Electronic Supplementary Information

Titanium-oxo clusters functionalized with catecholate-type ligands: modulating the optical properties through charge-transfer transitions

Hai-Ting Lv,* Hua-Min Li, Guo-Dong Zou, Ying Cui, Yang Huang, Yang Fan*

College of Chemistry and Chemical Engineering, Henan Province Key Laboratory of Utilization of Non-metallic Mineral in the South of Henan, Xinyang Normal University, Xinyang 464000, China

Contents

Table S1. Crystal data and structure refinements summary for **C1**, **C2**, **C3** and **C4**.

	C1	**C2**	**C3**	**C4**
Empirical formula	$C_{72}H_{112}O_{32}P_4Ti_8$	$C_{80}H_{116}O_{32}P_4Ti_8$	$C_{60}H_{100}O_{24}N_2P_2Ti_6$	$C_{58}H_{88}O_{24}N_2P_2Ti_6$
Formula weight	1996.68	2096.80	1582.76	1546.64
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	12.7384(11)	15.4222(3)	14.5622(9)	14.0170(6)
b (Å)	13.8895(8)	26.1161(6)	19.8886(8)	15.6940(8)
c (Å)	15.5231(14)	12.7525(3)	14.7162(9)	17.5353(8)
α (°)	115.032(7)	90	90	90
β (°)	103.585(8)	102.683(2)	110.627(7)	97.147(5)
γ (°)	95.731(6)	90	90	90
V (Å^3)	2356.2(4)	5011.0(2)	3988.9(4)	3827.5(3)
Z	1	2	2	2
ρ_{calcd} (g cm^{-3})	1.407	1.390	1.318	1.342
μ (mm^{-1})	0.783	0.740	0.679	0.707
F(000)	1036	2176	1656	1608
T (K)	295(2)	295(2)	295(2)	295(2)
Measured refls.	18054	43749	16063	16664
Independent refls.	9248	9806	7827	7507
R_{int}	0.0524	0.0545	0.0520	0.0334
GOF	1.022	1.023	1.022	1.116
R_1 [$I > 2\sigma(I)$][a]	0.0735	0.0590	0.0619	0.0599
wR_2 [$I > 2\sigma(I)$][b]	0.1877	0.1461	0.1247	0.1622

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

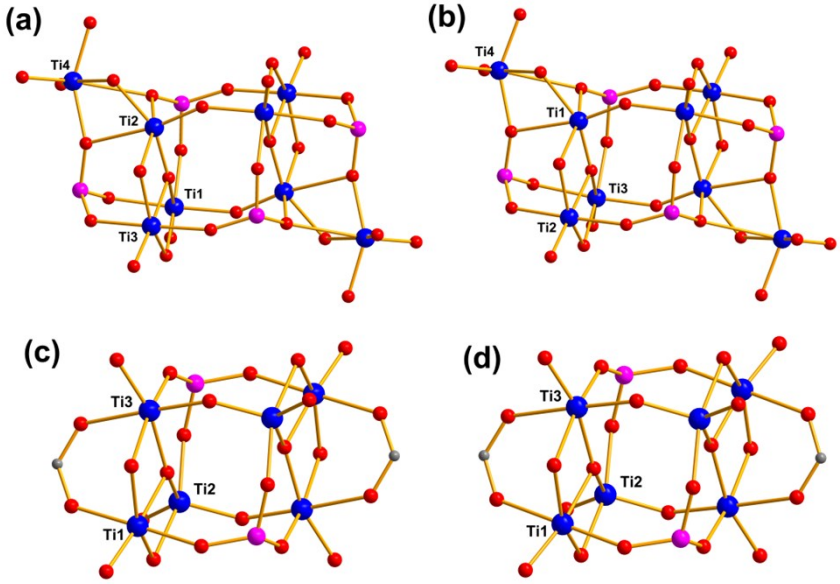

Fig. S1 Coordination mode of the TiO core for (a) **C1**, (b) **C2**, (c) **C3** and (d) **C4**. Color code: blue Ti; red O; magenta P; gray C.

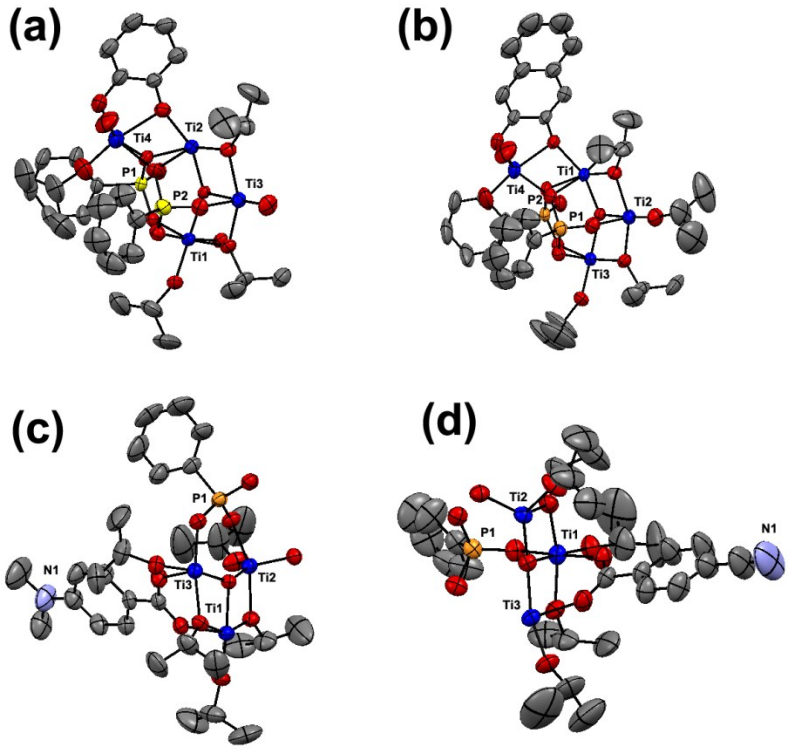

Fig. S2 Asymmetric unit of the clusters. Thermal ellipsoids given at 50% probability. H atoms are omitted for clarity.

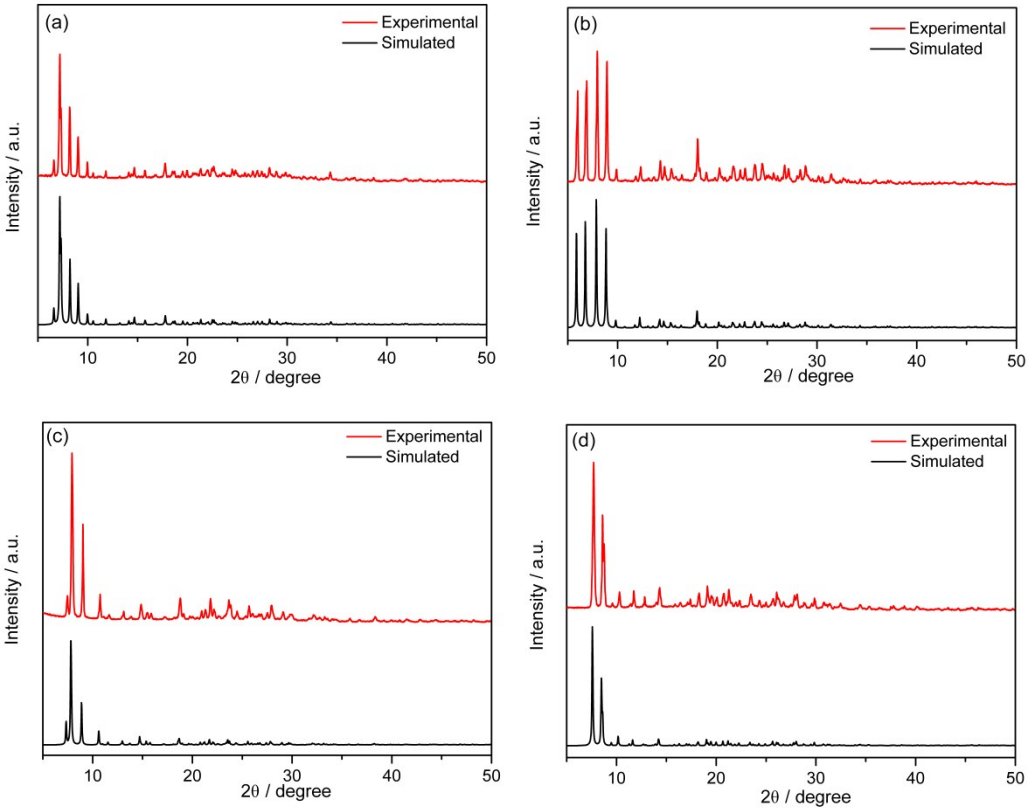

Fig. S3 XRD patterns of (a) **C1**, (b) **C2**, (c) **C3** and (d) **C4**.

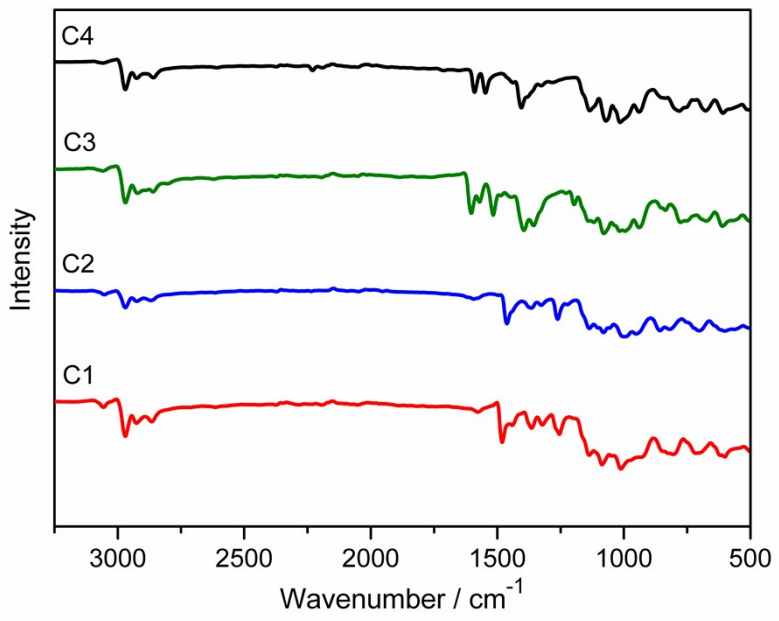

Fig. S4 FT-IR spectra of **C1**–**C4**.

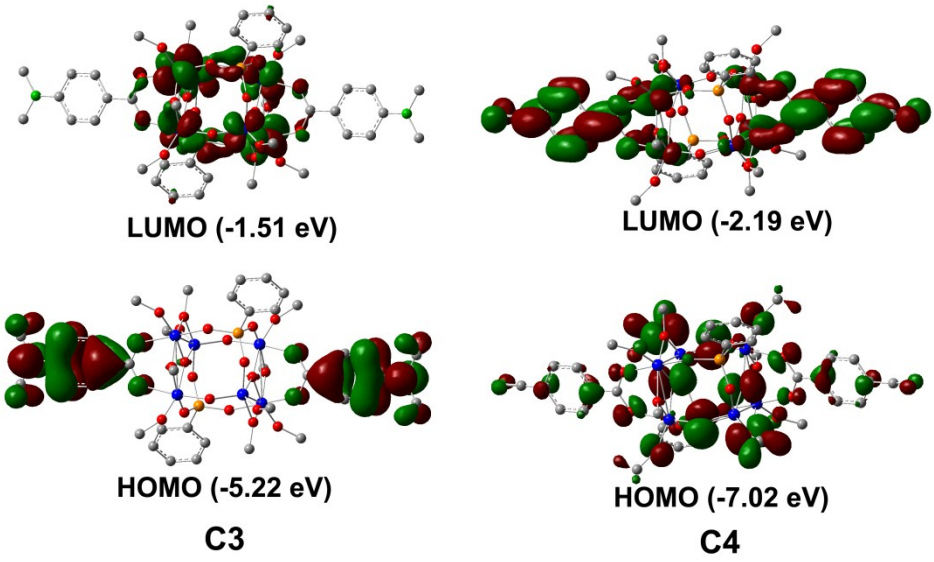

Fig. S5 HOMO and LUMO orbitals calculated for **C3** and **C4**.

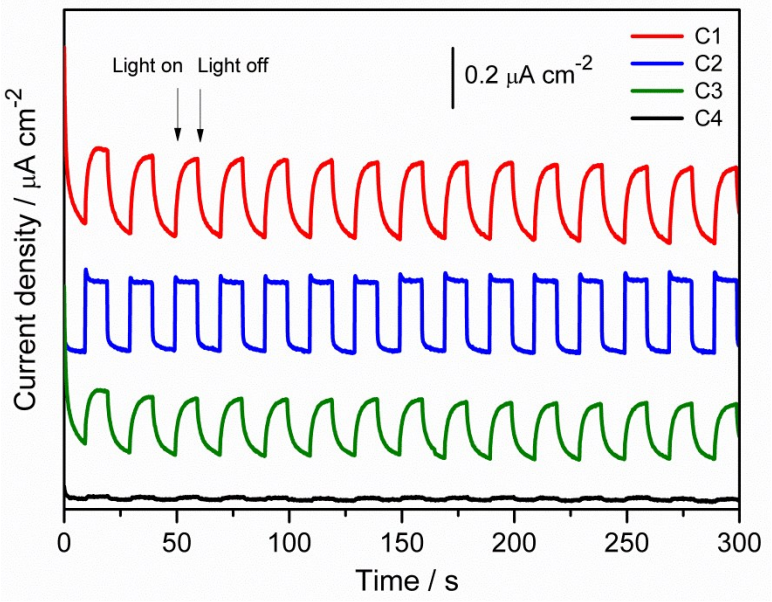

Fig. S6 Photocurrent responses of the photoelectrodes under visible light irradiation in dry CH_3CN containing 0.05 M $NaPF_6$ as the supporting electrolyte.

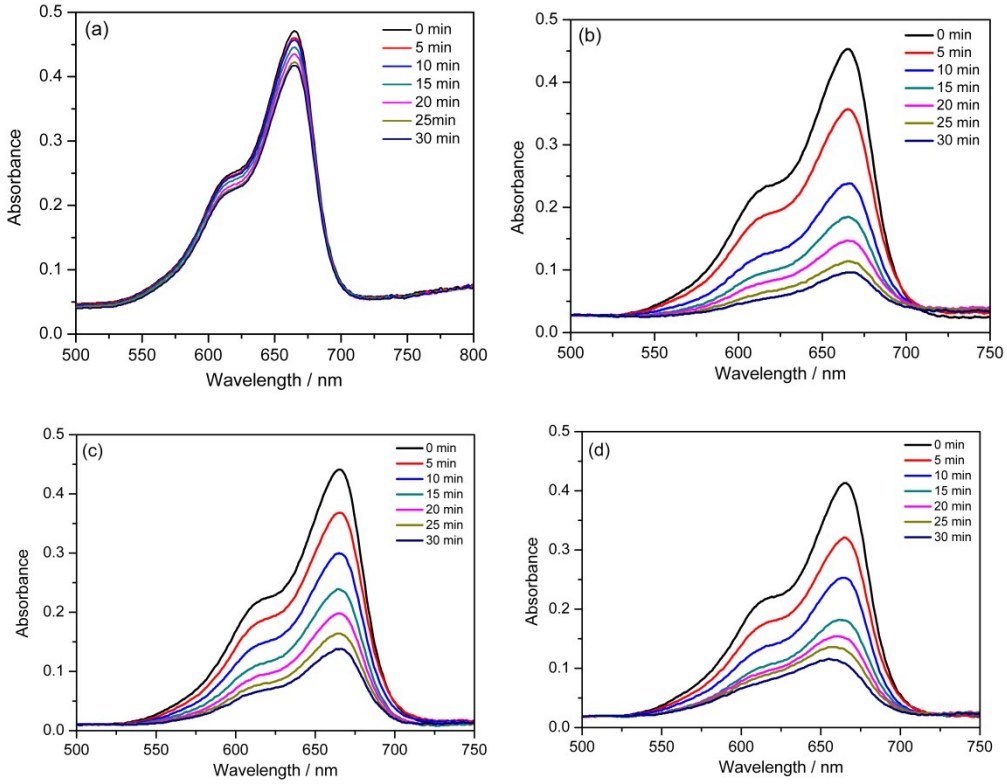

Fig. S7 Time-dependent absorption spectra for sunlight-driven photocatalytic MB degradation with (a) blank, (b) **C1**, (c) **C3** and (d) **C4**.

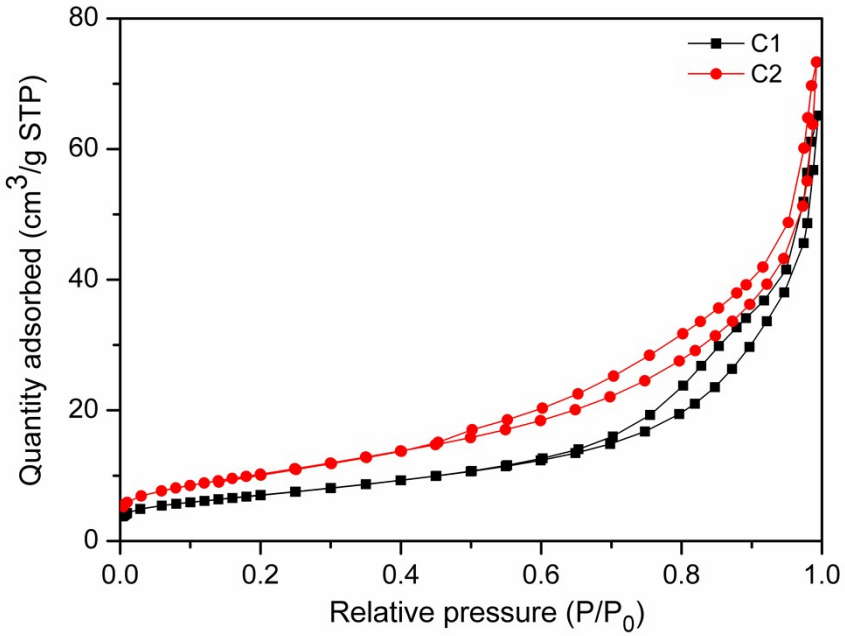

Fig. S8 N_2 adsorption–desorption isotherms of **C1** and **C2**.