Electronic Supplementary Material (ESI) for Dalton Transactions
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Supporting Information for:

Heterometallic Ag_2Ti_{10} and Ag_4Ti_8-oxo clusters with different silver doping models: synthesis, structure, and theoretical studies

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Table S1. Crystallographic data and structure refinement details for **PTC-221** and **PTC-222.**

Compounds	**PTC-221**	**PTC-222**
Empirical formula	$C_{132}H_{86}Ag_2O_{58}Ti_{10}$	$C_{74}H_{132}Ag_4N_2O_{39}Ti_8$
Formula weight	3294.74	2488.26
Temperature/K	100.0(2)	100.00(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
a/Å	15.4863(2)	15.5445(3)
b/Å	45.3078(6)	27.2039(6)
c/Å	19.2032(3)	25.2746(6)
α/°	90	90
β/°	103.069(2)	100.439(2)
γ/°	90	90
Volume/Å^3	13124.9(3)	10511.0(4)
Z	4	4
ρ_{calc}g/cm^3	1.667	1.537
μ/mm^{-1}	8.075	11.362
F(000)	6624.0	4936.0
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
Index ranges	-18 ≤ h ≤ 7, -55 ≤ k ≤ 44, -23 ≤ l ≤ 22	-12 ≤ h ≤ 18, -30 ≤ k ≤ 32, -30 ≤ l ≤ 29
Reflections collected	51803	18708
Independent reflections	24602 [R_{int} = 0.0647, R_{sigma} = 0.0806]	9525 [R_{int} = 0.0383, R_{sigma} = 0.0516]
Data/restraints/parameters	24602/784/1839	9525/0/565
Goodness-of-fit on F^2	1.052	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0899, wR_2 = 0.2289	R_1 = 0.0617, wR_2 = 0.1625
Final R indexes [all data]	R_1 = 0.1214, wR_2 = 0.2544	R_1 = 0.0850, wR_2 = 0.1823
Largest diff. peak/hole / e Å^{-3}	2.20/-1.54	1.77/-0.93

Table S2 Bond valence sum (BVS) analysis of metal ions [1] in **PTC-221** and **PTC-222**.

PTC-221	
Ag1 1.266	Ag2 1.557
Ag1-O00G 0.309 d=2.276(5)	Ag2-O00J 0.326 d=2.257(5)
Ag1A-O00G 0.309 d=2.277(5)	Ag2A-O00J 0.318 d=2.266(10)
Ag1-O00T 0.182 d=2.473(5)	Ag2-O01L 0.195 d=2.446(7)
Ag1-O00W 0.267 d=2.330(5)	Ag2A-O01L 0.562 d=2.055(12)
Ag1A-O00W 0.199 d=2.440(5)	Ag2-O01D 0.155 d=2.531(6)
Ag1 parameter: r1 = 1.842	Ag1 parameter: r1 = 1.842
Ti03 4.225	Ti04 4.157
Ti03-O00E 0.576 d=2.019(5)	Ti04-O00G 0.971 d=1.826(5)
Ti03-O00F 0.645 d=1.977(4)	Ti04-O00J 0.890 d=1.858(5)
Ti03-O00G 0.869 d=1.867(5)	Ti04-O00L 0.670 d=1.963(5)
Ti03-O00I 0.611 d=1.997(5)	Ti04-O00M 0.628 d=1.987(5)
Ti03-O00J 0.930 d=1.842(5)	Ti04-O00O 0.491 d=2.078(5)
Ti03-O00K 0.594 d=2.008(5)	Ti04-O00R 0.506 d=2.067(5)
Ti4 parameter: r1 = 1.815	Ti4 parameter: r1 = 1.815
Ti05 4.307	Ti06 4.377
Ti05-O00P 0.556 d=2.032(5)	Ti06-O00Q 0.568 d=2.024(5)
Ti05-O00S 0.539 d=2.044(6)	Ti06-O00W 0.547 d=2.038(6)
Ti05-O00U 0.550 d=2.036(5)	Ti06-O013 0.995 d=1.817(6)
Ti05-O00V 0.915 d=1.848(5)	Ti06-O014 0.637 d=1.982(6)
Ti05-O00Y 0.828 d=1.885(5)	Ti06-O016 0.692 d=1.951(6)
Ti05-O010 0.920 d=1.846(6)	Ti06-O01O 0.937 d=1.839(5)
Ti4 parameter: r1 = 1.815	Ti4 parameter: r1 = 1.815
Ti08 4.316	Ti09 4.389
Ti08-O00H 0.582 d=2.015(5)	Ti09-O00T 0.489 d=2.080(5)
Ti08-O012 0.968 d=1.827(6)	Ti09-O017 0.595 d=2.007(6)
Ti08-O01F 0.618 d=1.993(5)	Ti09-O019 0.616 d=1.994(5)

Ti08-O01I 0.674 d=1.961(6) Ti08-O01L 0.539 d=2.044(7) Ti08-O01Y 0.935 d=1.840(7) Ti4 parameter: r1 = 1.815	Ti09-O01E 0.867 d=1.868(6) Ti09-O01M 1.170 d=1.757(6) Ti09-O01N 0.652 d=1.973(6) Ti4 parameter: r1 = 1.815
Ti0A 4.339 Ti0A-O00Z 0.576 d=2.019(5) Ti0A-O018 0.553 d=2.034(6) Ti0A-O01A 0.883 d=1.861(6) Ti0A-O01B 0.871 d=1.866(6) Ti0A-O01G 0.539 d=2.044(6) Ti0A-O01Q 0.917 d=1.847(6) Ti4 parameter: r1 = 1.815	Ti0B 4.345 Ti0B-O00N 0.521 d=2.056(6) Ti0B-O015 0.540 d=2.043(6) Ti0B-O01D 0.541 d=2.042(6) Ti0B-O01J 0.945 d=1.836(6) Ti0B-O01S 0.902 d=1.853(7) Ti0B-O01V 0.895 d=1.856(7) Ti4 parameter: r1 = 1.815
Ti0C 4.300 Ti0C-O00X 0.567 d=2.025(6) Ti0C-O01C 0.498 d=2.073(5) Ti0C-O01H 0.530 d=2.050(6) Ti0C-O01K 0.930 d=1.842(6) Ti0C-O01T 0.902 d=1.853(7) Ti0C-O01U 0.874 d=1.865(7) Ti4 parameter: r1 = 1.815	Ti0D 4.344 Ti0D-O011 0.476 d=2.090(6) Ti0D-O01P 0.627 d=1.988(6) Ti0D-O01R 0.654 d=1.972(6) Ti0D-O01W 0.600 d=2.004(7) Ti0D-O01X 0.885 d=1.860(7) Ti0D-O021 1.102 d=1.779(7) Ti4 parameter: r1 = 1.815
PTC-222	
Ag01 1.000 Ag01-O008[1] 0.399 d=2.182(2) Ag01-O00G 0.164 d=2.511(2) Ag01-O00O 0.437 d=2.148(3) Ag1 parameter: r1 = 1.842	Ag02 1.065 Ag02-O009 0.239 d=2.371(2) Ag02-O00I 0.219 d=2.404(2) Ag02-O00Q 0.273 d=2.323(3) Ag1 parameter: r1 =1.842 Ag02-N00Z 0.334 d=2.256(4) Ag1 parameter: r1 = 1.85
Ti03 4.136 Ti03-O007[1] 0.759 d=1.917(2) Ti03-O008 0.853 d=1.874(2) Ti03-O009 1.014 d=1.810(2) Ti03-O00B[1] 0.494 d=2.076(2) Ti03-O00C 0.555 d=2.033(2) Ti03-O00E[1] 0.462 d=2.101(2) Ti4 parameter: r1 = 1.815	Ti04 4.189 Ti04-O008 0.864 d=1.869(2) Ti04-O009 0.769 d=1.912(2) Ti04-O00F 0.470 d=2.094(2) Ti04-O00G 0.963 d=1.829(2) Ti04-O00J 0.530 d=2.050(2) Ti04-O00N 0.592 d=2.009(3) Ti4 parameter: r1 = 1.815
Ti05 4.161 Ti05-O007 0.642 d=1.979(2) Ti05-O00A 0.981 d=1.8220(6) Ti05-O00H 0.531 d=2.049(3) Ti05-O00I 0.925 d=1.844(2) Ti05-O00K 0.384 d=2.169(2) Ti05-O00P 0.698 d=1.948(3) Ti4 parameter: r1 = 1.815	Ti06 4.212 Ti06-O007 0.739 d=1.927(2) Ti06-O00D 0.502 d=2.070(2) Ti06-O00G 0.960 d=1.830(2) Ti06-O00I 0.950 d=1.834(2) Ti06-O00L 0.524 d=2.054(2) Ti06-O00M 0.537 d=2.045(2) Ti4 parameter: r1 = 1.815

[1] $Vi = \Sigma S_{ij} = \Sigma \exp[(r_1-d)/B]$, where r_1 is the bond parameter between different atoms (eg. r1=1.815 for Ti^{IV}-O), d is the bond length between atoms i and j (eg. d_1 for Ti_1-O_1, d_2 for Ti_1-O_2); B is a constant, the "universal parameter" ~0.37 Å; S_{ij} is the valence of a bond between atoms i and j; V_i is the sum of all bond valences of the bonds formed by a given atom i.

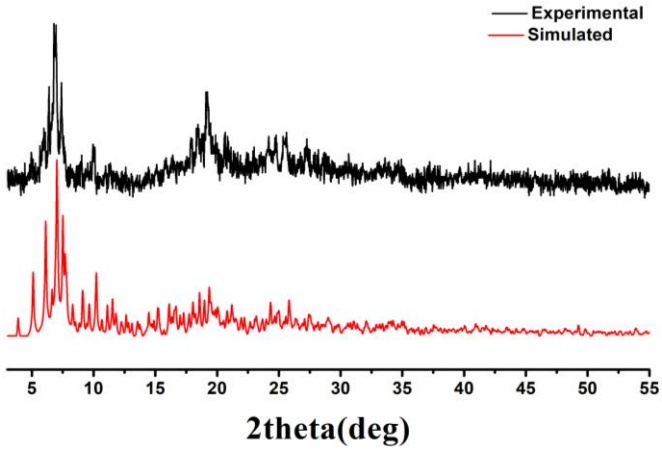

Figure S1. The simulated and experimental PXRD patterns of **PTC-221**.

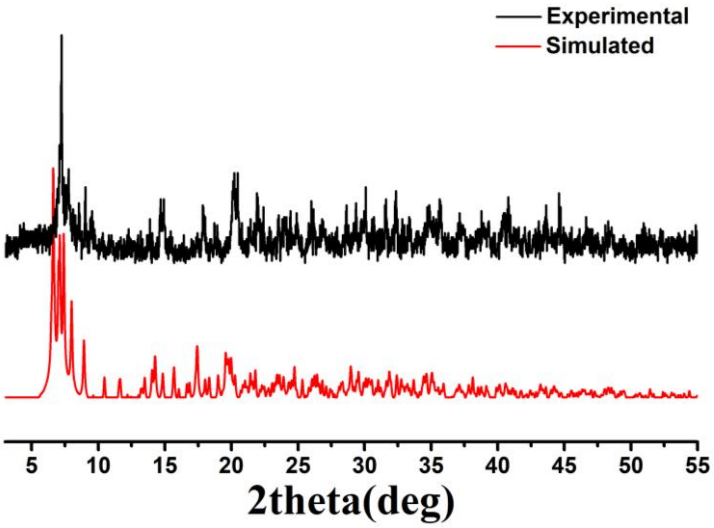

Figure S2. The simulated and experimental PXRD patterns of **PTC-222**.

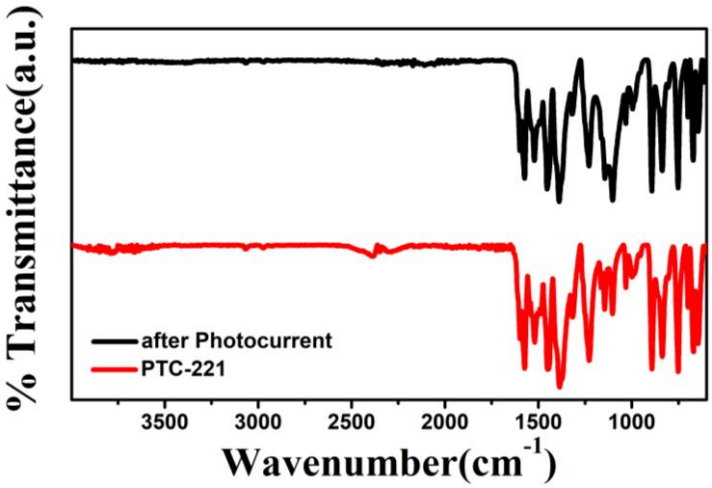

Figure S3. The IR spectra of **PTC-221** and the powder samples after photocurrent test.

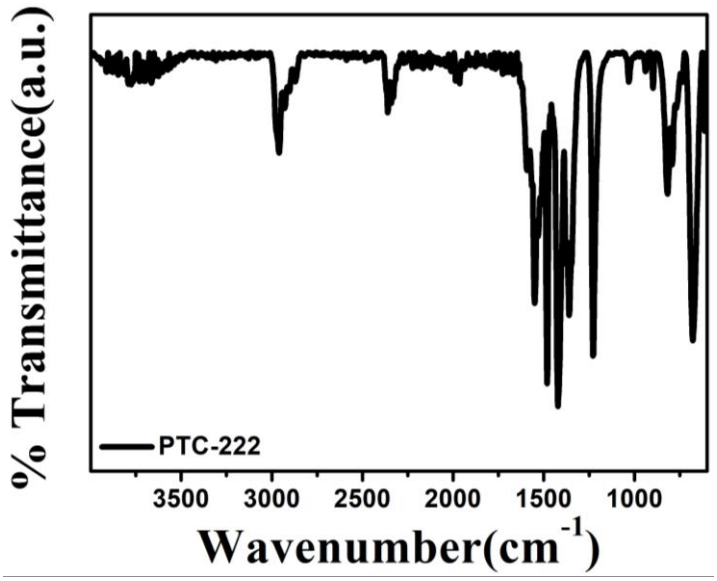

Figure S4. The IR spectrum of **PTC-222**.

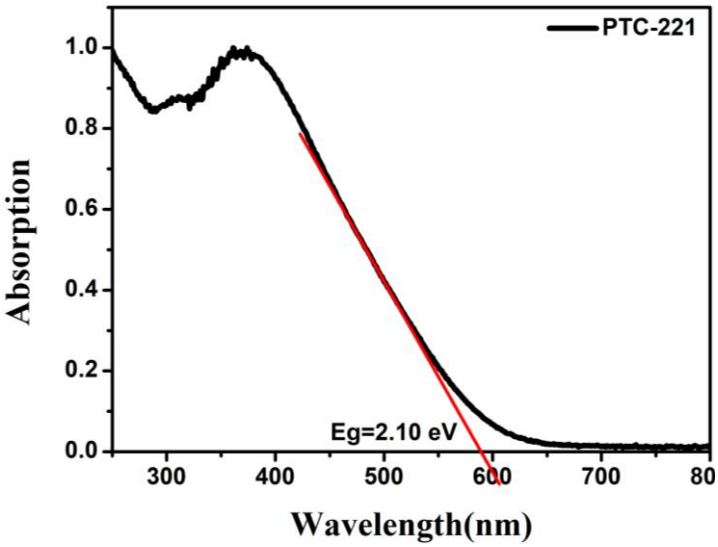

Figure S5. The solid-state UV-vis absorption spectrum of **PTC-221**.

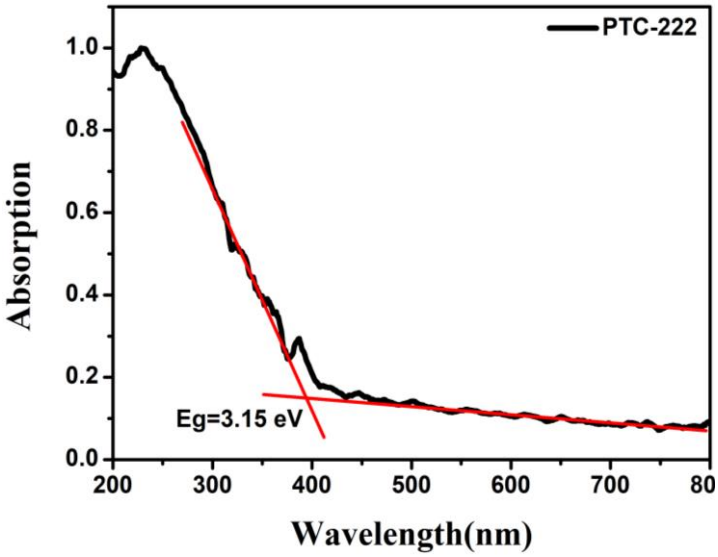

Figure S6. The solid-state UV-vis absorption spectrum of **PTC-222**.

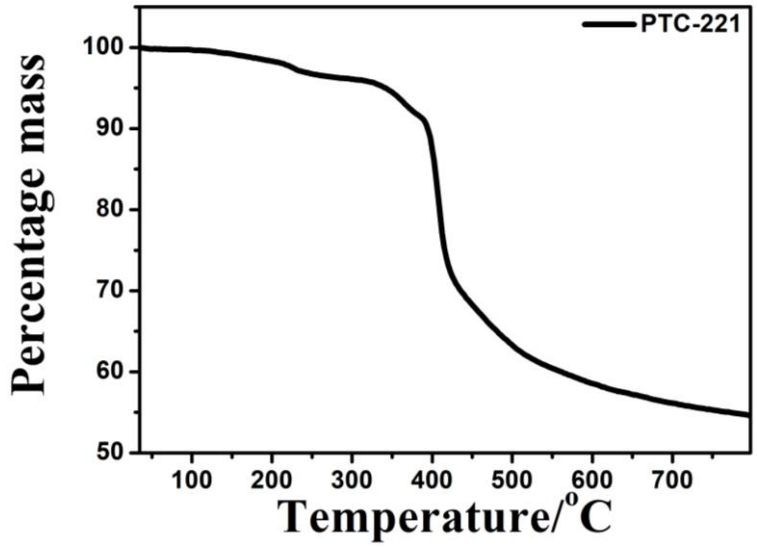

Figure S7. The TGA curve of **PTC-221**.