Electronic Supplementary Information

4-Dimethylaminobenzoate-functionalized Ti_6-oxo cluster with a narrow band gap and enhanced photoelectrochemical activity: a combined experimental and computational study

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Table S1 Crystal data and structure refinements summary for **C1**, **C2** and **C3**.

	C1	**C2**	**C3**
Empirical formula	$C_{86}H_{118}O_{24}N_6Ti_6$	$C_{84}H_{132}O_{24}Ti_6$	$C_{52}H_{110}O_{25}Ti_6$
Formula weight	1907.26	1813.29	1422.79
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1$/n	*C*2/*c*
a (Å)	23.6329(11)	15.6777(6)	23.3256(12)
b (Å)	16.0739(7)	16.4880(6)	19.2083(10)
c (Å)	27.4246(11)	18.4096(7)	18.3696(10)
β (°)	112.380(5)	103.720(4)	110.276(6)
V (Å^3)	9633.2(8)	4623.0(3)	7720.4(8)
Z	4	2	4
ρ_{calcd} (g cm^{-3})	1.315	1.303	1.224
μ (mm^{-1})	0.545	0.562	0.655
F(000)	4000	1920	3016
T (K)	295(2)	295(2)	295(2)
Measured refls.	23090	20893	28089
Independent refls.	9444	9058	7572
R_{int}	0.0378	0.0378	0.0409
GOF	1.066	1.037	1.044
R_1 [$I > 2\sigma(I)$][a]	0.0556	0.0765	0.0610
wR_2 [$I > 2\sigma(I)$][b]	0.1350	0.2069	0.1466

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S2 TDDFT calculated main orbital contributions to intense low-energy transitions of **C1** (E = energy, f = oscillator strength).

Main orbital contributions	E (eV)	λ (nm)	f
HOMO → LUMO+1 (52%) HOMO–2 → LUMO (22%) HOMO–1 → LUMO+2 (16%)	3.1186	397.57	0.2161
HOMO → LUMO+3 (42%) HOMO–2 → LUMO+2 (35%) HOMO–1 → LUMO (11%)	3.1251	396.74	0.2239
HOMO–5 → LUMO (40%) HOMO–4 → LUMO+1 (27%) HOMO–3 → LUMO+3 (14%)	3.1574	392.68	0.3985
HOMO–5 → LUMO+2 (33%) HOMO–4 → LUMO+3 (27%) HOMO–3 → LUMO+1 (16%)	3.1612	392.21	0.3997
HOMO–3 → LUMO+4 (79%) HOMO–5 → LUMO (12%)	3.2852	377.40	0.1684
HOMO–4 → LUMO+4 (79%) HOMO–5 → LUMO+2 (14%)	3.2867	377.23	0.1496
HOMO–3 → LUMO+5 (100%)	3.4272	361.76	0.0537
HOMO–2 → LUMO+8 (54%) HOMO–1 → LUMO+8 (22%) HOMO–2 → LUMO+8 (12%)	3.6059	343.83	0.1739

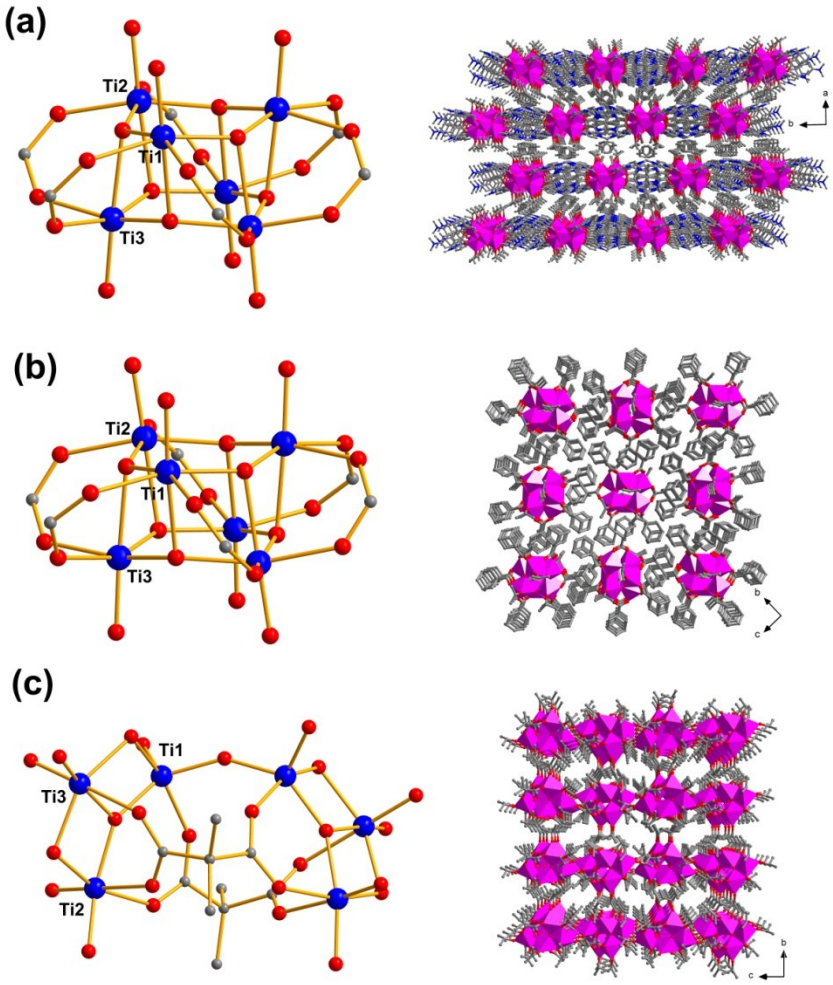

Fig. S1 Coordination mode of the TiO core and packing mode for (a) **C1**, (b) **C2** and (c) **C3**. Color code: blue Ti; red O; gray C. Polyhedral color code: pink TiO_6.

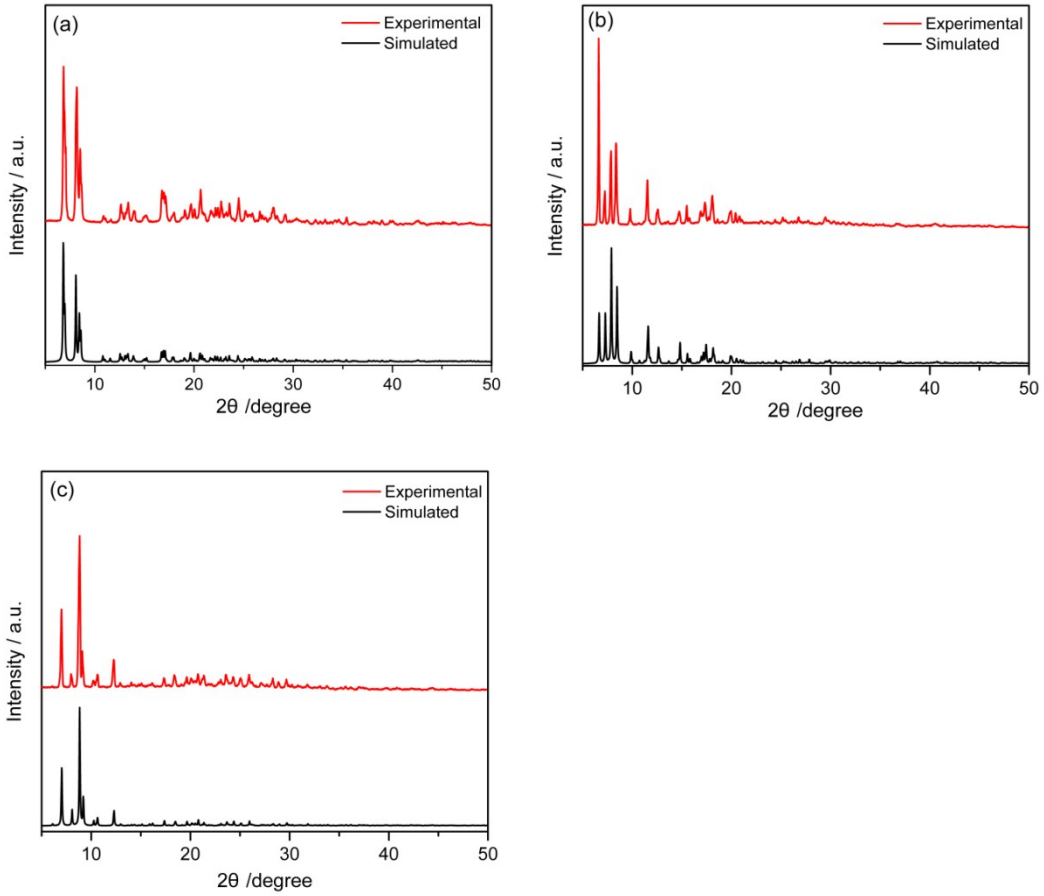

Fig. S2 XRD patterns of (a) **C1**, (b) **C2** and (c) **C3**.

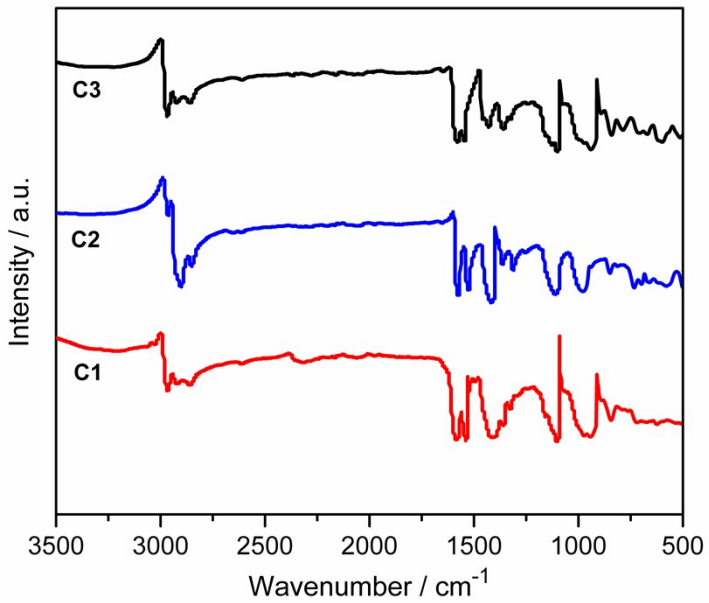

Fig. S3 FT-IR spectra of **C1**, **C2** and **C3**.

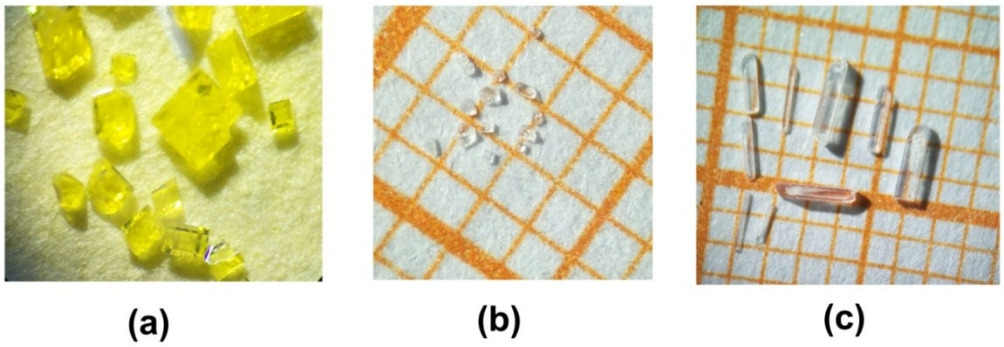

Fig. S4 Photo of the crystals (a) **C1**, (b) **C2** and (c) **C3**.

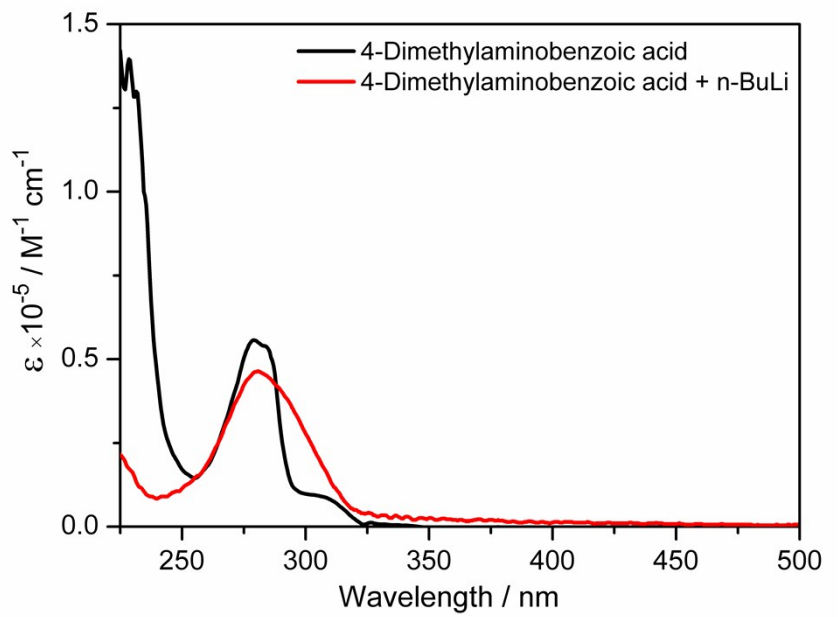

Fig. S5 UV-vis spectra of 4-dimethylaminobenzoic acid and the deprotonated acid (by adding n-BuLi to the acid in dry THF) in THF solutions.

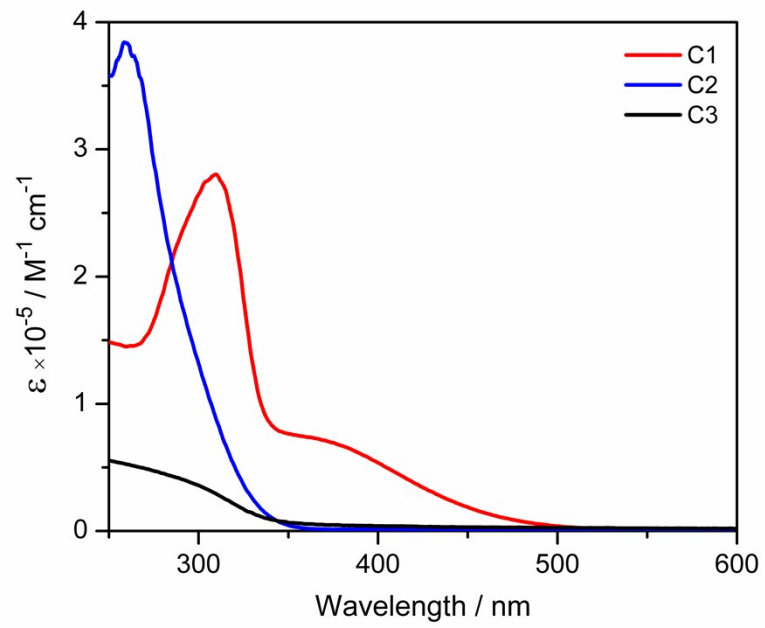

Fig. S6 UV-vis spectra of the clusters in CH_2Cl_2.

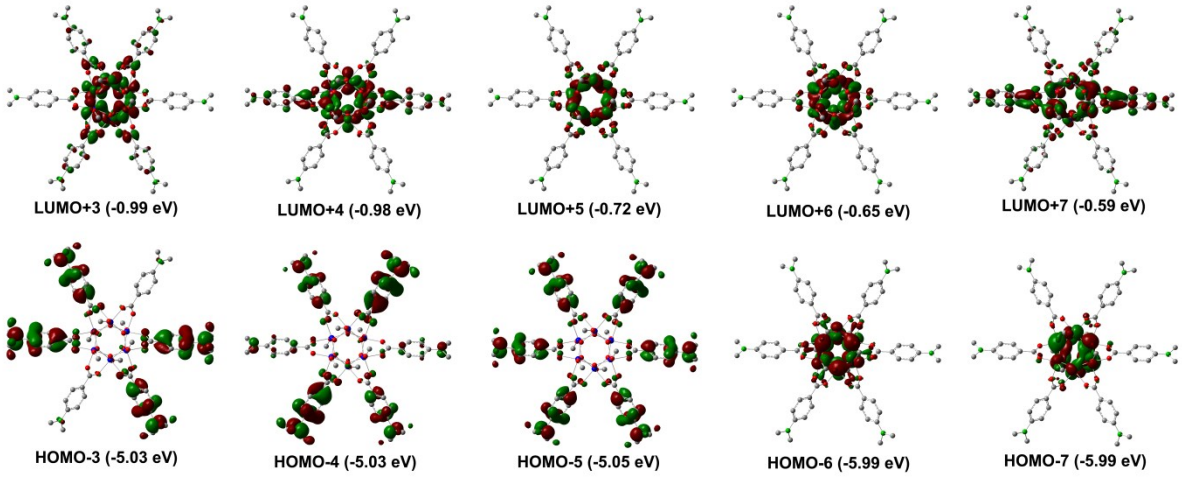

Fig. S7 Selected frontier orbital plots calculated for **C1**.

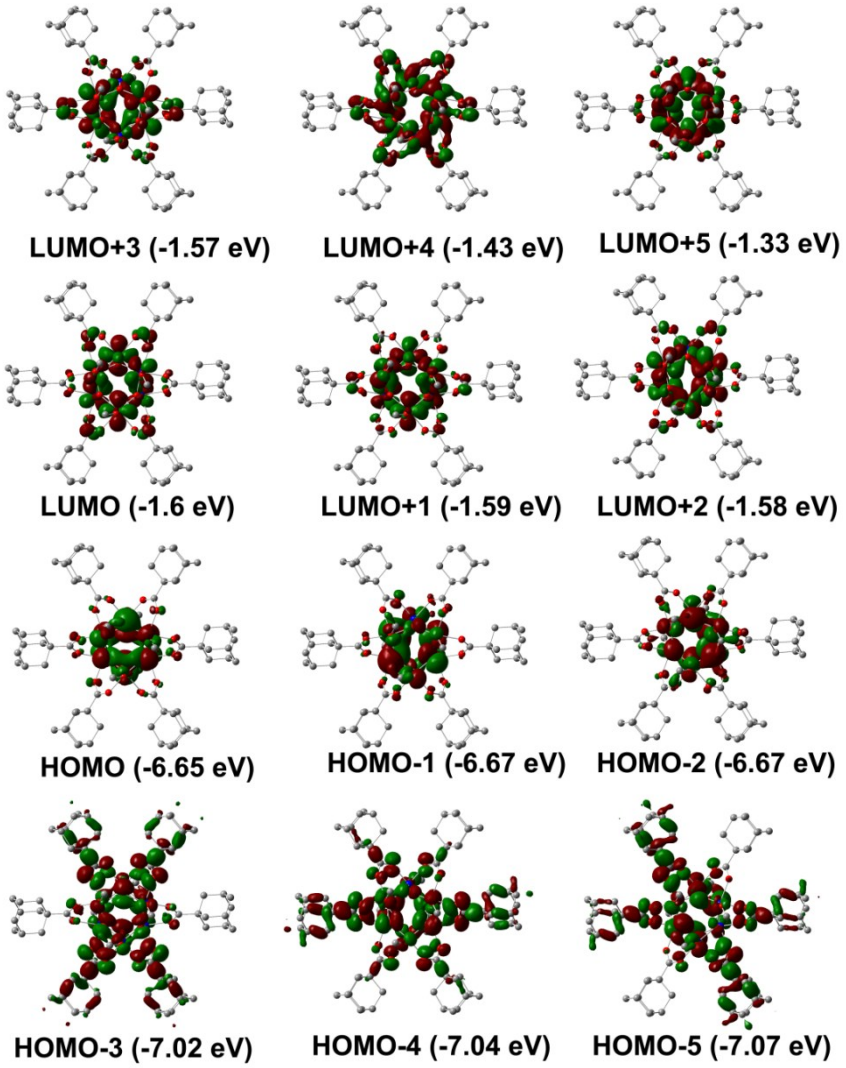

Fig. S8 Selected frontier orbital plots calculated for **C2.**

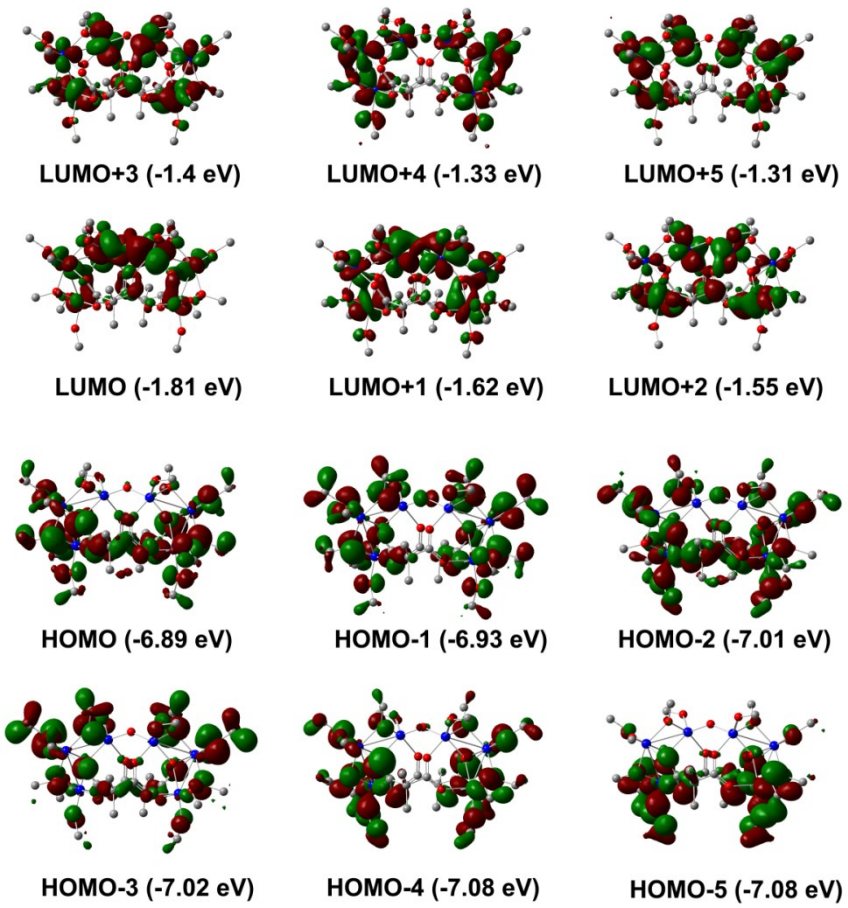

Fig. S9 Selected frontier orbital plots calculated for **C3.**

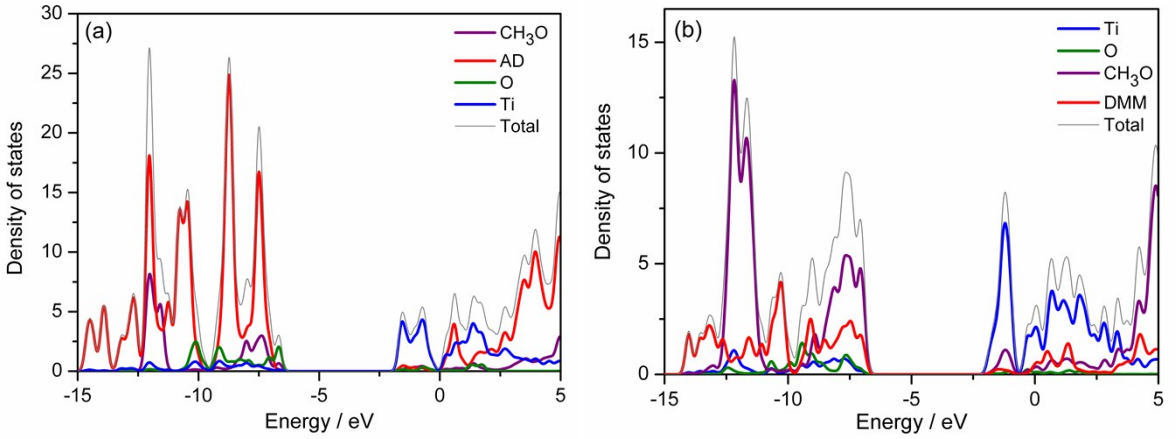

Fig. S10 DOS plots for (a) **C2** and (b) **C3.**