slab

Table S2. Relevant diabatic energy levels (in eV) of the TiO_2 slab and the dye molecules.

System	**TiO_2 VB**	**TiO_2 CB**	**Dye's HOMO**	**Dye's LUMO**	**Dye's LUMO+1**
$C2@TiO_2$	-7.52	-3.46	-5.69	-2.62	-2.25
$C4@TiO_2$	-7.50	-3.47	-5.95	-2.71	-2.32
$C2(D)@TiO_2$	-7.48	-3.44	-5.19	-2.12	-1.78
$C5@TiO_2$	-7.44	-3.50	-5.55	-2.16	-1.87

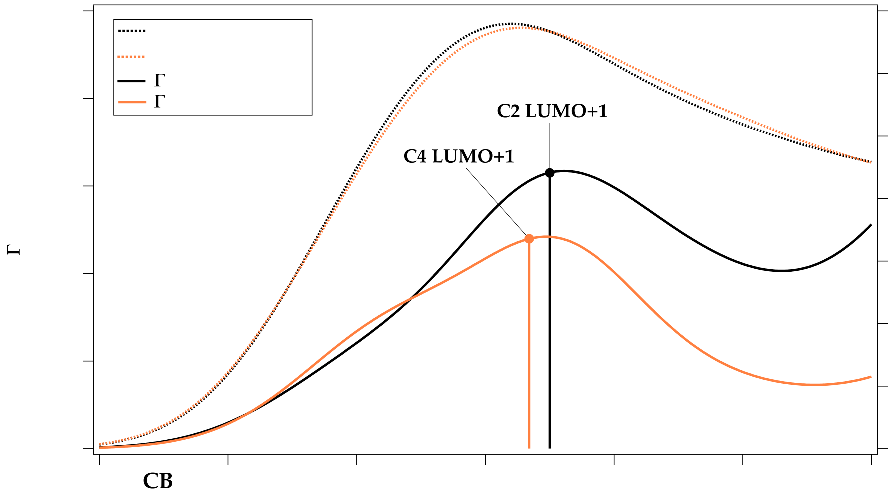


Figure S2. Probability distribution $\Gamma(\varepsilon_k)$, left scale, solid line, (eV); and diabatic Density of States (DOS, right scale, dashed lines eV^{-1}) for electron injection from the LUMO+1 of C2 and C4 to the TiO_2. The dye energy levels are also reported as vertical lines.

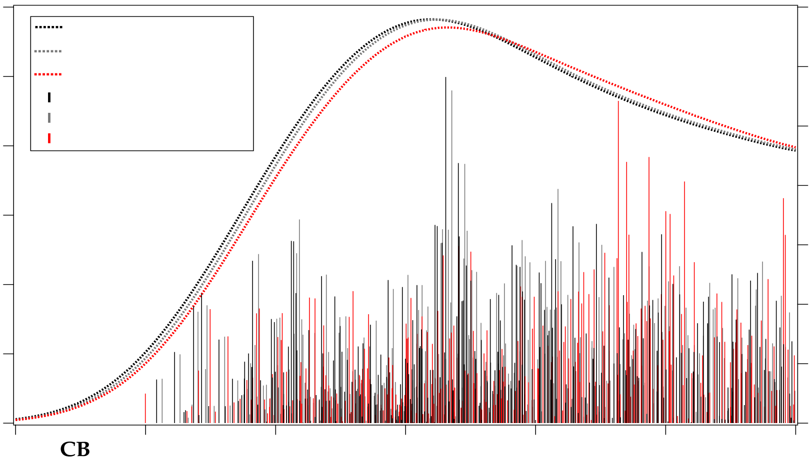


Figure S3. Calculated electronic coupling *V* (in eV) for the LUMO+1 of **C2** (black), LUMO of **C2(D)** (grey) and LUMO of **C5** (red) with the CB states of the TiO_2 (left axis) ; the diabatic TiO_2 DOS (states/eV) is also reported (right axis, dashed lines).

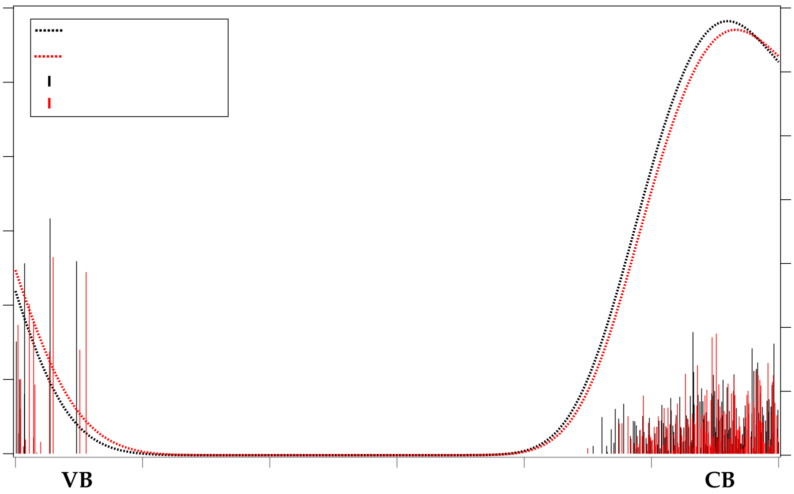


Figure S4. Calculated electronic coupling *V* (in eV) for the HOMO of **C2** (black) and **C5** (red) with the VB and CB states of the TiO_2 (left axis) ; the diabatic TiO_2 DOS (states/eV) is also reported (right axis, dashed lines).

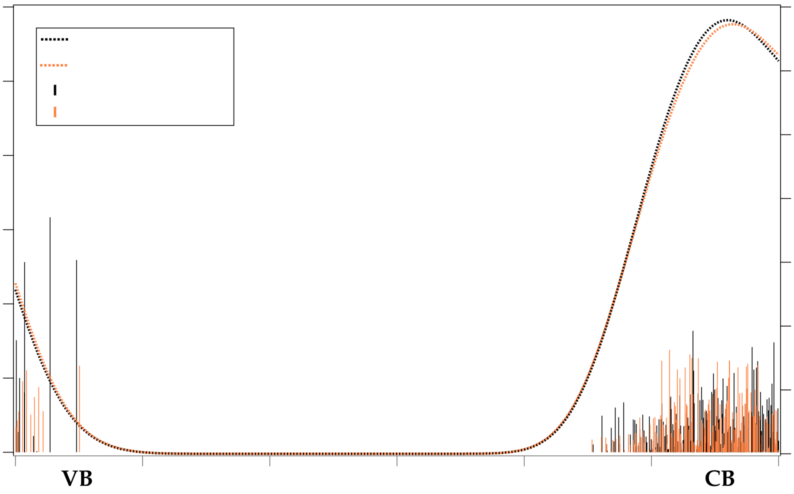


Figure S5. Calculated electronic coupling *V* (in eV) for the HOMO of **C2** (black) and **C4** (orange) with the VB and CB states of the TiO_2 (left axis) ; the diabatic TiO_2 DOS (states/eV) is also reported (right axis, dashed lines).

Photophysics in solution

C5, C6 and **C7** are studied in MeCN in exactly same conditions as in Refs. 2&5 by femtosecond transient absorption spectroscopy, with a time reslution of approx. 80 fs. After excitation in the maximum or on the red egde of the lowest energy ^{1}MLCT absorption band, the transient absorption is probed with a white light continuum covering the 320 – 750 nm range. The spectral features of ^{3}MLCT state are similar to **C2** and **C4** in MeCN as a narrow excited state absorption band around 350 nm and a broad excited state absorption band from 550-670 nm.[5] Figure S6 illustrates kinetic traces of **C5** (square curve), **C6** (circle curve) and **C7** (triangle curve) taken in the band of excited state absorption (red curves) and ground state bleaching (blue curves) with their fits (solid black curves). The kinetic traces are normalized at 1 ps in order to directly compare ^{3}MLCT state lifetimes.

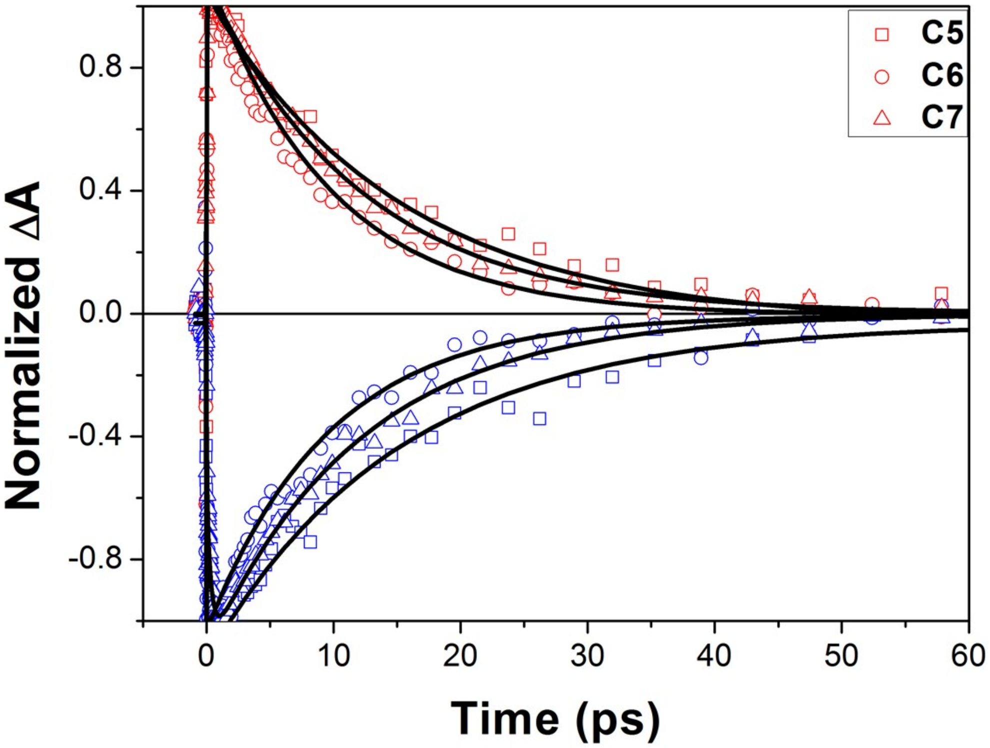


Figure S6. Kinetic traces of the excited state absorption (red) and ground state bleaching (blue) with their fits (solid black curves) normalized at 1 ps for **C5** (square dots), **C6** (circle dots) and **C7** (triangle dots). Parameters are same as shown in Table S3.

Table S3 presents the excited state lifetimes obtained by global analysis for three complexes as described previously. The sub-picosecond component is due to electronic and vibrational relaxation after excitation of the singlet ^{1}MLCT, while the second longer component is the ^{3}MLCT lifetime[2,5]. Despite different chemical structures, **C5, C6** and **C7** have a similar ^{3}MLCT state lifetimes in MeCN, namely in the 10~14ps range. Note that the **C5** ^{3}MLCT lifetime is mid way between the ones of **C2** and its de-carboxylated mother compound[1,2]. An increased stabilization of the ^{3}MLCT orbital away from the metal center, as observed for **C4** does not seem to apply for **C6** and **C7**.

Table S3. Excited state lifetimes of **C5, C6** and **C7** obtained by global analysis of the kinetic traces at all probe wavelengths.

	$(^3MLCT)^+$ in fs	^3MLCT (ps)
C5	300	14
C6	<IRF	10
C7	400	12

Table S4. Cartesian coordinates (Angstrom) of the $(TiO_2)_{82}$ cluster

O	-5.30715	-2.62909	8.92822
Ti	-5.43364	-0.78436	9.21238
O	-7.20825	-0.66706	9.93828
Ti	-8.96665	-0.71616	9.38856
O	-8.54862	-0.96348	7.41915
Ti	-9.07975	0.85908	6.95606
O	-9.48724	0.85641	5.17110
Ti	-8.08269	0.86556	3.86313
O	-8.04715	2.65785	3.20943
Ti	-8.21032	2.36836	1.41030
O	-8.29017	2.27075	-1.02570
Ti	-6.38030	2.26660	-1.39403
O	-6.32193	1.62570	-3.41304
Ti	-6.44746	3.29399	-4.08003
O	-8.39072	2.96655	-4.42603
Ti	-10.19473	2.90130	-4.25411
O	-10.57033	3.48030	-2.53247
Ti	-10.06275	2.53275	-0.94530
O	-10.60940	0.76123	-0.93014
Ti	-10.28882	-1.02935	-0.75857
O	-8.52193	-1.44539	-0.50535
Ti	-6.54743	-1.45059	-0.81002
O	-6.66081	-1.60864	1.17725
Ti	-4.75389	-1.88114	1.68083
O	-4.63619	0.26301	1.76330
Ti	-4.51327	1.96818	1.16254
O	-6.40127	2.48676	0.68362
Ti	-5.83262	-2.89800	7.16275
O	-4.48589	-3.57559	6.24837
Ti	-4.50369	-3.08904	4.30916
O	-2.77345	-3.62722	4.21532
Ti	-0.96924	-3.16856	4.18548
O	-0.80037	-3.66624	2.27598
Ti	-0.93954	-2.05583	1.49826
O	-0.82908	0.12265	1.56337
Ti	-0.74297	0.64112	3.57437
O	-0.93699	-1.44987	3.51035
O	-7.59021	-3.67176	7.59209
Ti	-9.13007	-2.84005	7.40924
O	-9.85009	-2.31669	9.12601
O	-5.79244	-0.93792	7.14479

Ti	-5.78794	0.93281	6.81489
O	-4.22841	1.34254	5.86520
Ti	-2.36152	0.97529	6.35026
O	-2.16004	1.59401	8.10760
Ti	-2.13756	-0.10071	8.93441
O	-0.43518	-0.63128	9.48353
Ti	1.19989	-0.98804	8.66511
O	1.29467	0.95112	7.93703
Ti	1.21453	0.72406	6.19241
O	1.17219	-1.12627	6.58182
Ti	0.98546	-3.03809	6.55591
O	1.07011	-2.84392	8.41382
O	-6.59641	-3.02040	4.94413
Ti	-8.25857	-2.85764	4.23129
O	-8.61789	-3.29782	2.42840
Ti	-8.63805	-1.59866	1.63908
O	-8.38494	-1.11600	3.60264
O	-9.54440	-3.07792	5.62282
O	-9.79029	0.81736	8.76158
O	-7.55026	1.72745	6.89520
O	-8.42789	0.57752	1.83773
O	-6.34884	0.69856	4.48852
Ti	-4.43816	0.77691	3.81658
O	-2.58110	0.68658	4.20461
O	-9.87586	3.09551	0.81801
O	-10.46041	-1.52608	1.04901
O	-10.69385	-1.56224	-2.54972
Ti	-10.15881	-0.59004	-4.04780
O	-9.93294	-1.33390	-5.76841
Ti	-8.29144	-0.72147	-6.38923
Ti	-8.04082	1.03174	-8.74174
O	-6.41583	0.98301	-9.43378
Ti	-4.61070	1.03466	-8.73346
O	-2.98165	0.88906	-9.51309
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Ti	2.16342	0.15577	-9.19204
O	2.20121	-1.53348	-8.35703
Ti	2.40387	-0.91587	-6.60822
O	4.25748	-1.35842	-6.13373
Ti	5.79702	-0.94867	-7.13854
O	6.39767	-0.80955	-4.80437
Ti	8.10887	-0.98540	-4.12646
O	8.05036	-2.77538	-3.43554
Ti	8.23568	-2.47759	-1.63782
O	8.35214	-2.21935	0.78262
Ti	10.09785	-2.61134	0.69950
O	10.75046	-0.86358	0.61722
Ti	10.40983	0.92402	0.47432
O	8.59755	1.31158	0.26977
Ti	6.64184	1.43409	0.60547
O	6.46827	-0.19527	1.29828
Ti	6.52250	0.44635	3.32513
O	6.66871	2.03782	2.42565
O	-8.36727	-0.22942	-4.03582
Ti	-6.50874	-0.44775	-3.52550
O	-4.72425	-0.40510	-4.11663
Ti	-4.72959	-0.63293	-6.25535

O	-4.77601	-0.82184	-8.04570
O	-10.78154	1.14986	-4.24706
O	-8.02220	1.18377	-6.73060
Ti	-8.43158	3.10405	-6.65960
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Ti	-4.67293	3.18420	-6.69675
O	-4.65276	3.60039	-4.62444
Ti	-2.75944	3.29921	-4.12338
O	-0.98060	3.51696	-4.69056
Ti	-0.95001	3.01506	-6.77007
O	-1.05843	2.81586	-8.63499
O	-6.57258	-1.12052	-5.70166
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O	-10.14461	3.56885	-6.09463
O	-8.62184	2.80965	-8.51394
O	-5.35489	1.12114	8.52165
O	-3.68540	-0.52328	9.86330
O	-4.45652	-1.32624	3.70305
O	-4.75708	-1.99295	-0.39251
Ti	-2.88088	-1.69322	-0.93546
O	-2.85585	-1.90269	1.14517
O	-4.99563	-3.49242	2.49985
O	-2.94721	-2.20569	-2.74232
Ti	-2.86984	-0.55371	-3.59995
O	-2.96089	-1.12838	-5.74042
Ti	-1.17813	-0.74930	-6.40233
O	-1.07385	-0.47491	-4.16343
Ti	0.79033	-0.66148	-3.82201
O	0.63822	-1.17240	-5.88628
O	-2.85305	0.01982	-1.59277
Ti	-2.69881	2.11223	-1.51116
O	-2.65402	2.22113	0.58880
Ti	-0.75258	1.82826	0.95201
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Ti	1.01190	2.02782	-1.74587
O	2.92962	1.86941	-1.37096
Ti	4.82699	1.83652	-1.89320
O	5.06145	3.44455	-2.73991
Ti	4.58997	3.03172	-4.55830
O	4.55599	1.27320	-3.95780
Ti	4.49491	-0.80398	-4.08541
O	4.50121	-2.46147	-3.22392
Ti	4.56654	-1.99497	-1.41073
O	6.42022	-2.57568	-0.89602
Ti	6.43156	-2.27478	1.15619
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Ti	2.74995	-2.14608	1.26862
O	2.72789	-2.28030	-0.83251
Ti	0.82369	-1.87960	-1.21990
O	0.73624	-2.37389	-3.01939
O	-1.03318	-2.15349	-0.58832
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O	-2.69709	3.80156	-2.34245
O	-2.89048	3.55093	-6.36255
O	-0.87841	1.93375	-1.13085
O	-2.39048	-0.68124	7.13939
O	-0.75498	-3.27903	6.15755
O	1.03424	-3.52842	4.46997

Ti	2.80678	-3.30033	3.90319
O	2.76152	-3.81765	2.12370
O	2.92202	-3.58141	6.14537
Ti	4.70362	-3.21159	6.48435
O	6.67986	-3.69368	6.01633
Ti	8.46740	-3.14476	6.43225
O	10.19928	-3.60831	5.85623
Ti	10.20123	-2.99761	4.00942
O	10.76348	-1.24657	3.95728
Ti	10.18086	0.50584	3.78611
O	10.01924	1.24907	5.52249
Ti	8.34478	0.69087	6.11888
O	6.58873	1.10631	5.46439
Ti	4.76760	0.61277	6.04604
O	4.74758	0.33887	3.90264
Ti	2.89719	0.52303	3.36170
O	2.99792	2.17684	2.52077
Ti	2.95717	1.66424	0.70753
O	2.91296	-0.03752	1.34860
O	2.85692	-1.58483	3.28799
O	4.68756	-3.62299	4.40645
Ti	6.46976	-3.31641	3.84095
O	8.40293	-3.07576	4.19558
O	2.99831	1.11034	5.51851
O	1.12219	0.42188	3.93319
O	4.84394	1.96182	0.18272
O	4.72370	-0.29071	-2.01390
O	6.73302	1.56549	-1.38067
Ti	8.69021	1.46364	-1.89695
O	8.47526	-0.69429	-2.08583
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O	0.88501	3.64067	-2.51231
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O	4.75570	-3.02402	8.29820
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O	6.48939	-3.92463	2.08686
O	6.37297	-1.65203	3.19471
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O	8.50075	0.75141	7.97144
Ti	8.06713	-1.03817	8.46978
O	8.65689	-2.81426	8.26565
O	8.05696	-1.20946	6.47249
O	6.45786	-1.00150	9.18810
O	10.57005	-3.58094	2.26946
O	9.88148	-3.24175	-1.01784
O	9.43709	-1.03243	-5.46387
Ti	9.10175	-0.88682	-7.27616
O	8.59536	0.95336	-7.68753
Ti	9.19774	2.82825	-7.66239
O	7.66218	3.65601	-7.80240
Ti	5.90496	2.88693	-7.39991
O	5.35738	2.68687	-9.16976

Ti	5.44288	0.84058	-9.49096
O	7.22626	0.69126	-10.20773
Ti	8.98393	0.71839	-9.66952
O	9.86967	2.32115	-9.42400
O	8.43401	0.99021	-3.87290
Ti	8.32716	2.74200	-4.47987
O	8.67684	3.17119	-2.69441
O	9.79164	-0.84473	-9.08116
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O	9.62047	2.99614	-5.87254
O	6.66795	2.93534	-5.17854
O	2.83538	3.54644	-4.45670
O	4.58083	3.59089	-6.47233
O	4.77474	0.78825	7.82782
O	3.01061	-0.93681	9.29762
O	0.92915	-1.94514	0.88106
O	-4.45141	2.44782	2.96475
O	-4.57042	2.16640	-0.94199
O	-6.42638	0.20582	-1.49870
O	-6.45437	3.91836	-2.33617
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O	-4.63274	1.25081	-6.67056
O	-4.71726	2.97713	-8.50501
O	-1.13972	1.10312	-6.79080
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O	10.75759	1.43019	2.28125
O	10.51012	1.37162	-1.35497
O	2.42214	0.74355	-7.41122
O	3.68336	0.62250	-10.14119
O	5.81960	0.94253	-7.43413
O	5.28705	-1.08565	-8.82246

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