Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Syntheses, Structures and Ligand Binding Modes of Titanium-Oxide Complexes of 2-Picolinate

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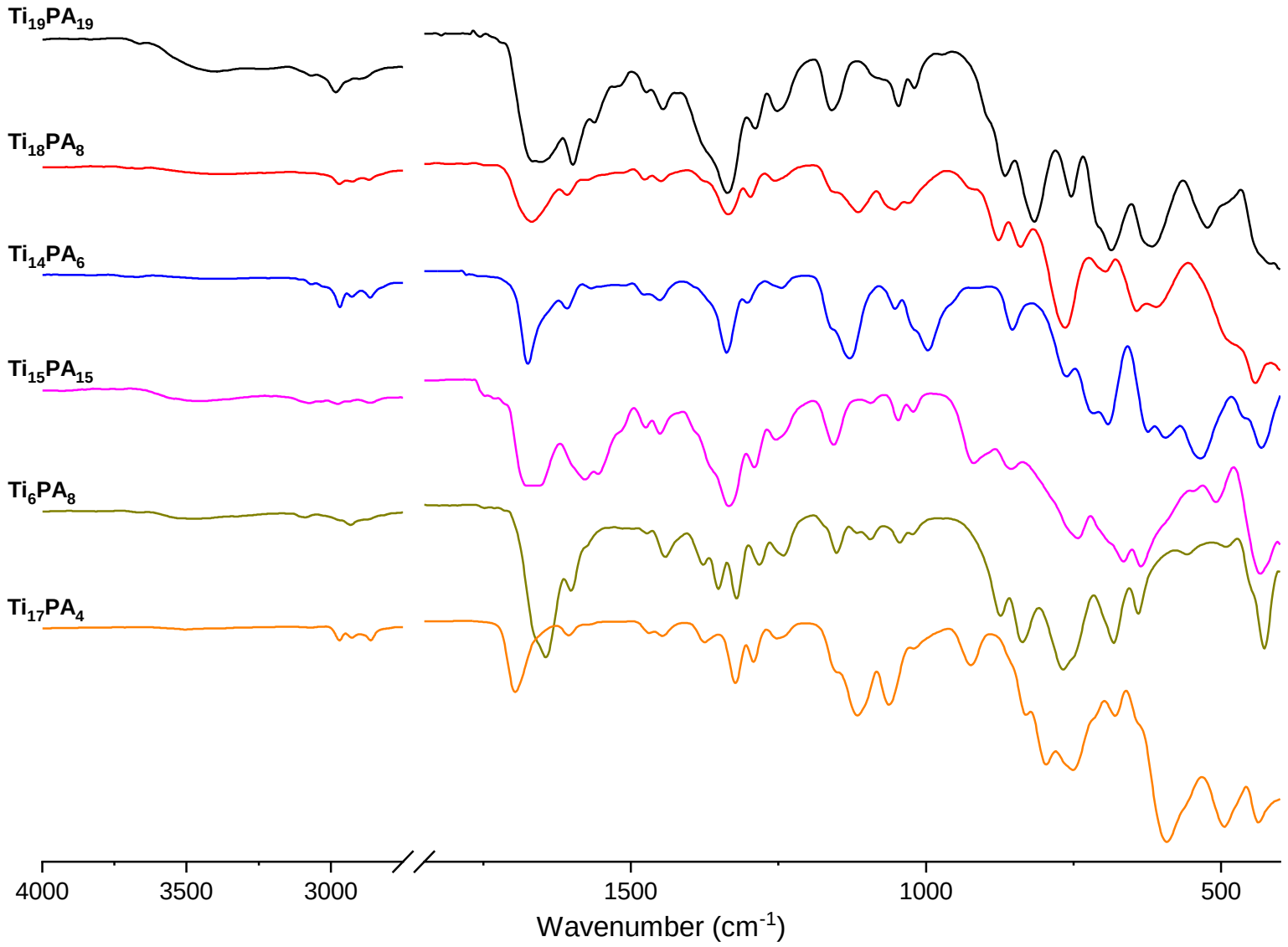
S1. The table of crystallographic data

Compound	**$Ti_{19}(PA)_{19}$**	**$Ti_{18}(PA)_{8}$**	**$Ti_{14}(PA)_{6}$**
Formula unit	$Ti_{19}O_{70}N_{26.5}C_{137}H_{125.5}$	$Ti_{18}O_{61}N_{8}C_{69}H_{92}$	$Ti_{14}O_{46}N_{10}C_{90}H_{154}$
CCDC number	2126650	2126649	2126646
Moieties	$[H_4Ti_{19}O_{30}(O_2NC_6H_4)_{19}(OC_3H_7)_2]\cdot(NC_4H_{12})\cdot 6.5(NC_2H_3)$	$[Ti_{18}O_{22}(O_2NC_6H_4)_8(OCH_3)_{18}]\cdot 2(O_2CH)\cdot(OCH_4)$	$[H_2Ti_{14}O_{20}(O_2NC_6H_4)_6(OC_3H_7)_{12}]\cdot 2(NC_4H_{11})\cdot 2(NC_2H_3)\cdot 2(OC_3H_8)$
Formula weight (g/mol)	4172.57	2871.09	2782.82
Crystal system	orthorhombic	cubic	monoclinic
Space group (Nr.)	*$Pmn2_1$*	*I432*	*$P2_1/n$*
a (Å)	22.0234(10)	32.0910(3)	19.4181(2)
b (Å)	15.8771(5)	32.0910(3)	16.6427(2)
c (Å)	28.8999(6)	32.0910(4)	20.1511(4)
α (°)	90	90	90
β (°)	90	90	107.688(2)
γ(°)	90	90	90
Volume ($Å^3$)	10105.4(6)	33048.3(9)	6204.36(17)
Z	2	6	2
$Density_{calc}$ (g/cm^3)	1.282	0.829	1.489
Abs. Coeff. μ (mm^{-1})	6.691	5.639	7.946
Temperature (K)	173	173	173
Total reflections	35091	18693	44175
Min-max 2θ (°)	5.566 to 154.982	5.508 to 152.928	5.536 to 153.418
Unique reflections	13913	5244	12329
R_1 [I>=2σ]	0.0704	0.0904	0.0706
wR_2 (all data)	0.2147	0.3016	0.1953
R_{int}	0.0575	0.0857	0.0838
Goodness of fit on F^2	1.038	1.041	1.049
Parameters	1208	255	742
Restraints	518	179	22
Largest diff. peak/hole (e $Å^{-3}$)	0.66/-0.43	0.60/-0.49	0.92/-0.72

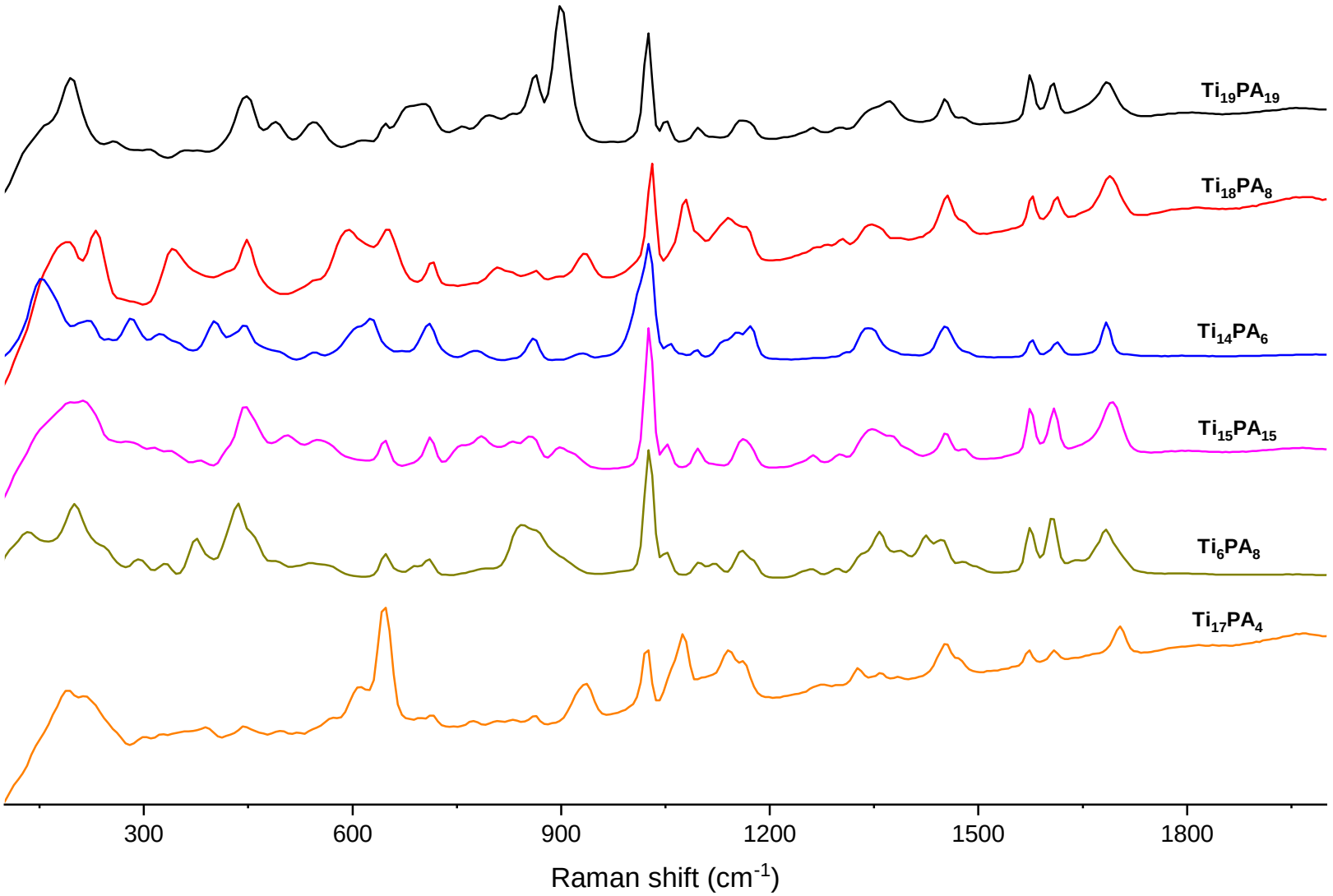
Compound	**$Ti_{15}(PA)_{15}$**	**$Ti_6(PA)_8$**	**$Ti_{17}(PA)_4$**
Formula unit	$Ti_{15}O_{61}N_{27}C_{121}H_{111}$	$Ti_6O_{28}N_{12}C_{60}H_{60}$	$Ti_{17}O_{48}N_4C_{56}H_{96}$
CCDC number	2126647	2126645	2126648
Moieties	$[H_2Ti_{15}O_{21}(O_2NC_6H_4)_{15}(O_2CH)_5](NC_4H_{11})\cdot 11(NC_2H_3)$	$Ti_6O_8(O_2NC_6H_4)_8(ONC_3H_7)_4$	$Ti_{17}O_{24}(O_2NC_6H_4)_4(OC_2H_5)_{16}$
Formula weight (g/mol)	3637.33	1684.60	2407.1
Crystal system	triclinic	tetragonal	monoclinic
Space group (Nr.)	*P-1*	*I-4*	$P2_1/m$
a (Å)	15.9539(6)	15.2721(2)	14.1453(18)
b (Å)	17.4707(9)	15.2721(2)	25.9558(14)
c (Å)	29.0128(9)	15.8807(3)	14.178(2)
α (°)	89.709(3)	90	90
β (°)	80.240(3)	90	112.466(15)
γ(°)	81.263(4)	90	90
Volume ($Å^3$)	7875.3(6)	3703.97(12)	4810.3(11)
Z	2	2	2
$Density_{calc}$ (g/cm^3)	1.343	1.510	1.662
Abs. Coeff. μ (mm^{-1})	6.825	6.016	12.086
Temperature (K)	173	173	173
Total reflections	73602	5116	15616
Min-max 2θ (°)	5.924 to 153.186	8.032 to 152.328	6.762 to 156.22
Unique reflections	29824	3062	7758
R_1 [I>=2σ]	0.0831	0.0301	0.1015
wR_2 (all data)	0.2729	0.0757	0.3121
R_{int}	0.1059	0.0322	0.0544
Goodness of fit on F^2	0.944	1.013	1.021
Parameters	1725	243	641
Restraints	2097	0	180
Largest diff. peak/hole (e $Å^{-3}$)	0.57/-0.55	0.33/-0.30	1.48/-1.11

S2. Additional characterization data

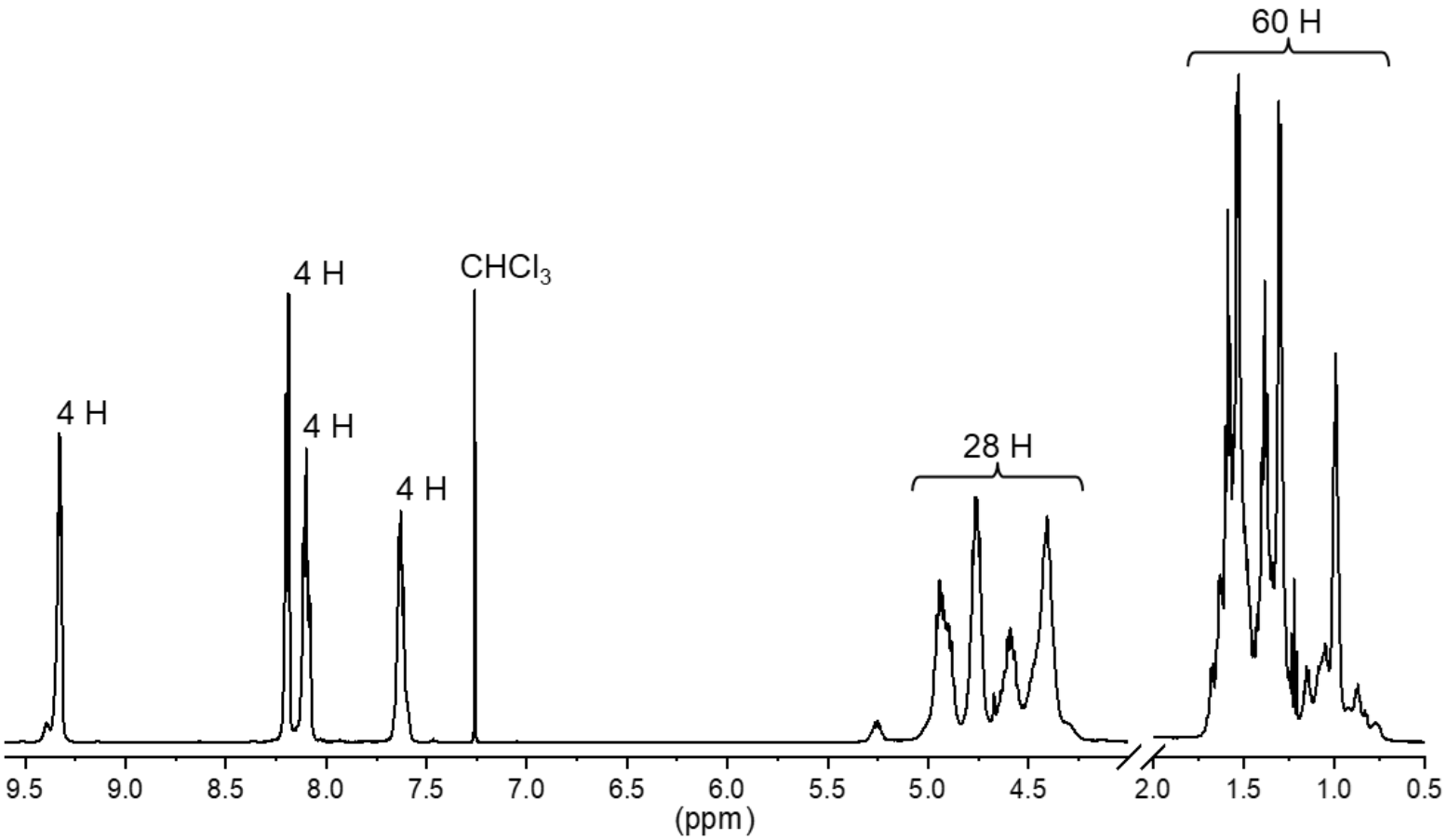
FTIR spectra. The FTIR spectra of the clusters are shown below.



Raman spectra. The representative Raman spectra of the clusters are shown below.

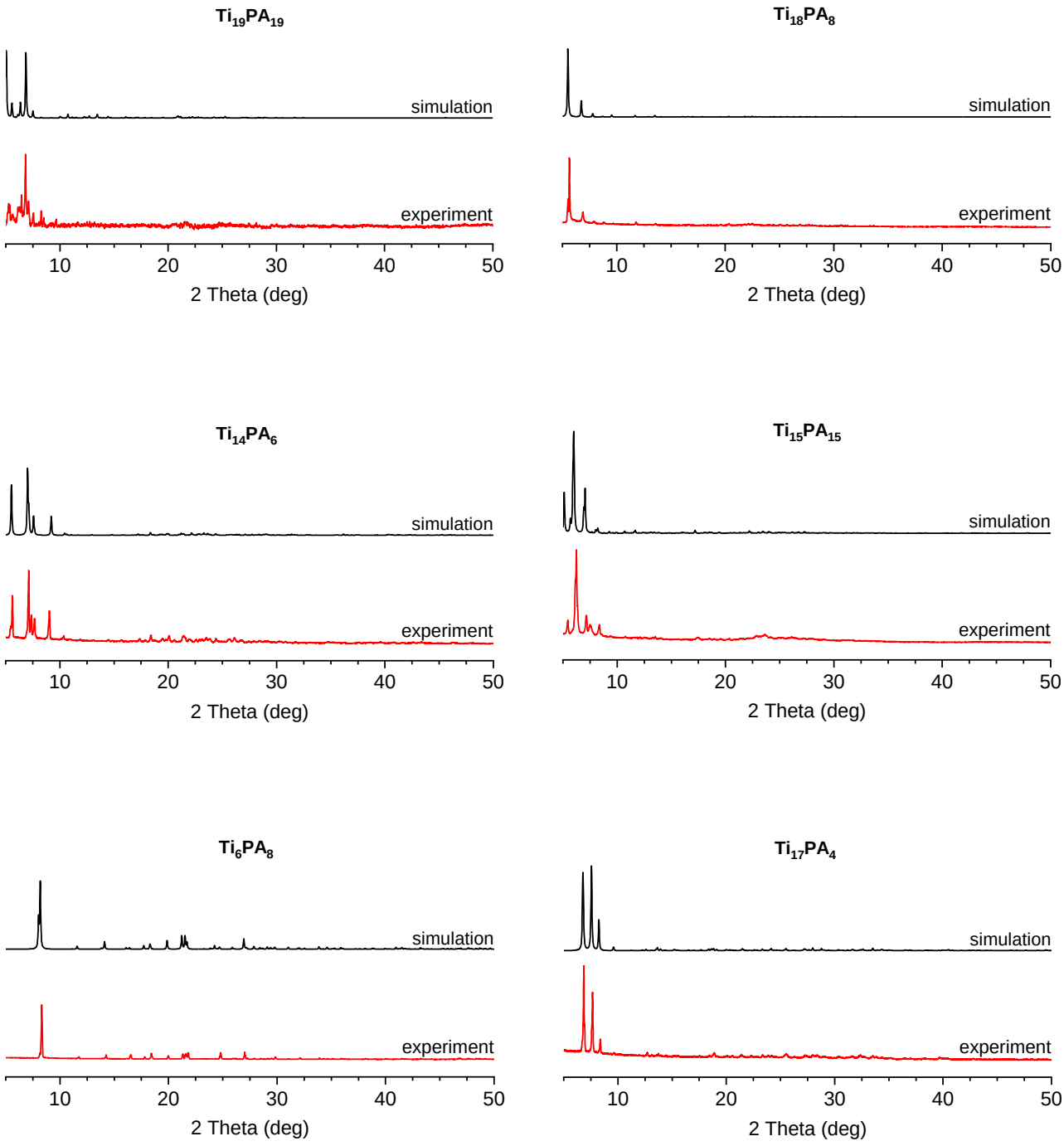


^{1}H NMR spectrum. ^{1}H NMR spectrum of **$Ti_{17}PA_4$**, measured on a Bruker AV-500 spectrometer using $CDCl_3$ as the solvent.

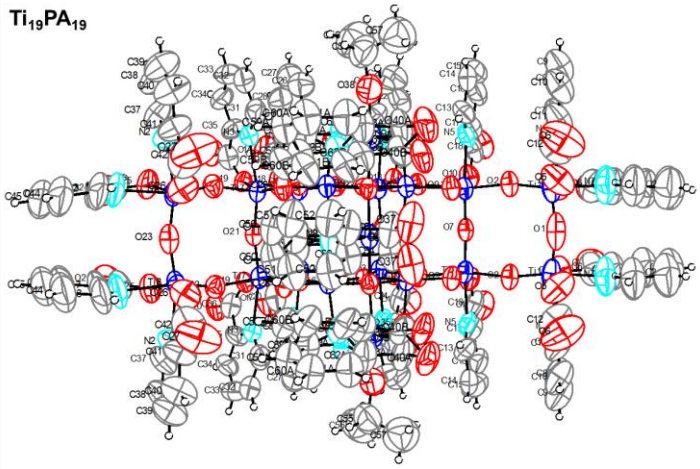


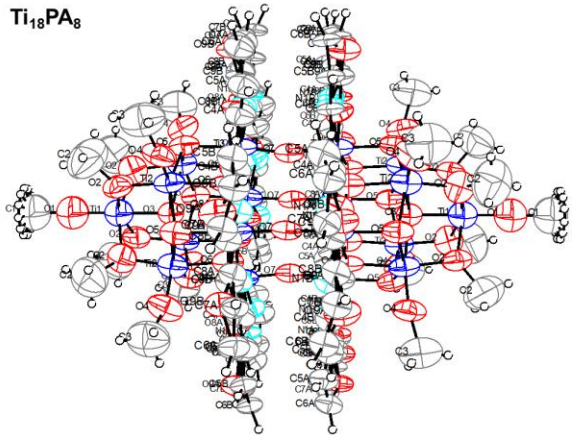
The peaks ranging 4-5.2 are assigned as CH and CH_2. Those ranging 1-1.8 are assigned as CH_3. According to the ratio of the two groups, i.e., 28 : 60, we postulate that $Ti_{17}PA_4$ contains approximately 12 OEt and 4 O^{i}Pr groups. However, there may be some uncertainties since some disordered alcohol solvent molecules may be present in the samples which could not be determined by SC−XRD.

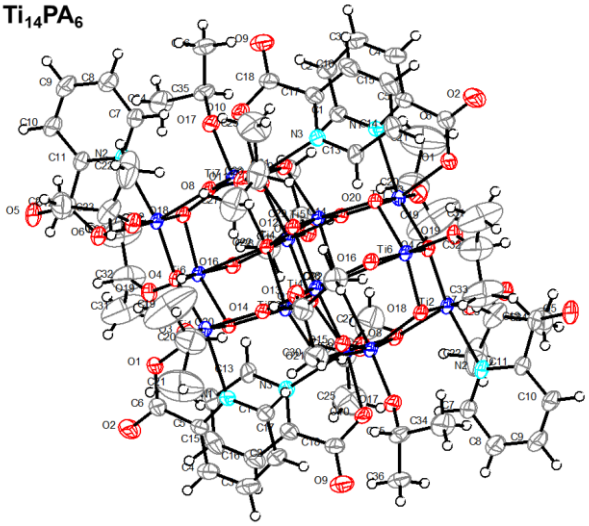
Powder X-ray diffraction data. The spectra were recorded using a Rigaku SmartLab 9KW X-ray diffraction instrument.

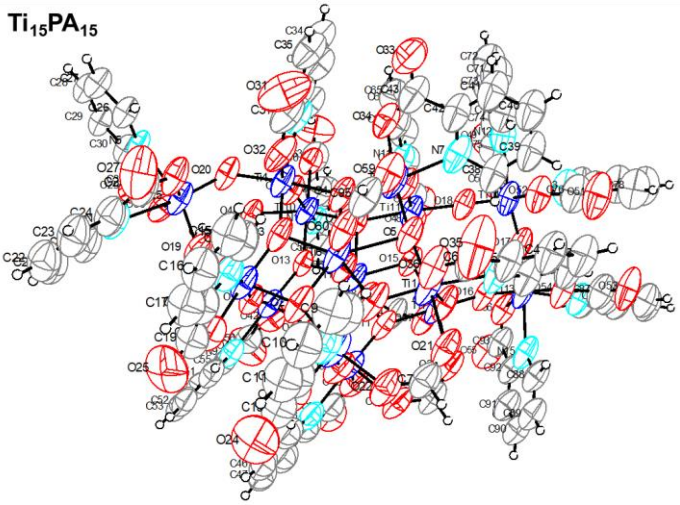


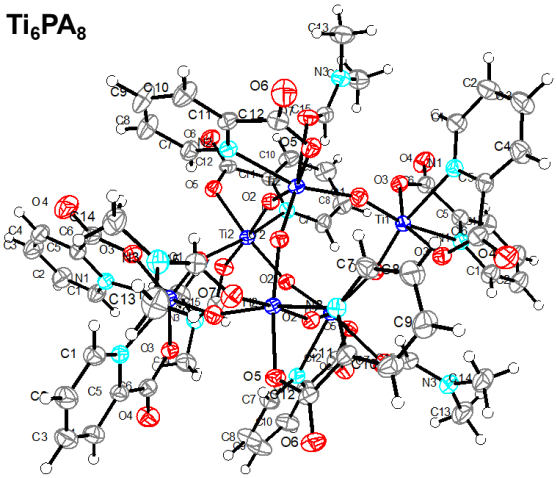
Ellipsoidal model. The ellipsoidal models the molecules showing 50% of probability

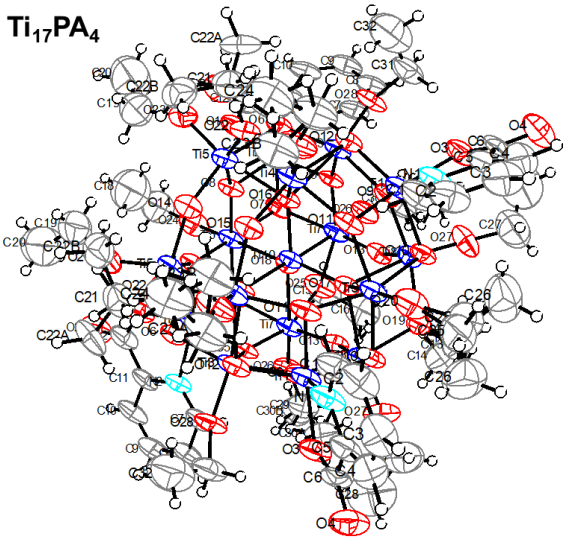












S3. Supplementary figures and discussion

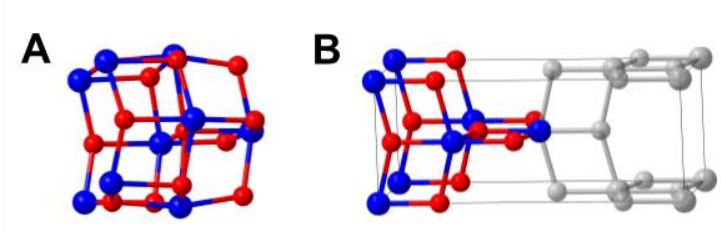


Figure S1. The structure of Ti_9O_{13} unit and Ti_7O_9 half-cell of anatase TiO_2.

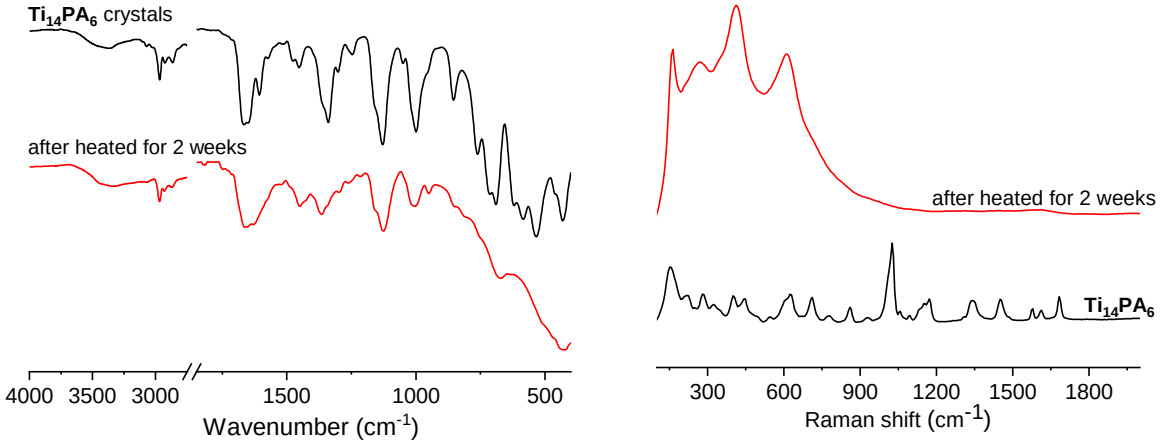


Figure S2. FTIR spectra and Raman spectra of the rutile TiO_2 obtained by increasing the solvothermal reaction time of **$Ti_{14}PA_6$** to ca. 2 weeks.

Figure S3. The photos of the crystals.

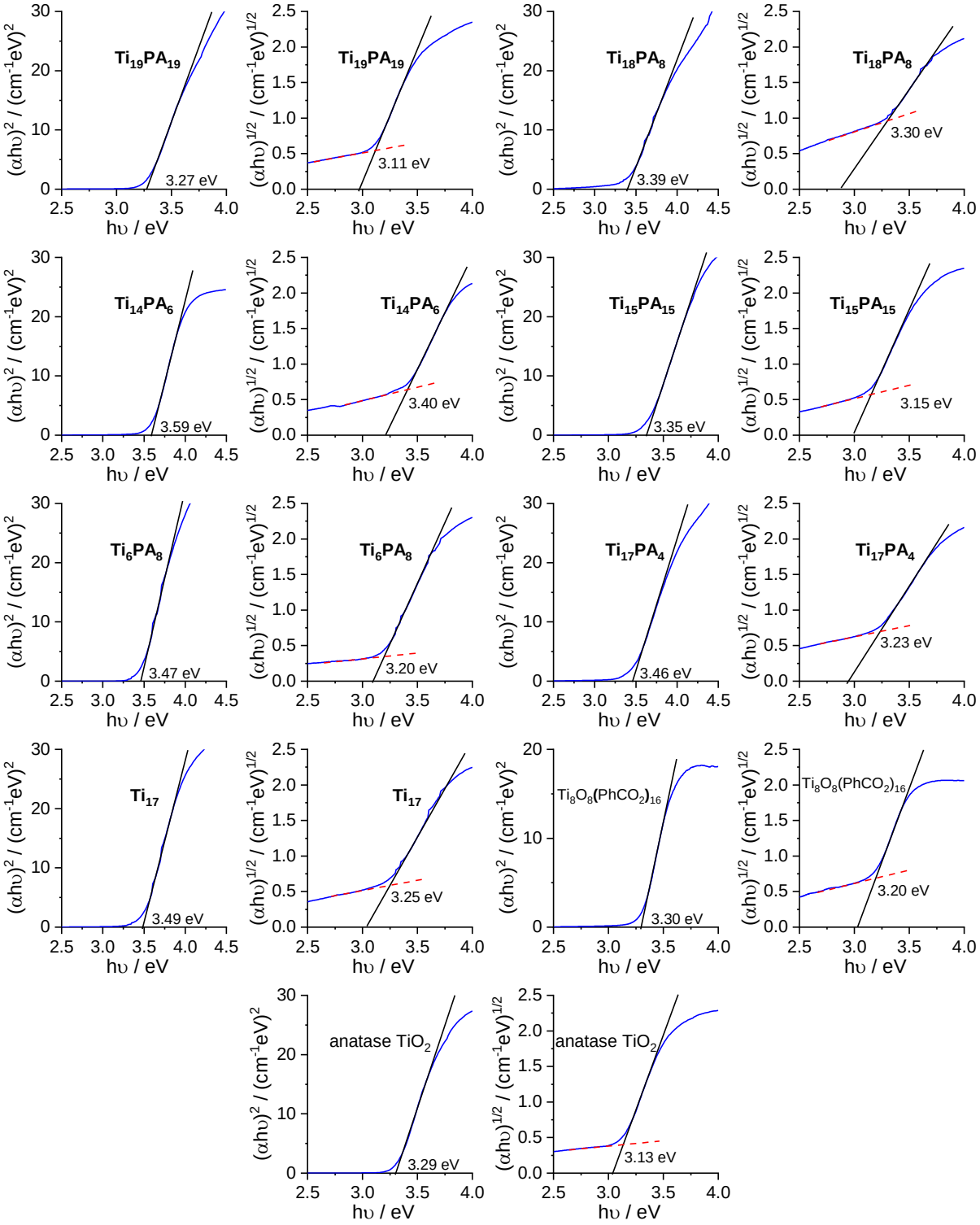


Figure S4. Calculations of direct band gap and indirect band gap values based on UV-vis diffuse reflectance spectra.

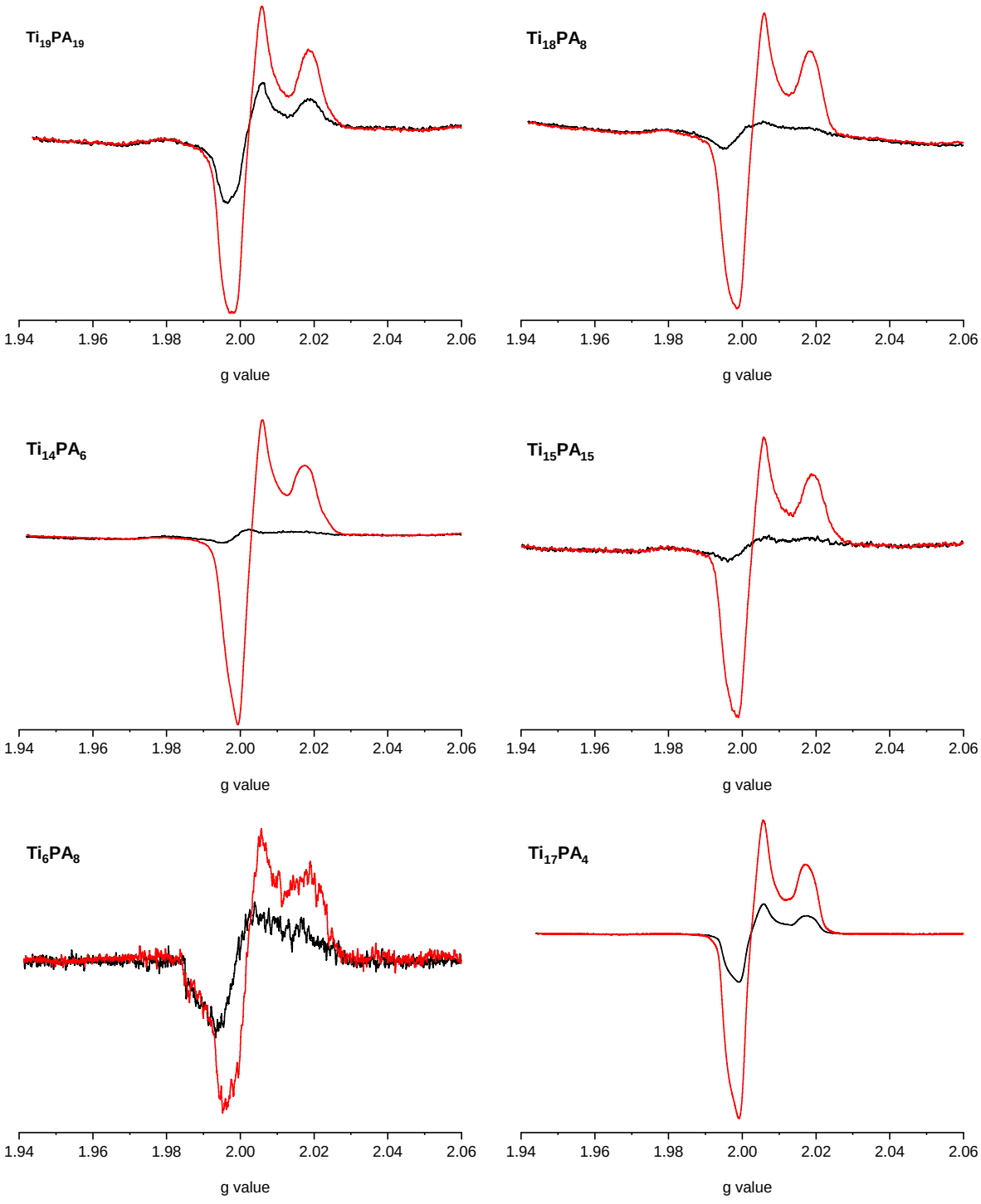


Figure S5. EPR spectra of the TOCs in dark (black) and after irradiation (red curve) under 1 atm N_2.

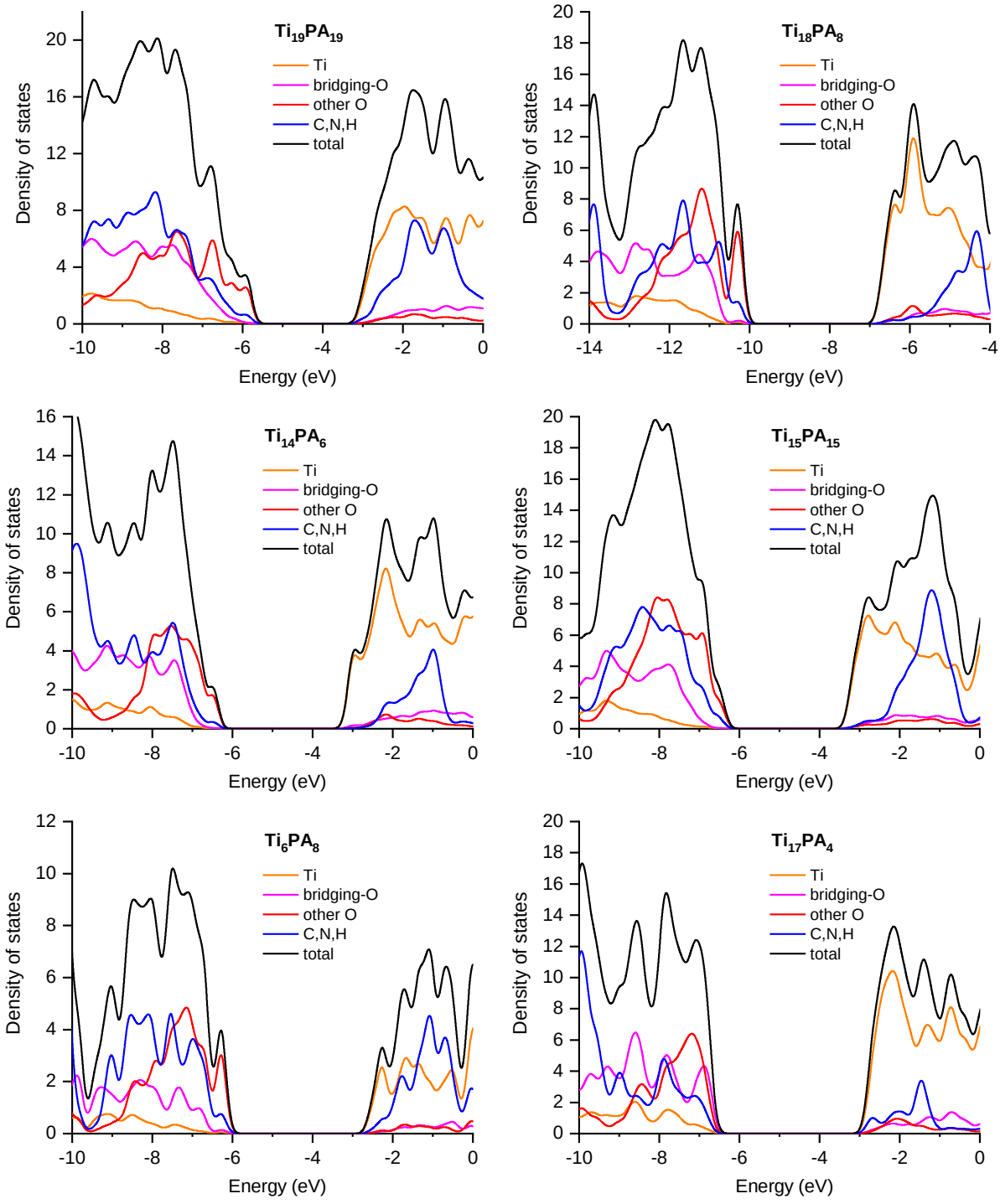


Figure S6. Density of states of the TOCs illustrating the contributions of various moieties to the frontier orbitals. Figure 8B is reproduced here for comparison.