Supplementary Information

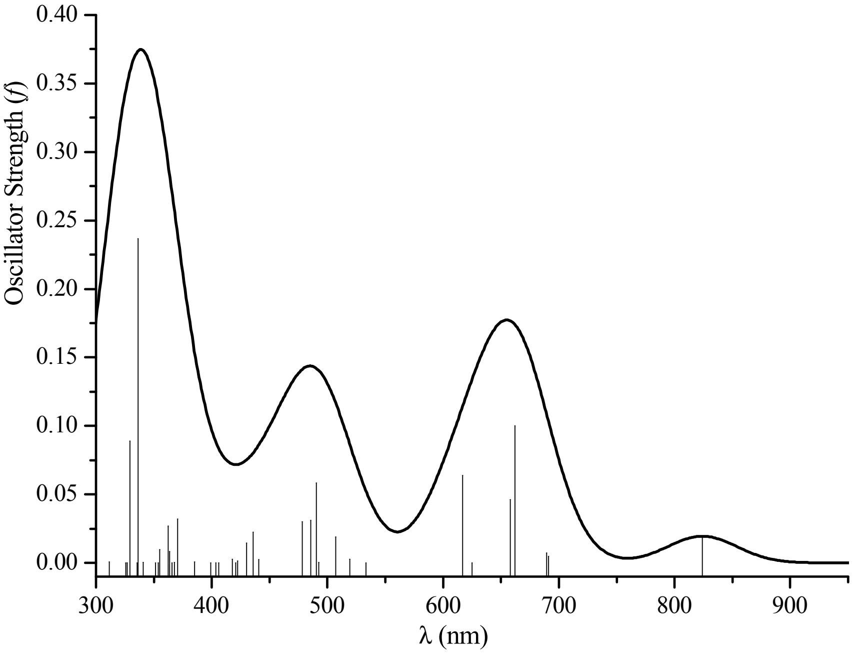

Fig. S1 Simulated absorption spectra in methanol for **1** obtained from the TD-B3LYP/PCM calculations.

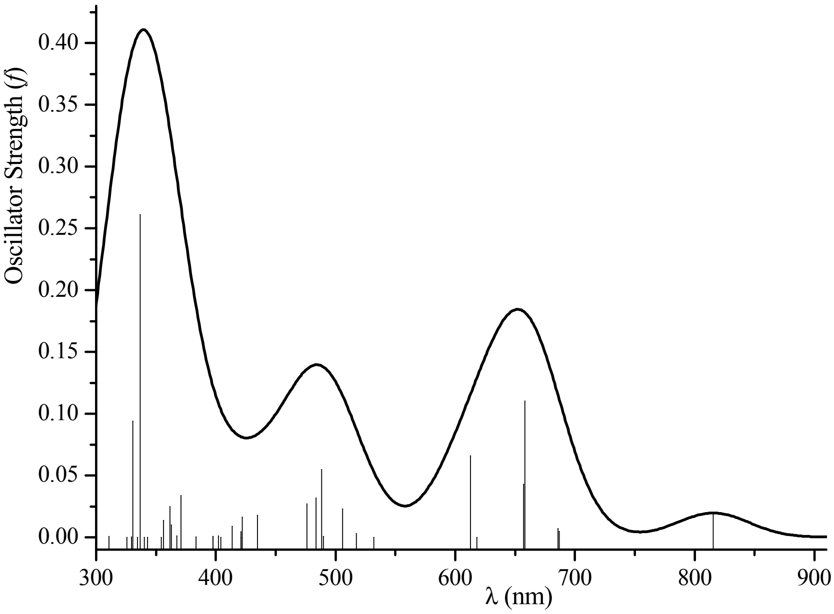

Fig. S2. Simulated absorption spectra in methanol for **2** obtained from the TD-B3LYP/PCM calculations.

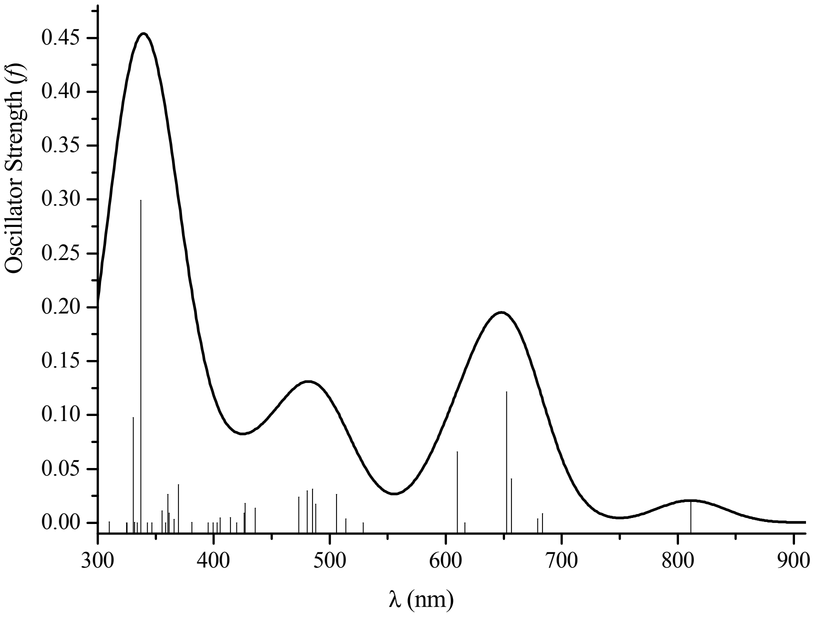

Fig. S3. Simulated absorption spectra in methanol for **3** obtained from the TD-B3LYP/PCM calculations.

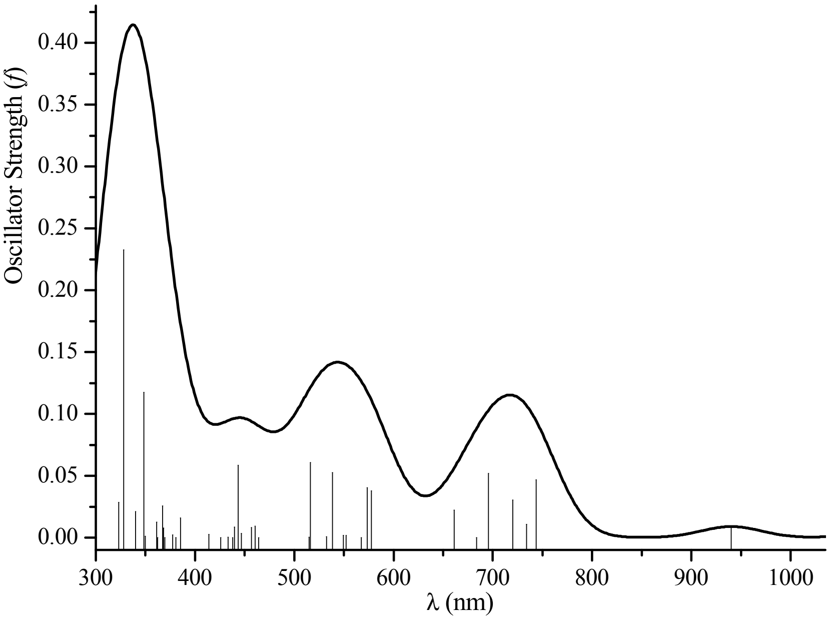

Fig. S4. Simulated absorption spectra in methanol for **4** obtained from the TD-B3LYP/PCM calculations.

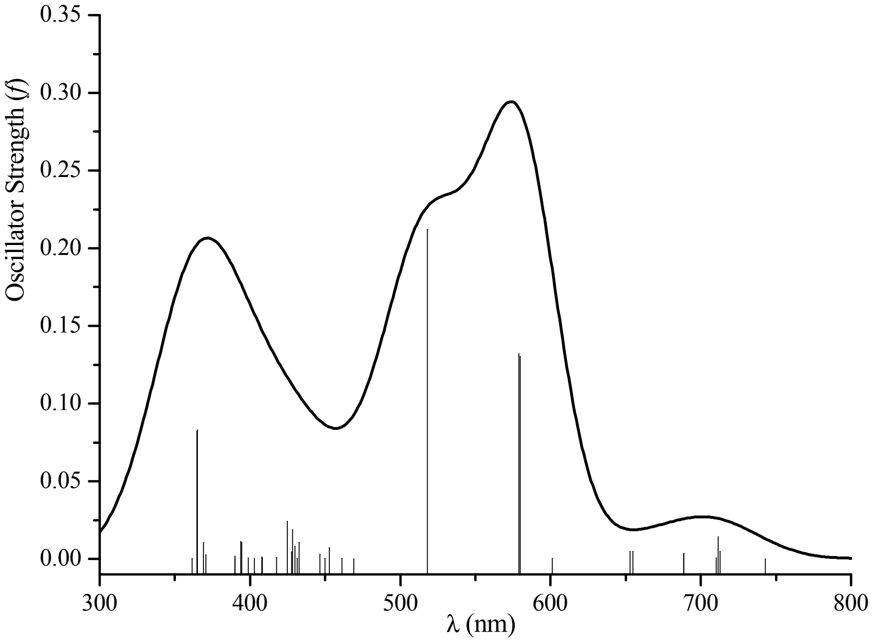

Fig. S5 Simulated absorption spectra in methanol for **5** obtained from the TD-B3LYP/PCM calculations.

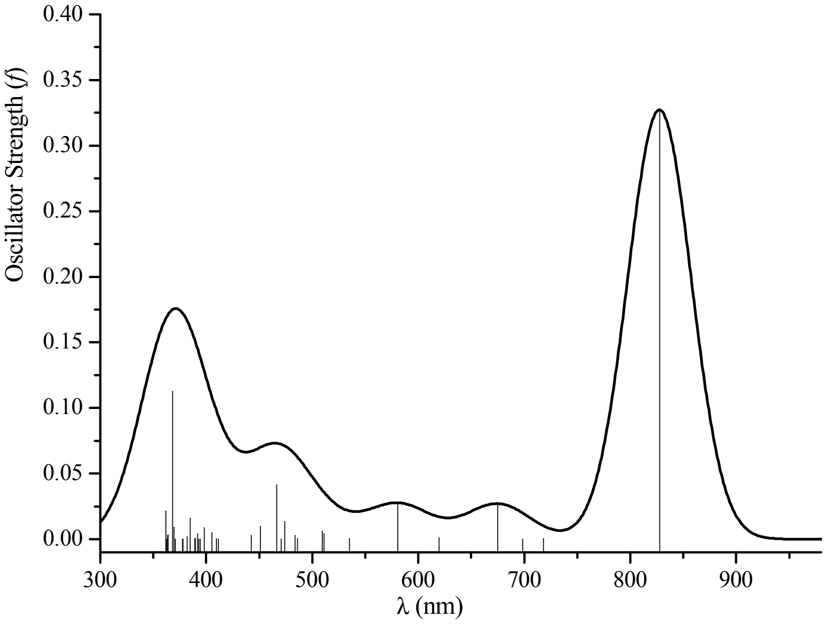

Fig. S6. Simulated absorption spectra in methanol for $\mathbf{1}^+$ obtained from the TD-B3LYP/PCM calculations.

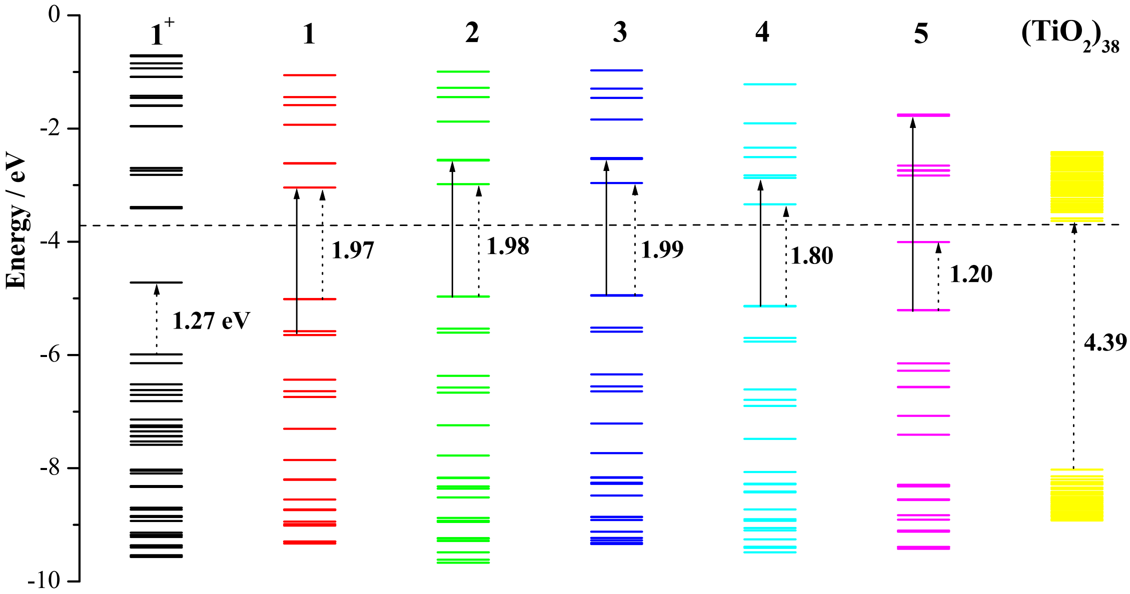

Fig. S7 Diagrams of frontier molecular orbitals of **1-5** in the methanol solution obtained from the TD-B3LYP/PCM calculations. The solid arrows represent the stronger low-energy visible absorption transitions while the dotted arrows denote the lowest-energy transitions. The HOMO-LUMO energy gaps are also shown in the diagram (eV).

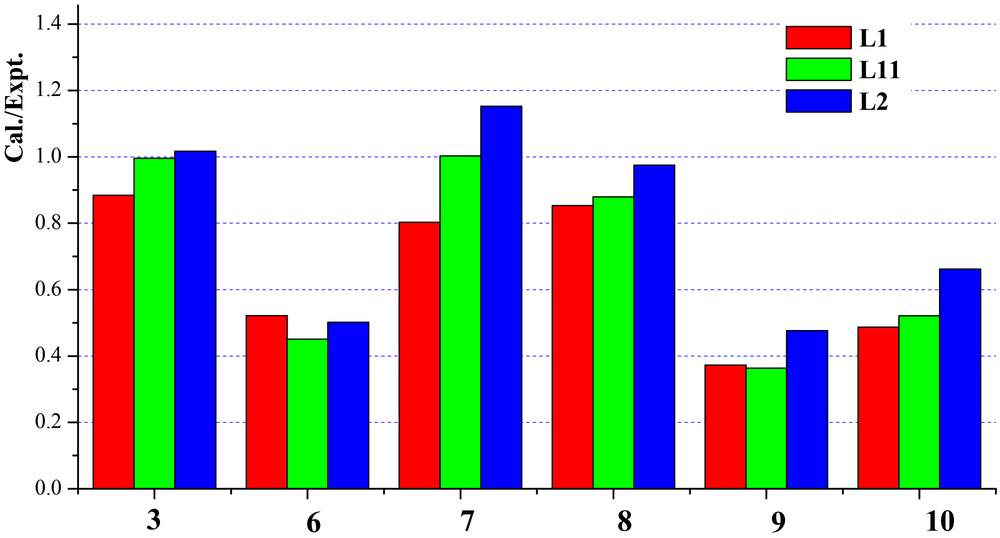

Fig. S8. Diagram of the ratio of the calculated $E^{0(}$sol) and experimental values.

Table S1 The calculated frequencies (cm^{-1}) of complexes **1-5** in the molecular (Mol.), univalent cationic (Cat.) and triplet excited (Exc.) states.

	Freq.	IR. Int.	Freq.	IR. Int.	Freq.	IR. Int.	Assignm.	Expt.	Ratio
1	Mol.		Cat.		Exc.				
	881	1.68E+03	899	1.28E+03	874	1.67E+03	ν(C-S)	795	0.9
	894	1.25E+04	918	1.03E+04	894	1.37E+04			
	1767	6.44E+03	1783	3.14E+04	1757	1.10E+04	ν(C=O)	1710	0.97
	1768	7.32E+04	1784	4.65E+04	1760	6.71E+04			
	2085	3.54E+02	2029	2.64E+04	2065	9.85E+01	ν(C≡N)	2097	1.01
	2088	3.08E+04	2039	4.00E+01	2068	2.92E+04			
	3649	1.37E+05	3636	7.30E+04	3651	2.56E+04	ν(O-H)	3371	0.92
	3650	1.42E+05	3636	2.09E+05	3651	2.50E+05			
2	Mol.		Cat.		Exc.				
	879	1.70E+03	898	1.44E+03	873	1.66E+03	ν(C-S)	795	0.9
	892	1.41E+04	917	1.12E+04	894	6.20E+03			
	1766	1.12E+04	1782	2.82E+04	1755	8.05E+03	ν(C=O)	1710	0.97
	1767	6.83E+04	1783	4.97E+04	1759	7.00E+04			
	2087	2.83E+02	2032	2.66E+04	2067	1.15E+02	ν(C≡N)	2097	1.01
	2090	3.11E+04	2041	4.25E+01	2069	2.93E+04			
	3650	1.09E+05	3636	1.11E+05	3651	6.22E+04	ν(O-H)	3371	0.92
	3650	1.69E+05	3637	1.70E+05	3652	2.13E+05			
3	Mol.		Cat.		Exc.				
	878	1.68E+03	897	1.36E+03	873	1.66E+03	ν(C-S)	795	0.91
	893	5.88E+03	915	1.20E+04	893	9.49E+03			
	1765	1.12E+04	1781	2.88E+04	1754	6.25E+03	ν(C=O)	1710	0.97
	1767	6.83E+04	1783	4.92E+04	1758	7.19E+04			
	2088	2.90E+02	2035	2.67E+04	2067	1.10E+02	ν(C≡N)	2097	1.00
	2091	3.11E+04	2043	4.46E+01	2070	2.94E+04			
	3650	9.43E+04	3637	4.40E+04	3652	8.37E+04	ν(O-H)	3371	0.92
	3651	1.83E+05	3638	2.37E+05	3653	1.92E+05			
4	Mol.		Cat.		Exc.				
	884	1.60E+03	899	1.57E+03	878	1.67E+03	ν(C-S)		
	898	8.61E+03	917	1.15E+04	897	1.07E+04			
	1769	2.43E+04	1784	2.30E+04	1763	2.40E+04	ν(C=O)		
	1770	4.32E+04	1784	3.99E+04	1765	9.52E+03			
	1781	1.99E+04	1788	3.12E+04	1768	1.63E+04			
	1782	2.92E+04	1792	2.04E+04	1772	6.50E+04			
	2081	3.36E+02	2027	2.60E+04	2063	1.32E+02	ν(C≡N)		
	2084	2.94E+04	2037	3.18E+01	2064	2.82E+04			
	3642	4.32E+04	3631	4.03E+04	3645	3.77E+04	ν(O-H)		
	3644	7.69E+04	3633	7.39E+04	3648	5.56E+04			
	3649	8.15E+04	3635	2.72E+04	3649	8.26E+04			
	3649	2.05E+05	3636	2.71E+05	3650	2.27E+05			

5	Mol.		Cat.		Exc.		
	860	6.54E+03	877	3.96E+03	858	6.89E+03	ν(C-S)
	917	1.30E+04	930	1.33E+04	920	1.29E+04	
	1765	5.45E+03	1780	7.53E+03	1763	8.34E+03	ν(C=O)
	1768	1.19E+04	1780	5.20E+02	1765	2.73E+04	
	1769	5.75E+03	1781	3.58E+04	1765	2.96E+03	
	1770	6.89E+04	1783	4.77E+04	1769	5.21E+04	
	2044	1.28E+04	2003	9.59E+03	2035	8.93E+03	ν(C≡N)
	2081	1.27E+04	2020	1.56E+04	2050	1.87E+04	
	3646	9.13E+04	3626	1.17E+05	3648	1.46E+04	ν(O-H)
	3647	3.12E+04	3634	1.46E+04	3648	9.54E+04	
	3648	4.25E+03	3635	4.00E+04	3649	3.56E+04	
	3648	1.94E+05	3635	1.56E+05	3649	1.74E+05	

Table S2 Calculated bond orders of complexes **1-5** in the molecular (Mol.), univalent cationic (Cat.) and triplet excited (Exc.) states obtained using the four-component scalar relativistic method implemented in the Priroda code with all-electron DZP basis and the PBE functional.

		Ru-N1	Ru-N2	Ru-N3	N≡C	C-S
1	Mol.	0.72	0.45	0.70	2.26	1.74
	Cat.	0.77	0.43	0.64	2.22	1.76
	Exc.	0.75	0.48	0.60	2.27	1.72
2	Mol.	0.72	0.45	0.70	2.26	1.73
	Cat.	0.77	0.44	0.64	2.22	1.76
	Exc.	0.74	0.48	0.60	2.27	1.72
3	Mol.	0.72	0.45	0.70	2.27	1.73
	Cat.	0.77	0.44	0.64	2.22	1.75
	Exc.	0.74	0.48	0.60	2.27	1.72
4	Mol.	0.72	0.46	0.69	2.25	1.74
	Cat.	0.77	0.43	0.65	2.21	1.76
	Exc.	0.75	0.50	0.60	2.26	1.72
5	Mol.	0.74	0.61	0.62	2.23	1.77
		0.69			2.26	1.74
	Cat.	0.80	0.58	0.58	2.18	1.78
		0.73			2.22	1.78
	Exc.	0.78	0.63	0.63	2.21	1.76
		0.71			2.27	1.74

Table S3 Calculated electronic absorptions of **1** in the methanol solution obtained at the TD-DFT (B3LYP) level.

λ (nm) [a]	E (eV) [a]	*f* [b]	Configurations	|CI Coef.| > 0.2
824	1.50	0.020	130→131	0.570
			129→132	-0.335
662	1.87	0.100	130→132	0.508
			129→133	0.393
658	1.88	0.046	128→131	0.603
			126→131	0.313
617	2.01	0.064	129→132	0.515
			130→131	0.256
			130→133	-0.215
507	2.44	0.019	126→131	0.518
			127→132	0.332
			128→131	-0.235
490	2.53	0.058	127→132	0.558
			126→131	-0.285
			127→133	-0.230
485	2.55	0.031	129→134	0.692
478	2.59	0.030	130→134	0.674
441	2.81	0.002	129→135	0.606
			124→131	0.312
436	2.84	0.022	130→135	0.682
430	2.88	0.015	124→131	0.594
			129→135	-0.338
371	3.35	0.032	125→132	0.642
			125→133	-0.204
362	3.42	0.027	130→137	0.608
			125→133	-0.260
336	3.69	0.237	123→131	0.607
			124→133	-0.257
329	3.76	0.089	124→132	0.512
			125→131	0.204

[a] Calculated absorption spectra in nm and eV. [b] Oscillator strength.

Table S4 Calculated electronic absorptions of **2** in the methanol solution at the TD-DFT (B3LYP) level.

λ (nm) [a]	E (eV) [a]	*f* [b]	Configurations	|CI Coef.| > 0.2
816	1.52	0.020	138→139	0.565
			137→140	-0.351
687	1.80	0.005	138→141	0.653
			137→140	0.219
686	1.81	0.007	137→141	0.555
			138→140	-0.408
658	1.88	0.110	138→140	0.517
			137→141	0.400
657	1.89	0.043	136→139	0.599
			134→139	0.321
613	2.02	0.066	137→140	0.525
			138→139	0.263
			138→141	-0.204
517	2.40	0.003	136→141	0.652
506	2.45	0.023	134→139	0.529
			135→140	0.313
			136→139	-0.252
488	2.54	0.055	135→140	0.578
			134→139	-0.260
			135→141	0.222
484	2.56	0.032	137→142	0.691
476	2.60	0.027	138→142	0.675
435	2.85	0.018	132→139	0.652
422	2.94	0.016	138→143	0.625
			133→139	-0.305
371	3.34	0.034	133→140	0.655
363	3.42	0.010	137→145	0.660
361	3.43	0.025	138→145	0.632
			133→141	-0.223
356	3.48	0.014	132→141	0.595
			131→139	-0.269
337	3.68	0.261	131→139	0.615
			132→141	0.246
331	3.75	0.094	132→140	0.522
			133→139	0.213

[a] Calculated absorption spectra in nm and eV. [b] Oscillator strength.

Table S5 Calculated electronic absorptions of **3** in the methanol solution at the TD-DFT (B3LYP) level.

λ (nm) [a]	E (eV) [a]	f [b]	Configurations	|CI Coef.| > 0.2	Expt. (nm) [c]
811	1.53	0.021	162→163	0.544	
			161→164	-0.329	
683	1.81	0.009	162→165	0.521	
			162→164	0.386	
679	1.83	0.004	161→165	0.546	
			162→165	0.310	
			162→164	-0.247	
657	1.89	0.041	160→163	0.598	
			158→163	0.323	
652	1.90	0.121	162→164	0.429	637
			162→165	-0.314	
			161→165	0.307	
			161→164	0.247	
610	2.03	0.066	161→164	0.479	
			162→163	0.252	
			161→165	-0.224	
			162→164	-0.202	
514	2.41	0.004	160→165	0.658	
506	2.45	0.026	158→163	0.542	515
			159→164	0.272	
			160→163	-0.266	
488	2.54	0.017	159→164	0.512	
			159→165	0.448	
485	2.56	0.031	159→165	0.542	
			159→164	-0.386	
481	2.58	0.030	161→166	0.648	
			162→166	-0.256	
473	2.62	0.024	162→166	0.632	
			161→166	0.251	
436	2.84	0.013	156→163	0.597	465
			161→167	0.274	
427	2.90	0.018	162→167	0.650	
370	3.35	0.035	157→164	0.667	382
361	3.44	0.026	162→169	0.600	359
			157→165	-0.229	
			161→169	0.208	
356	3.49	0.011	156→165	0.569	341
			155→163	0.294	
337	3.68	0.299	155→163	0.600	327
			156→165	-0.253	
331	3.75	0.098	156→164	0.507	
			157→163	0.211	

[a] Calculated absorption spectra in nm and eV. [b] Oscillator strength. [c] Experimental absorptions from ref. [27].

Table S6 Calculated electronic absorptions of **4** in the methanol solution at the TD-DFT (B3LYP) level.

λ (nm) [a]	E (eV) [a]	*f* [b]	Configurations	|CI Coef.| > 0.2
940	1.32	0.009	152→153	0.606
			151→154	-0.253
744	1.67	0.047	152→154	0.648
			151→155	0.217
734	1.69	0.011	152→155	0.508
			151→154	-0.459
720	1.72	0.031	151→155	0.656
696	1.78	0.052	150→153	0.625
			148→153	0.252
661	1.87	0.022	151→154	0.421
			152→155	0.419
577	2.15	0.038	151→156	0.609
			152→156	0.251
574	2.16	0.040	152→156	0.622
			151→156	-0.249
538	2.30	0.053	152→157	0.640
516	2.40	0.061	148→153	0.479
			149→154	-0.307
			150→155	-0.328
443	2.80	0.059	146→153	0.656
385	3.22	0.016	147→154	0.690
367	3.38	0.026	152→159	0.649
361	3.43	0.013	146→155	0.606
			151→159	0.246
348	3.56	0.117	145→153	0.624
			147→156	-0.205
340	3.64	0.021	146→154	0.453
			147→157	0.334
			147→155	0.285
328	3.78	0.233	147→156	0.657
323	3.84	0.029	146→156	0.647

[a] Calculated absorption spectra in nm and eV. [b] Oscillator strength.

Table S7 Calculated electronic absorptions of **5** in the methanol solution at the TD-DFT (B3LYP) level.

λ (nm) [a]	E (eV) [a]	*f* [b]	Configurations	|CI Coef.| > 0.2
712	1.74	0.014	148→152	0.573
			151→154	0.281
			150→155	-0.236
580	2.14	0.130	151→156	0.639
579	2.14	0.132	150→156	0.640
518	2.39	0.212	150→155	0.422
			151→154	0.412
433	2.87	0.011	148→154	0.663
428	2.89	0.019	151→157	0.477
			148→155	0.360
			149→156	0.301
425	2.92	0.024	150→158	0.674
395	3.14	0.011	147→153	0.676
394	3.15	0.011	146→153	0.643
369	3.36	0.011	150→159	0.558
			150→160	0.304
365	3.40	0.083	147→156	0.674
365	3.40	0.082	146→156	0.667

[a] Calculated absorption spectra in nm and eV. [b] Oscillator strength.

Table S8 Calculated electronic absorptions of **1**$^+$ in the methanol solution at the TD-DFT (B3LYP) level.

λ (nm) [a]	E (eV) [a]	*f* [b]	Configurations	|CI Coef.| > 0.2
828	1.50	0.3272	128β→130β	0.903
675	1.84	0.0266	126β→130β	0.933
			124β→130β	0.216
581	2.14	0.0264	130α→131α	0.750
			129β→131β	0.510
			124β→130β	-0.287
474	2.62	0.0134	128α→131α	0.886
			125α→131α	0.360
			127β→131β	0.245
467	2.66	0.0413	130α→132α	0.754
			129β→133β	-0.598
385	3.22	0.0159	125α→131α	0.882
			128α→131α	-0.361
			125β→131β	0.260
368	3.37	0.1126	124β→131β	0.630
			129β→134β	-0.454
			126α→131α	-0.398
			126β→131β	-0.209
362	3.43	0.0214	129β→134β	0.575
			118β→130β	-0.382
			124β→131β	0.300
			123β→131β	-0.287
			126α→132α	0.251

[a] Calculated absorption spectra in nm and eV. [b] Oscillator strength.

Table S9 The calculated HOMO-LUMO gaps of anatase clusters with B3LYP functional and PCM solvent-effect models.

Basis Sets / solvent	Priroda optimized geometry	HOMO-LUMO gap (eV)	
LanL2DZ / Methanol	$(TiO_2)_{16}$	4.53	This work
	$(TiO_2)_{28}$	4.55	This work
	$(TiO_2)_{38}$	4.39	This work
3-21G* / Water	$(TiO_2)_{16}$	4.68	This work
	$(TiO_2)_{28}$	4.72	This work
	$(TiO_2)_{38}$	4.57	This work
3-21G* / Methanol	$(TiO_2)_{38}$	4.54	This work
	CP optimized geometry	HOMO-LUMO gap (eV)	
3-21G* / Water	$(TiO_2)_{38}$	3.78	Ref. [86] in the text.[a]
	Geometry cut from anatase crystalline	HOMO-LUMO gap (eV)	
3-21G* / Water	$(TiO_2)_{38}$	1.46	This work

[a] F. De Angelis, A. Tilocca, A. Selloni, *J. Am. Chem. Soc.* **2004**, *126*, 15024-15025.

Table S10. Dimensions of orbital (wavefunction) and density basis sets used in AE calculations.

Atoms	Basis Sets	Orbital Basis		Density Basis	
		Contracted	Primitive	Contracted	Primitive
H	L1	$2s, 1p$	$6s, 2p$	$2s, 1p$	$6s, 3p$
	L11	$2s, 1p$	$6s, 2p$	$2s, 1p$	$6s, 3p$
	L2	$3s, 2p, 1d$	$8s, 4p, 2d$	$3s, 2p, 1d$	$8s, 6p, 3d$
C, N, O	L1	$3s, 2p, 1d$	$10s, 7p, 3d$	$6s, 4p, 3d, 1f$	$10s, 9p, 7d, 4f$
	L11	$4s, 3p, 1d$	$10s, 7p, 3d$	$7s, 5p, 4d, 1f$	$10s, 9p, 7f, 4g$
	L2	$4s, 3p, 2d, 1f$	$12s, 8p, 4d, 2f$	$7s, 6p, 5d, 3f, 1g$	$12s, 10p, 9d, 6f, 4g$
S	L1	$4s, 3p, 1d$	$15s, 11p, 3d$	$9s, 7p, 5d, 2f$	$14s, 13p, 11d, 6f$
	L11	$5s, 4p, 2d$	$15s, 11p, 6d$	$10s, 9p, 7d, 3f$	$14s, 13p, 11d, 9f$
	L2	$4s, 3p, 2d, 1f$	$12s, 8p, 4d, 2f$	$11s, 9p, 7d, 4f, 2g$	$18s, 17p, 15d, 11f, 9g$
Ru	L1	$7s, 6p, 4d, 1f$	$26s, 23p, 16d, 5f$	$15s, 14p, 13d, 9f, 6g, 2h$	$23s, 22p, 20d, 17f, 14g, 7h$
	L11	$7s, 6p, 4d, 1f$	$26s, 23p, 16d, 5f$	$15s, 14p, 13d, 9f, 6g, 2h$	$23s, 22p, 20d, 17f, 14g, 7h$
	L2	$9s, 8p, 6d, 3f, 1g$	$29s, 26p, 18d, 9f, 5g$	$17s, 16p, 15d, 12f, 8g, 5h, 2i$	$27s, 25p, 23d, 20f, 17g, 11h, 6i$

Table 11 Calculated oxidation potentials (OPs) of **1-11** dyes obtained with the SC-ECP/PBE/BSI/PCM and ZORA/PBE/TZP/COSMO approaches implemented in the Gaussian 03 and ADF suite of programs.

Redox Couple	Dye/Dye$^+$							Dye*/Dye$^+$	
Basis Sets	L1		L11		L2		Expt.^{a}	L1	
OPs	E^0(SC/PCM)	E^0(ZORA/COSMO)	E^0(SC/PCM)	E^0(ZORA/COSMO)	E^0(SC/PCM)	E^0(ZORA/COSMO)		E^0(SC/PCM)	E^0(ZORA/COSMO)
1	0.1679	0.2594	0.0805	0.1720	0.2715	0.3630		-0.9345	-0.8152
2	0.1210	0.2191	0.1504	0.2484	0.2197	0.3177		-0.9413	-0.8173
3	0.3199	0.2328	0.3622	0.2751	0.3704	0.2832	0.38	-1.0122	-0.8288
4	0.2153	0.2929	0.2422	0.3198	0.2778	0.3555		-0.7947	-0.7145
5	0.3430	0.3461	0.3426	0.3457	0.3784	0.3814		-0.1294	-0.1372
6	0.3097	0.3175	0.2745	0.2823	0.2997	0.3075	0.50		
7	0.2199	0.2169	0.2640	0.2610	0.2968	0.2937	0.22		
8	0.7295	0.7929	0.7501	0.8134	0.8277	0.8910	0.81		
9	0.2480	0.2372	0.2435	0.2327	0.2989	0.2880	0.49		
10	0.1827	0.1875	0.1933	0.1981	0.2369	0.2417	0.31		
11	-0.1238	-0.0527					0.31		

^{a} Experimental data from refs. [24-27]. Reported vs SCE, corrected with respect to the Fc/Fc$^+$ electrode by subtraction of 0.35 V, see refs. [89-90].