Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Thiocyanate-Free Cyclometalated Ruthenium(II) Sensitizers for DSSC: A Combined Experimental and Theoretical Investigation

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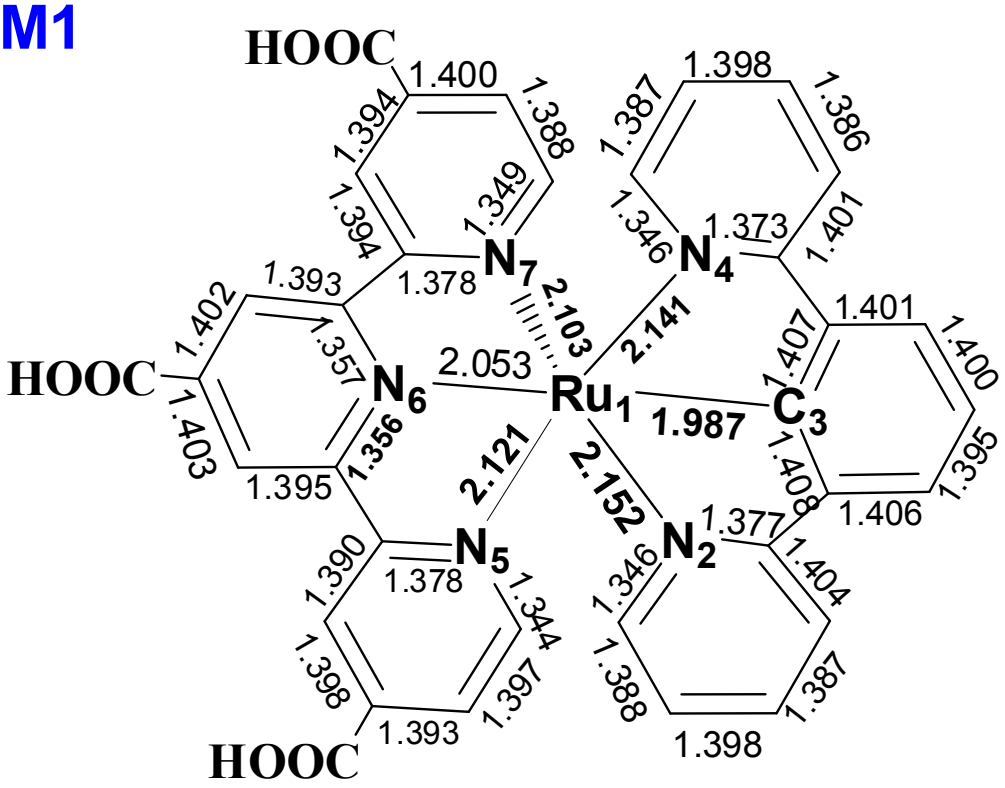
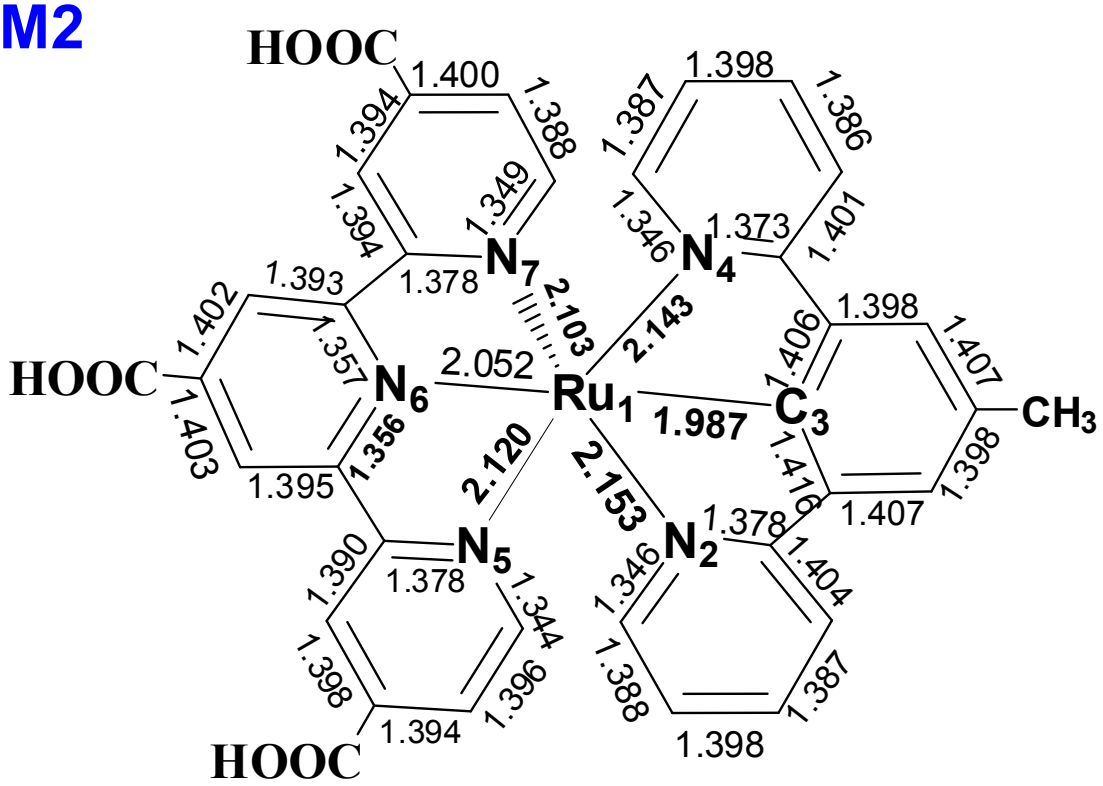
Scheme S1: Optimized Geometrical parameters of the dyes **M1-M4.**

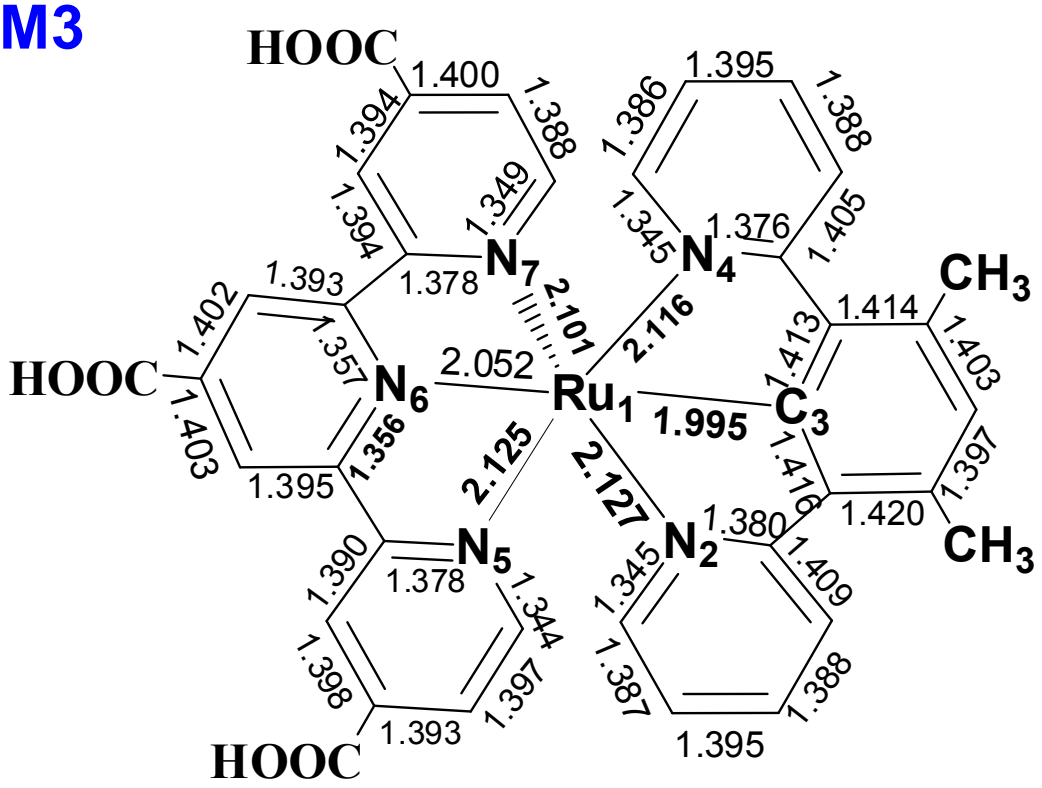
M1



M2



M3


HOOC
HOOC
HOOC
CH3
CH3
N7
N6
N5
N4
N2
Ru1
C3
2.101
2.116
2.052
2.125
2.127
1.995
1.356
1.400
1.394
1.388
1.349
1.394
1.378
1.393
1.402
1.357
1.403
1.395
1.390
1.378
1.344
1.398
1.397
1.393
1.395
1.386
1.388
1.345
1.376
1.405
1.414
1.413
1.403
1.410
1.397
1.420
1.380
1.409
1.345
1.387
1.388
1.395

M4

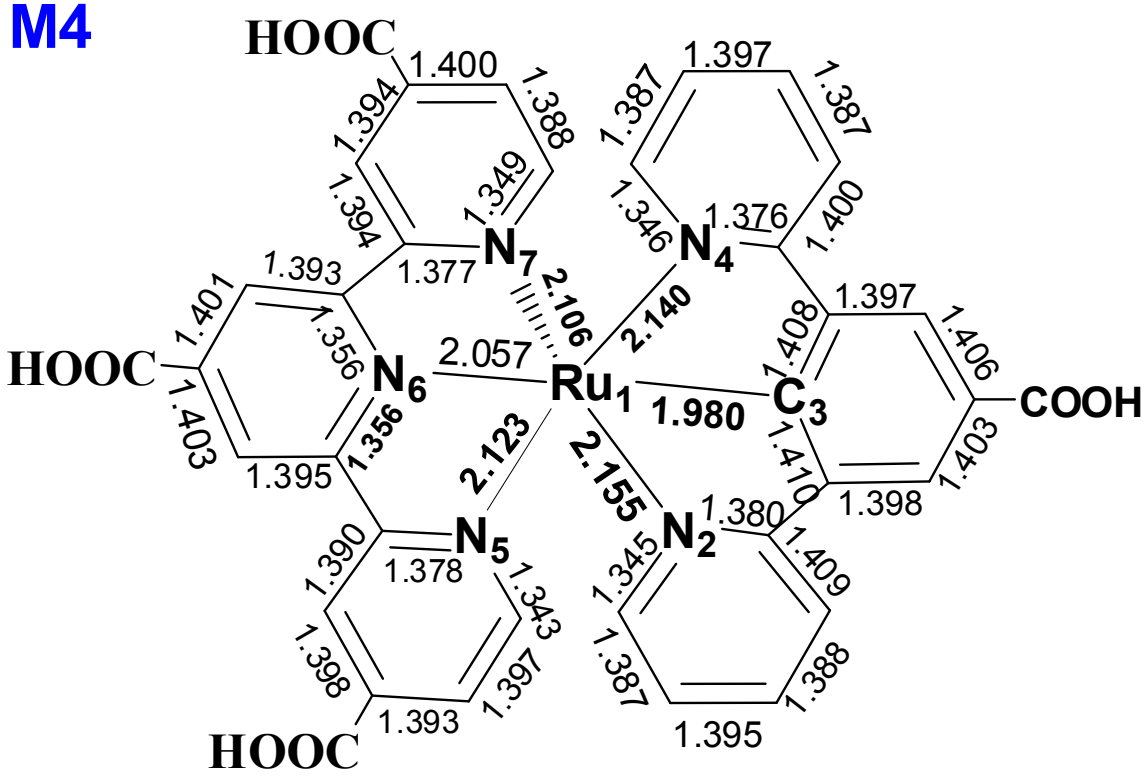

HOOC
HOOC
HOOC
COOH
N7
N6
N5
N4
N2
Ru1
C3
2.106
2.140
2.057
2.123
2.155
1.980
1.356
1.400
1.394
1.388
1.349
1.394
1.377
1.393
1.401
1.356
1.403
1.395
1.390
1.378
1.343
1.398
1.397
1.393
1.397
1.387
1.387
1.346
1.376
1.400
1.397
1.408
1.406
1.403
1.410
1.398
1.380
1.409
1.345
1.387
1.388
1.395

Table S1: Selected FMOs (Isosurface=0.02), their Energies (eV) and Molecular orbital composition (%) of the dye **M1**.

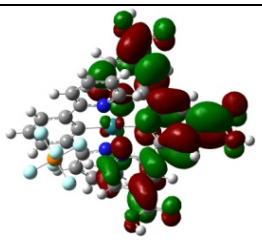
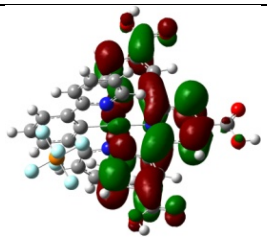
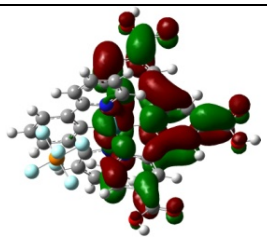
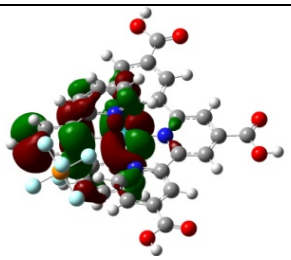
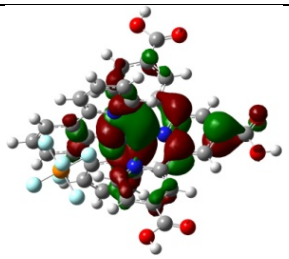
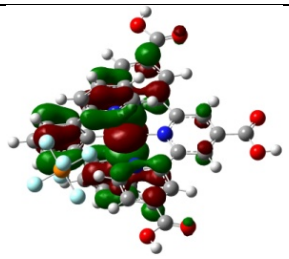
	FMO	MO Composition (%)
L+2	 -2.09	TPY (97.5)
L+1	 -2.43	Ru (5.0) TPY (94.0)
L	 -2.73	Ru (12.5) TPY (81.9) TPY-C (5.6)
H	 -5.24	Ru (49.8) TPY (14.5) TPY-C (35.7)
H-1	 -5.55	Ru (60.6) TPY (22.3) TPY-C (17.0)
H-2	 -5.63	Ru (66.7) TPY (13.4) TPY-C (19.8)

Table S2: Selected FMOs (Isosurface=0.02) and their Energies (eV). Molecular orbital composition (%) of the dye **M2**.

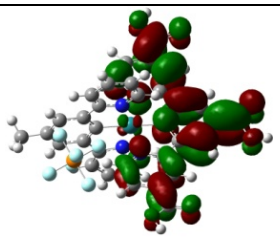
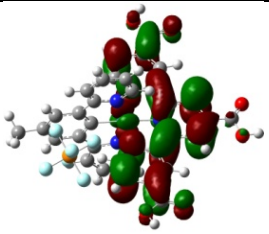
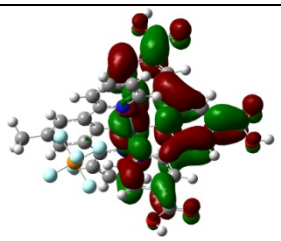
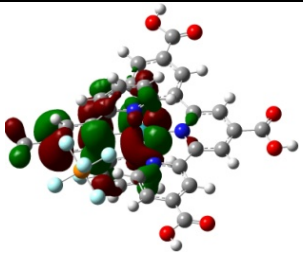
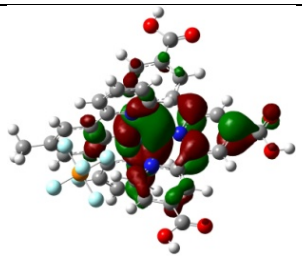
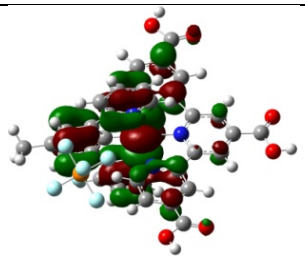
	FMO	MO Composition (%)
L+2	 -2.09	TPY (97.4)
L+1	 -2.42	Ru (5.1) TPY (93.9)
L	 -2.73	Ru (12.5) TPY (81.8) TPY-C (5.6)
H	 -5.15	Ru (45.9) TPY (13.7) TPY-C (40.4)
H-1	 -5.54	Ru (60.3) TPY (22.0) TPY-C (17.7)
H-2	 -5.62	Ru (65.9) TPY (13.8) TPY-C (20.2)

Table S3: Selected FMOs (Isosurface=0.02) and their Energies (eV). Molecular orbital composition (%) of the dye **M4**.

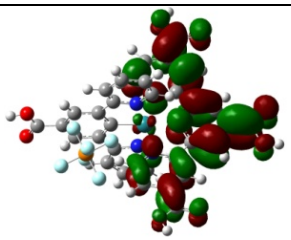
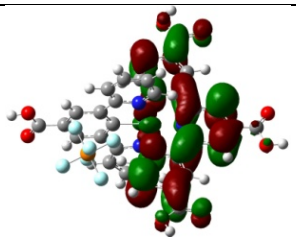
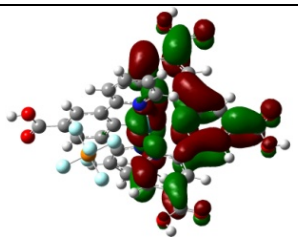
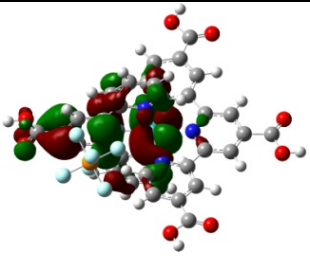
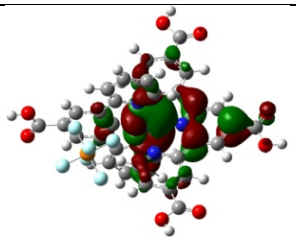
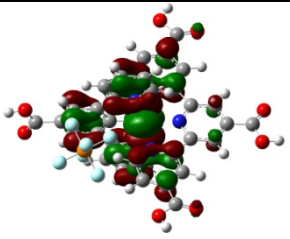
	FMO	MO Composition (%)
L+2	 -2.12	TPY (97.6)
L+1	 -2.46	Ru (5.2) TPY (93.9)
L	 -2.78	Ru (11.7) TPY (82.8) TPY-C (5.5)
H	 -5.42	Ru (51.1) TPY (13.8) TPY-C (35.1)
H-1	 -5.65	Ru (61.1) TPY (21.1) TPY-C (17.8)
H-2	 -5.73	Ru (68.9) TPY (13.6) TPY-C (17.4)

Table S4: TD-DFT data of **M1@**$(TiO_2)_{38}$ with 1-COOH and 2-COOH adsorption.

Dye Adsorbed with	State	Wavelength (nm)	Excitation Energy (eV)	Oscillator Strength	Dominant contribution
2-COOH	S7	653	1.90	0.0303	H-2→L+7 (15%), H-2→L+8 (12%) & H-2→L+9 (12%)
	S13	593	2.09	0.0122	H-1→L+7 (19%), H-1→L+8 (12%) &H-1→L+9 (11%)
	S21	560	2.21	0.1341	H-1→L+21 (10%) &H-1→L+28 (10%),
	S47	509	2.44	0.0105	H-1→L+10 (28%), H-2→L+7 (27%), H-1→L+9 (10%) &H-1→L+11 (10%)
1-COOH	S6	647	1.92	0.0217	H-2→L+11(36%) &H-2→L+17(16%)
	S18	567	2.19	0.0675	H-1→L+11(25%), H-1→L+17(12%) &H-2→L+32(10%)
	S32	522	2.38	0.0301	H-2→L+5(34%), H-1→L+7(14%), H-1→L+32(13%) &H-1→L+31(10%)
	S34	519	2.39	0.0230	H-1→L+7(37%), H-2→L+6 (14%) &H-2→L+5 (13%)

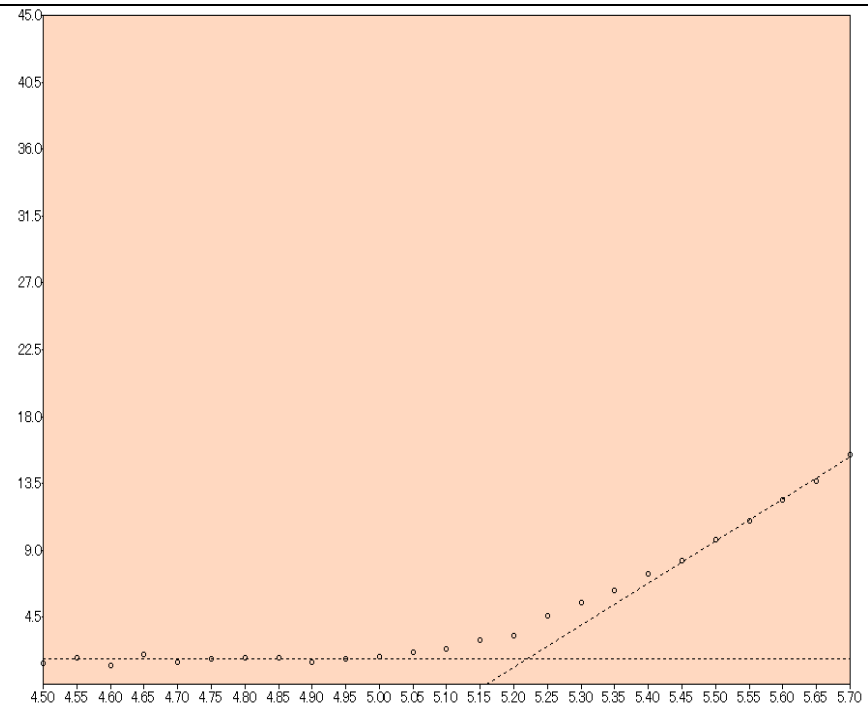
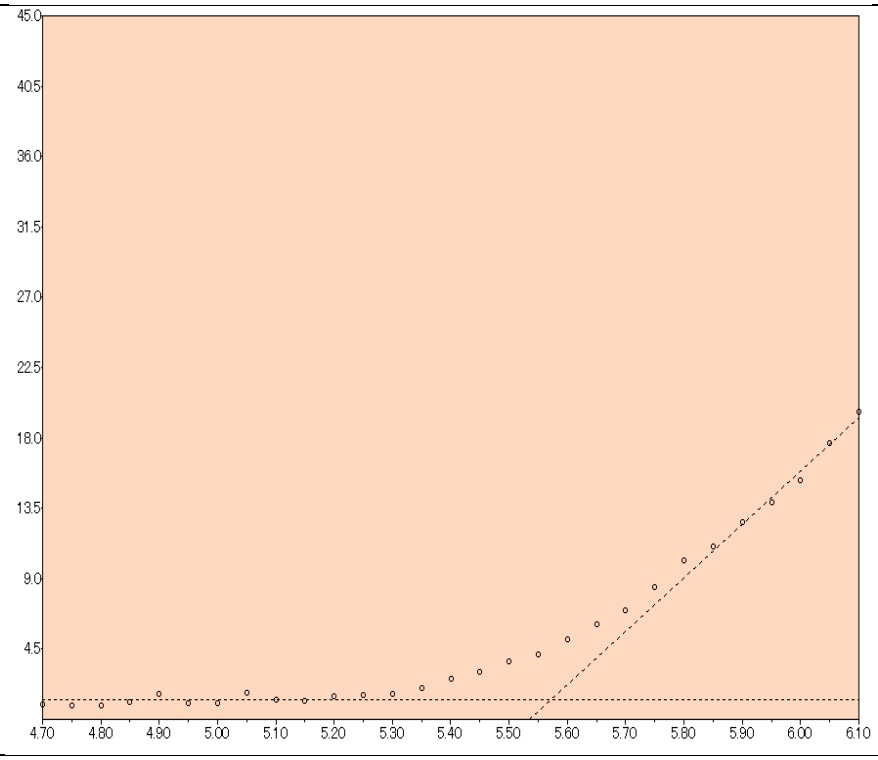
Table S5: TD-DFT data of **M2@**$(TiO_2)_{38}$ with 1-COOH and 2-COOH adsorption.

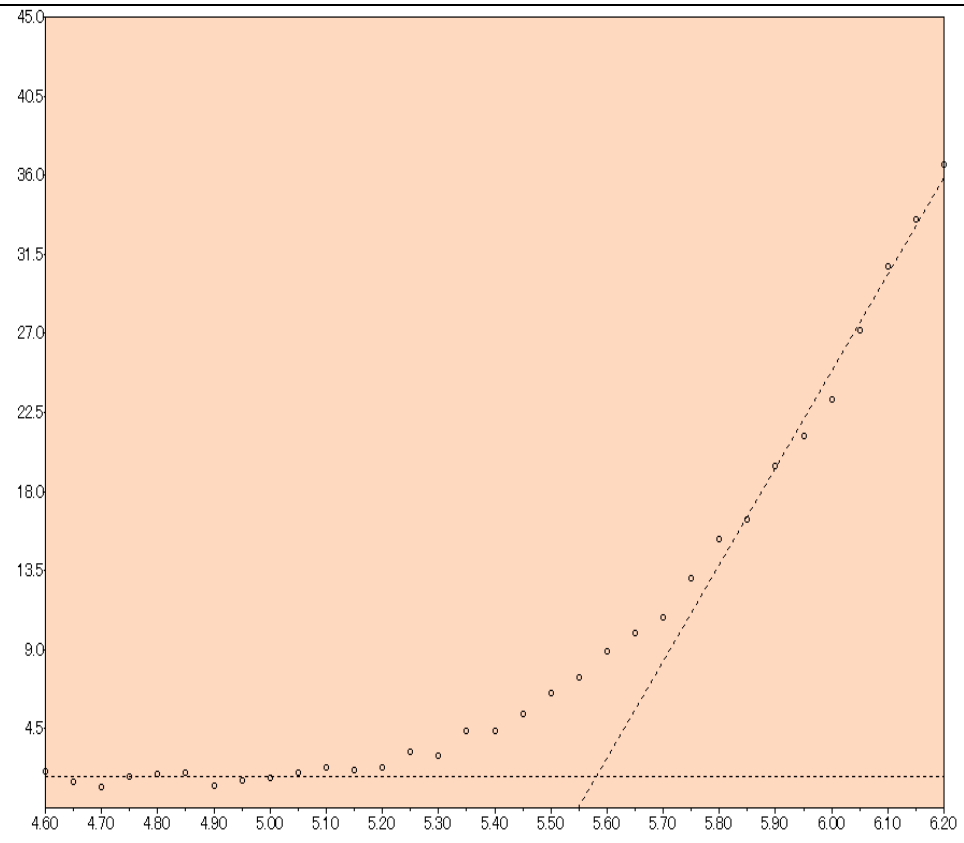
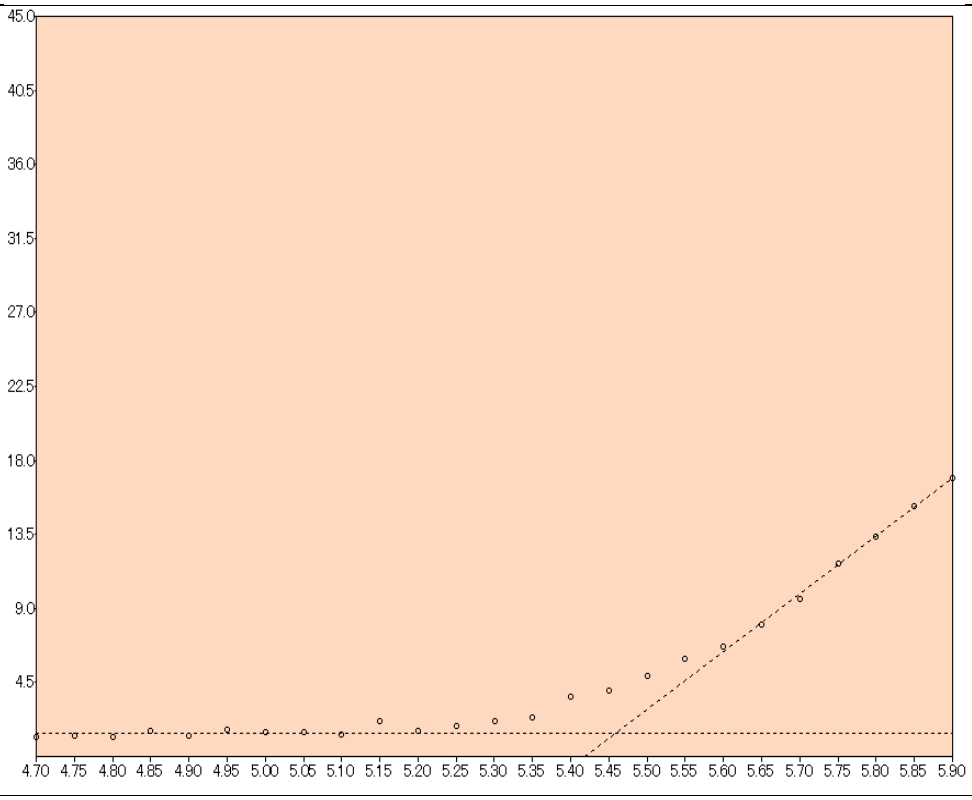
Dye Adsorbed with	State	Wavelength (nm)	Excitation Energy (eV)	Oscillator Strength	Dominant contribution
2-COOH	S9	659	1.88	0.0305	H-2→L+7 (18%), H-2→L+9 (14%) &H-2→L+8 (12%)
	S16	599	2.07	0.0164	H-1→L+7 (20%), H-1→L+9 (12%) &H-1→L+8 (11%)
	S26	566	2.19	0.1313	H-1→L+29 (15%) &H-1→L+21 (10%)
1-COOH	S3	641	1.94	0.0166	H-2→L+10(19%), H-2→L+14(12%) &H-2→L+16(12%)
	S15	562	2.21	0.0497	H-1→L+1(52%)
	S16	560	2.22	0.0432	H-1→L+1 (46%)
	S35	517	2.40	0.0151	H-1→L+8 (77%)
	S38	515	2.41	0.0162	H-1→L+9(24%), HOMO→L+18(18%) &HOMO→L+19(16%)
	S43	505	2.45	0.0166	H-1→L+9 (28%) &H-1→L+10(17%)

Table S6: TD-DFT data of **M4**@$(TiO_2)_{38}$ with 1-COOH and 2-COOH adsorption.

Dye Adsorbed with	State	Wavelength (nm)	Excitation Energy (eV)	Oscillator Strength	Dominant contribution
2-COOH	S3	633	1.96	0.0305	H-2→L+6 (24%),
	S8	578	2.15	0.0210	H-1→L+6 (22%) &H-1→L+5 (10%)
	S12	548	2.26	0.1235	H-1→L+24 (19%), H-1→L+19 (13%), &H-1→L+22 (11%)
	S42	491	2.52	0.0195	H-1→L+7 (13%), H-1→L+6 (11%), H-2→L+7 (10%) &H-1→L+9 (10%)
1-COOH	S4	632	1.96	0.0223	H-2→L+10(44%) &H-1→L+10(13%)
	S14	556	2.23	0.0782	H-1→L+10(31%) &H-2→L+10(10%)
	S27	508	2.44	0.0626	H-1→L+30(25%) &H-1→L+31(22%)
	S46	475	2.61	0.0256	H-1→L+10(21%), H-1→L+15(18%), H-1→L+13(15%) &H-1→L+17(12%)

Table S7: Ionization potential (IP) of **M1, M2, M3** and **M4** determined by using the photoemission yield spectrometer (Riken Keiki, AC-3E).

Dye	Photoelectron Spectrum	Ionization Potential (V)
M1		**-5.22**
M2		**-5.57**

M3	 45.0 40.5 36.0 31.5 27.0 22.5 18.0 13.5 9.0 4.5 4.60 4.70 4.80 4.90 5.00 5.10 5.20 5.30 5.40 5.50 5.60 5.70 5.80 5.90 6.00 6.10 6.20	**-5.58**
M4	 45.0 40.5 36.0 31.5 27.0 22.5 18.0 13.5 9.0 4.5 4.70 4.75 4.80 4.85 4.90 4.95 5.00 5.05 5.10 5.15 5.20 5.25 5.30 5.35 5.40 5.45 5.50 5.55 5.60 5.65 5.70 5.75 5.80 5.85 5.90	**-5.46**