Electronic Supporting Information

Series of Silver Doped Butterfly-like Ti_8Ag_2 Clusters with Two Ag ions Panelled in Ti_8 Surface

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Table S1. Crystal data and structure refinement for compound **1**

Identification code	**1**
CCDC No	1916923
Empirical formula	$C_{138}H_{106}Ag_2N_2O_{38}P_2Ti_8$
Formu weight	3061.12
Temperature	292 K
Wavelength	1.54184 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a =14.2611(3) Å α = 90°
	b = 18.0847(5) Å β= 92.723(2)°
	c = 26.3595(8) Å γ= 90°
Volume	6790.7(3) A^3
Z, Calcuted density	2, 1.497 Mg/m^3
Absorption coefficient	6.943 mm^{-1}
F(000)	3104
Crystal size	0.25x 0.19 x 0.11 mm
Theta range for data collection	3.950 to 72.444°
Limiting indices	-17<=h<=15, -16<=k<=22, -29<=l<=32
Reflections collected / unique	27007 / 13161 [R(int) = 0.0388]
Completeness to theta = 25.02	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13161/0/857
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 =0.1068
R indices (all data)	R1 =0.0760, wR2 = 0.1250
Largest diff. peak and hole	0.614 and -0.573 $e.A^3$

Table S2. Crystal data and structure refinement for compound **2**

Identification code	**2**
CCDC No	1916928
Empirical formula	$C_{198}H_{224}Ag_2N_4O_{38}P_2Ti_8$
Formu weight	3928.68
Temperature	170 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a =16.6988(3) Å α = 107.8060(10)°
	b = 18.6668(3) Å β= 112.2850(10)°
	c = 19.6322(3) Å γ= 104.1300(10)°

Volume	4920.38(15) A^3
Z, Calcuted density	1, 1.326 Mg/m^3
Absorption coefficient	0.588 mm^{-1}
F(000)	2044
Crystal size	0.27 x 0.24 x 0.19 mm
Theta range for data collection	1.444 to 28.282°
Limiting indices	-21<=h<=22, -24<=k<=24, -26<=l<=26
Reflections collected / unique	78386 / 24290 [R(int) = 0.0188]
Completeness to theta = 25.02	99.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	24290 / 0 / 1158
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0988
R indices (all data)	R1 = 0.0415, wR2 = 0.1059
Largest diff. peak and hole	1.362 and -0.692 $e.A^3$

Table S3. Crystal data and structure refinement for compound **3**

Identification code	**3**
CCDC No	1916929
Empirical formula	$C_{154}H_{138}Ag_2N_3O_{52}P_2Ti_8$
Formu weight	3523.32
Temperature	170 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a =15.6045(2)Å α = 92.6270(10)°
	b = 17.2291(3) Å β= 99.8580(10)°
	c = 31.2468(5) Å γ= 109.6870(10)°
Volume	7744.2(2)A^3
Z, Calcuted density	1, 1.511 Mg/m^3
Absorption coefficient	0.744 mm^{-1}
F(000)	3598
Crystal size	0.34 x 0.29 x 0.24 mm
Theta range for data collection	1.263 to 28.281°
Limiting indices	-19<=h<=20, -22<=k<=22, -41<=l<=41
Reflections collected / unique	124427 / 38311 [R(int) = 0.0271]
Completeness to theta = 25.02	99.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	38311 / 64 / 2088

Goodness-of-fit on F^2	1.111
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0881
R indices (all data)	R1 = 0.0463, wR2 = 0.0997
Largest diff. peak and hole	0.771 and -0.937 e.A^3

Table S4. Crystal data and structure refinement for compound **4**

Identification code	**4**
CCDC No	1916931
Empirical formula	$C_{164}H_{152}Ag_2N_8O_{38}P_2Ti_8$
Formu weight	3505.82
Temperature	170 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a =15.2916(2) Å α = 67.8580(10)°
	b = 16.8434(3) Å β= 82.7640(10)°
	c = 17.8849(3) Å γ= 78.7810(10)°
Volume	4178.20(12) A^3
Z, Calcuted density	1, 1.393 Mg/m^3
Absorption coefficient	0.684 mm^{-1}
F(000)	1798
Crystal size	0.31 x 0.28 x 0.23 mm
Theta range for data collection	1.738 to 28.282°
Limiting indices	-20<=h<=20, -22<=k<=22, -23<=l<=23
Reflections collected / unique	54838 / 20281 [R(int) = 0.0159]
Completeness to theta = 25.02	98.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20281 / 3 / 1014
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0281, wR2 = 0.0775
R indices (all data)	R1 = 0.0339, wR2 = 0.0857
Largest diff. peak and hole	0.448 and -0.857 e.A^3

Table S5. Crystal data and structure refinement for compound **5**

Identification code	**5**
CCDC No	1916932
Empirical formula	$C_{144}H_{118}Ag_2N_2O_{38}P_2Ti_8$
Formu weight	3145.28
Temperature	170 K

Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 14.1578(2) Å α = 88.5520(10)°
	b = 15.2500(2) β= 67.5800(10)°
	c = 17.4641(3) Å γ= 79.1470(10)°
Volume	3418.76(9) A^3
Z, Calcuted density	1, 1.528 Mg/m^3
Absorption coefficient	0.826 mm^{-1}
F(000)	1600
Crystal size	0.22 × 0.15 × 0.14 mm
Theta range for data collection	3.208 to 50°
Limiting indices	$-16 \le h \le 15$, $-18 \le k \le 18$, $-20 \le l \le 20$
Reflections collected / unique	25788 / 12008 [R(int) = 0.0192]
Completeness to theta = 25.02	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12008/594/875
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R_1 = 0.0643, wR_2 = 0.1739
R indices (all data)	R_1 = 0.0800, wR_2 = 0.1984
Largest diff. peak and hole	3.39 and -2.52 $e.A^3$

Table S6. Crystal data and structure refinement for compound **6**

Identification code	**6**
CCDC No	1916933
Empirical formula	$C_{144}H_{118}Ag_2N_2O_{38}P_2Ti_8$
Formu weight	3145.28
Temperature	292 K
Wavelength	1.54184 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a =14.2246(9) Å α = 67.905(6)°
	b = 15.4590(9) Å β= 82.025(5)°
	c = 18.8915(11) Å γ= 65.532(6)°
Volume	3502.7(4) A^3
Z, Calcuted density	1, 1.491 Mg/m^3
Absorption coefficient	6.746 mm^{-1}
F(000)	1600
Crystal size	0.27 x 0.25 x 0.18 mm
Theta range for data collection	3.414 to 72.141°

Limiting indices	-12<=h<=17, -18<=k<=19, -23<=l<=22
Reflections collected / unique	24469 / 13449 [R(int) = 0.0352]
Completeness to theta = 25.02	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13449 / 0 / 887
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1269
R indices (all data)	R1 = 0.0629, wR2 = 0.1385
Largest diff. peak and hole	1.912 and -1.079 e.A^3

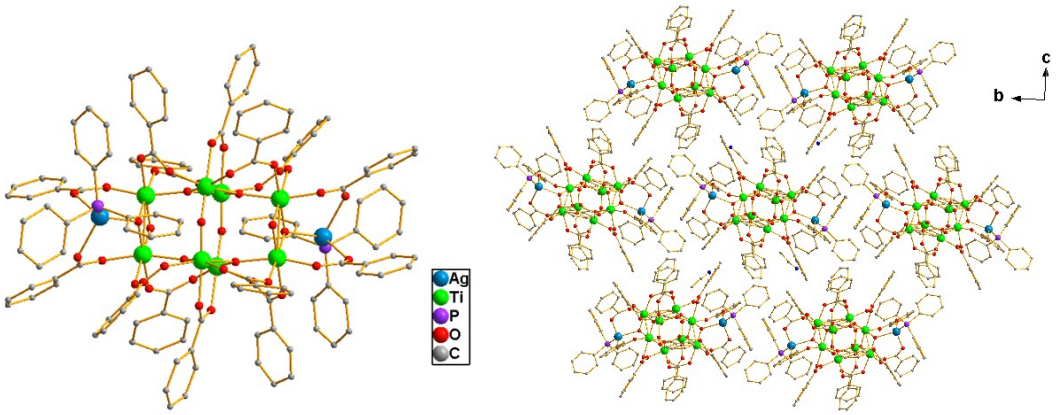

Fig. S1 Crystal structure and packing-mode of **1**.

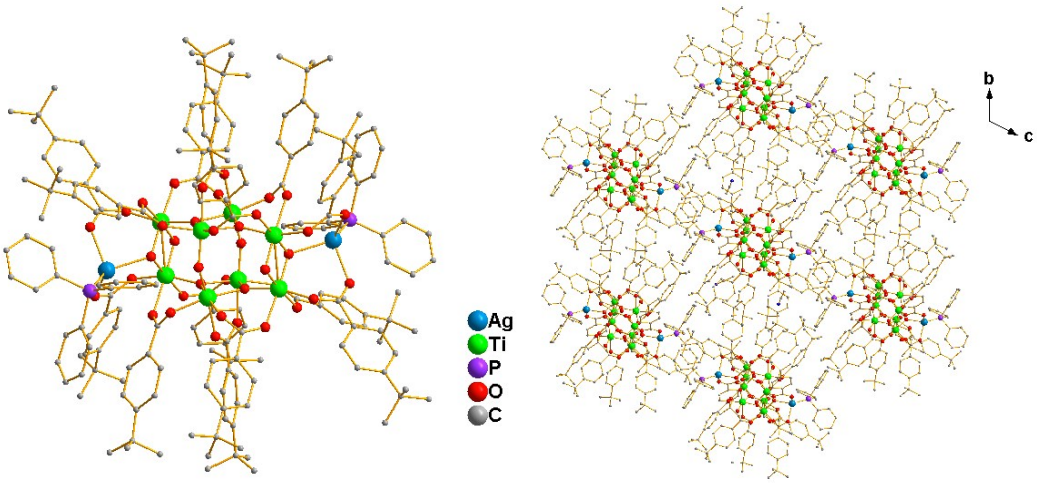

Fig. S2 Crystal structure and packing-mode of **2**.

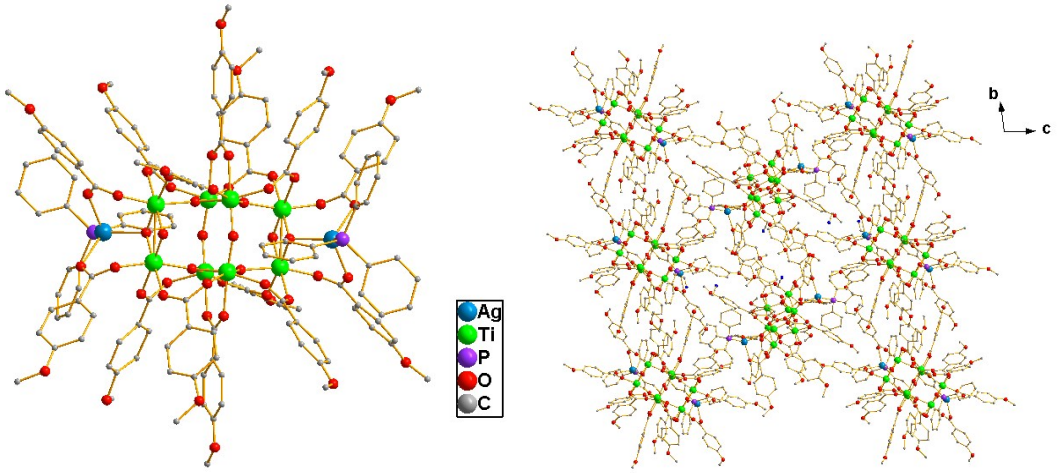

Fig. S3 Crystal structure and packing-mode of **3**.

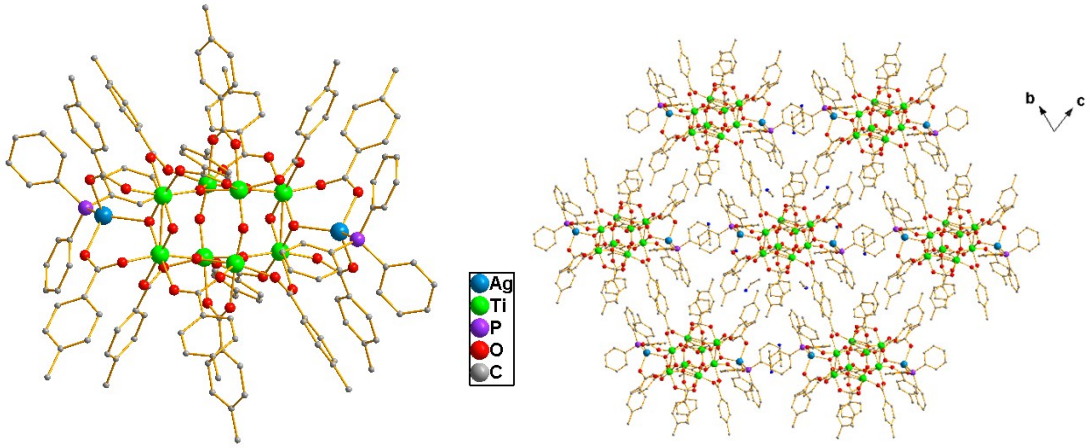

Fig. S4 Crystal structure and packing-mode of **4**.

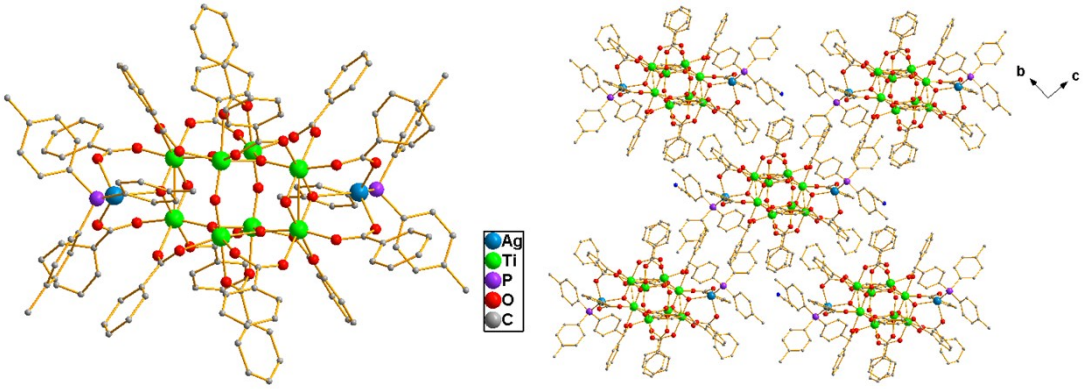

Fig. S5 Crystal structure and packing-mode of **5**.

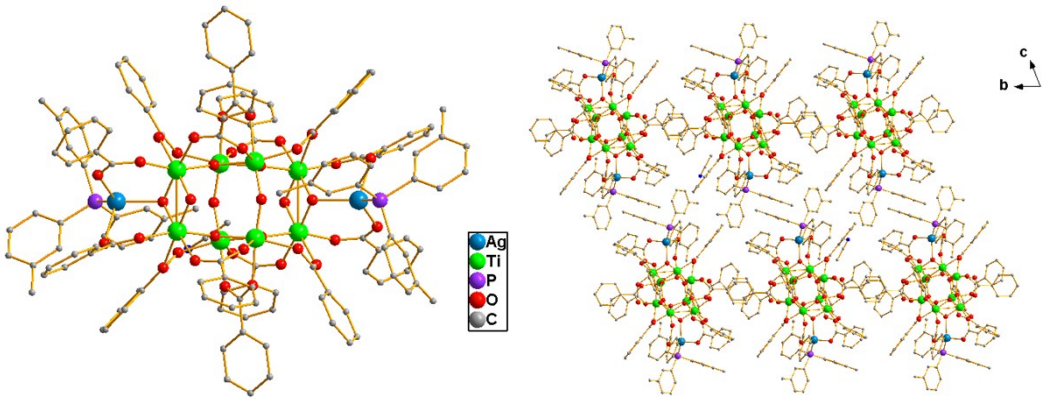

Fig. S6 Crystal structure and packing-mode of **6**.

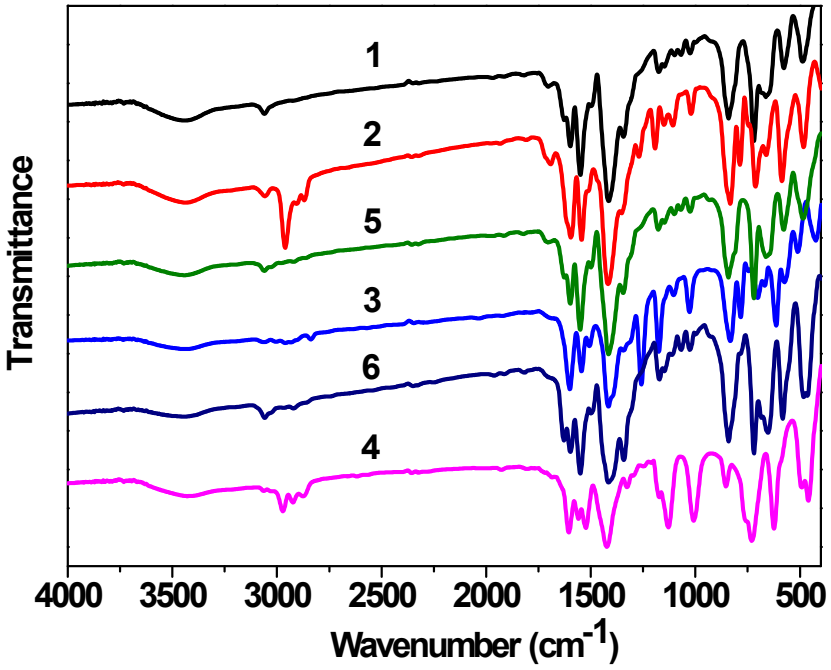

Fig. S7 The FT-IR spectra of **1-6**.

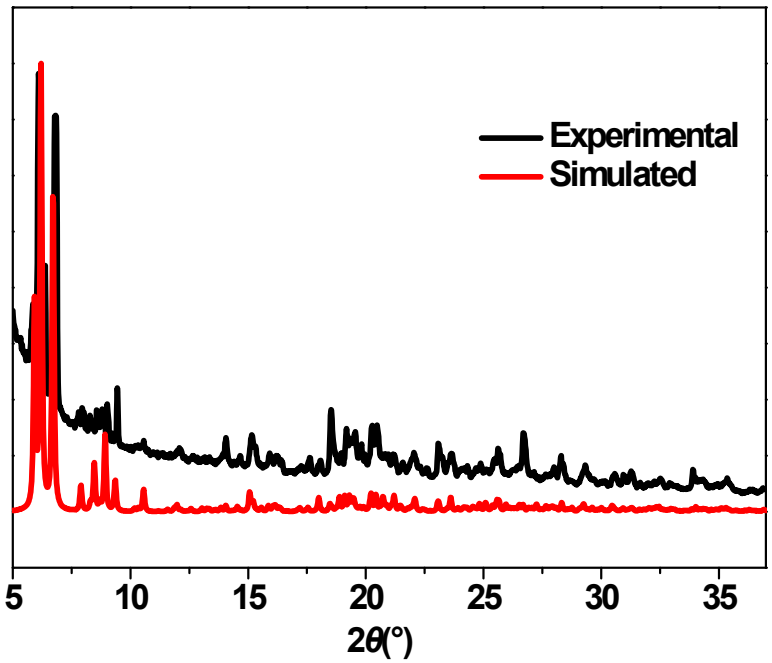

Fig. S8 The PXRD of the simulated and experimental patterns of **1**.

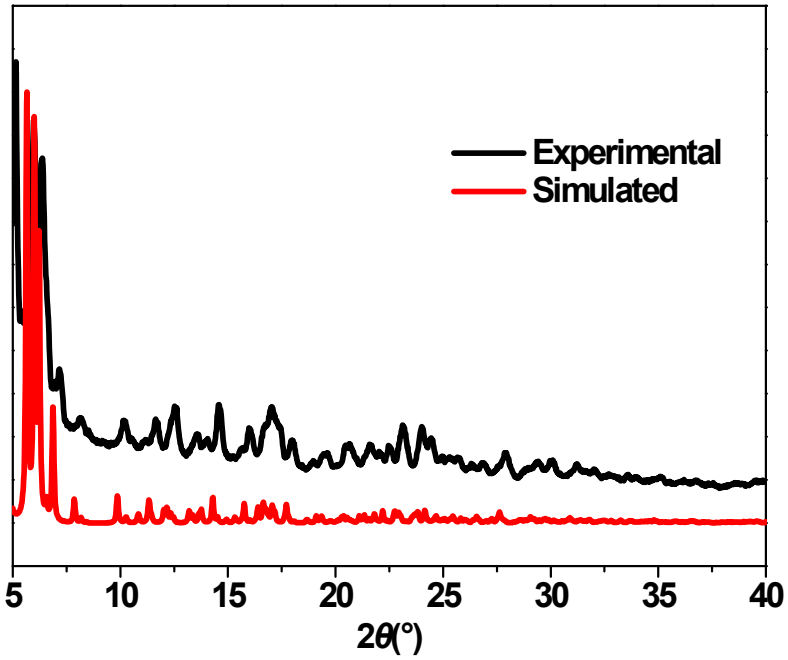

Fig. S9 The PXRD of the simulated and experimental patterns of **2**.

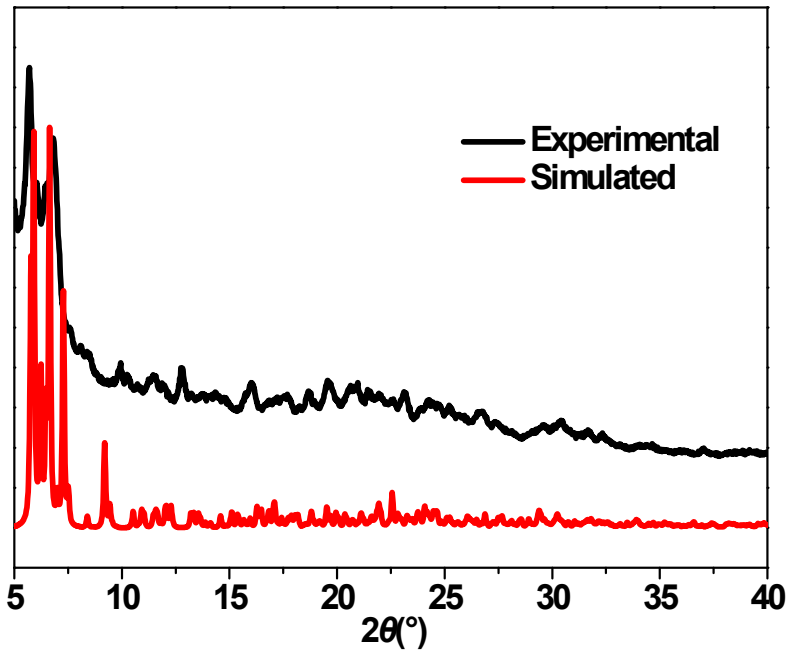

Fig. S10 The PXRD of the simulated and experimental patterns of **3**.

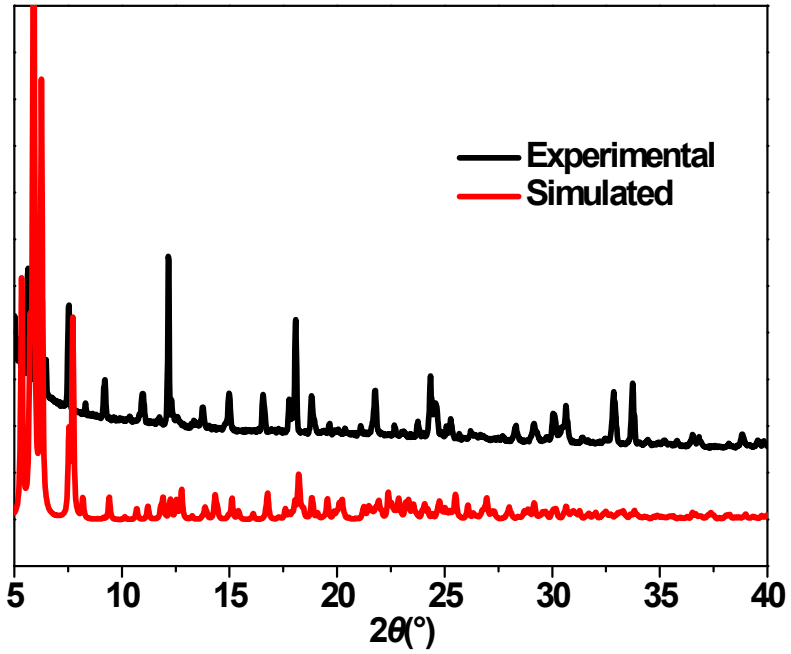

Fig. S11 The PXRD of the simulated and experimental patterns of **4**.

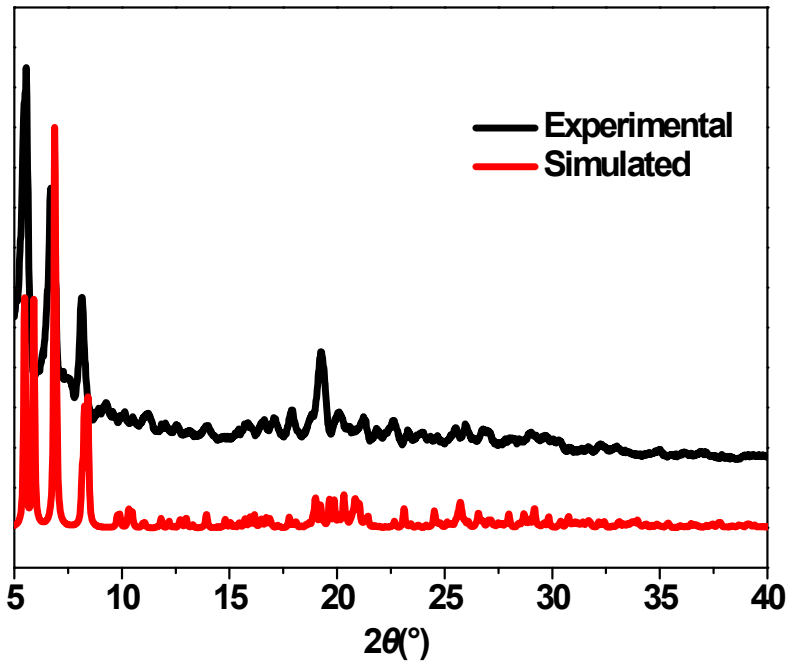

Fig. S12 The PXRD of the simulated and experimental patterns of **5**.

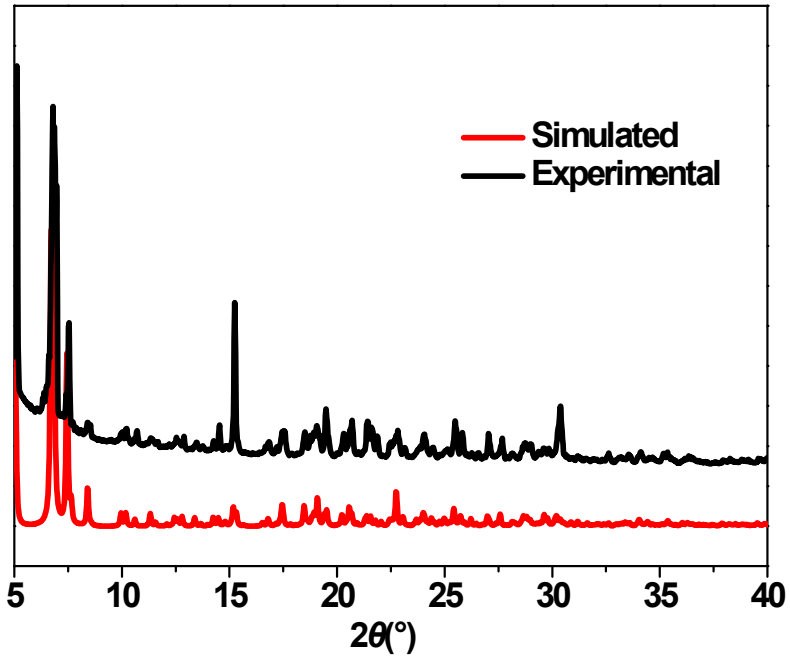

Fig. S13 The PXRD of simulated and experimental patterns of **6**.

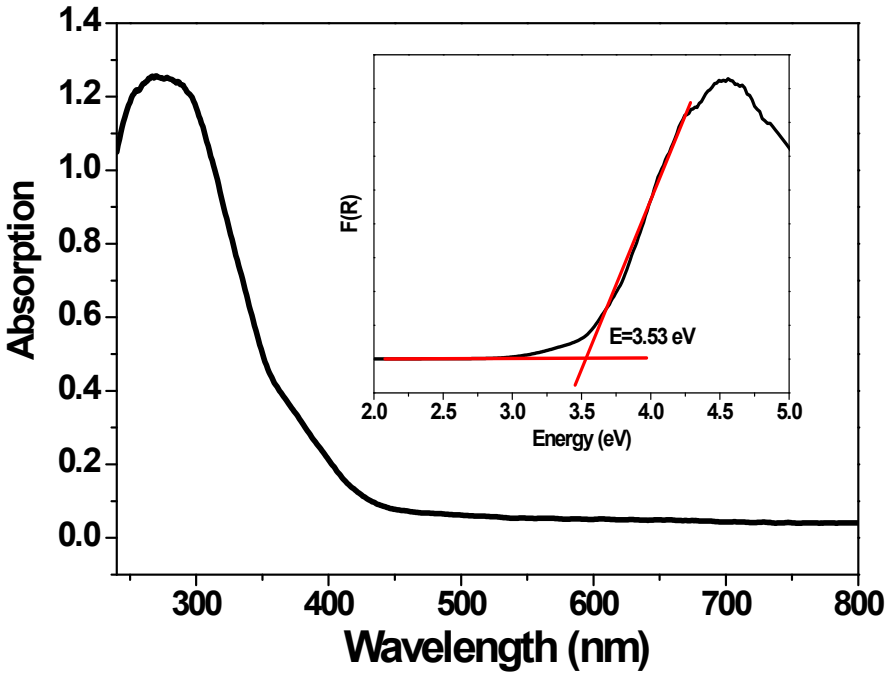

Fig. S14 UV/Vis spectrum for **1**

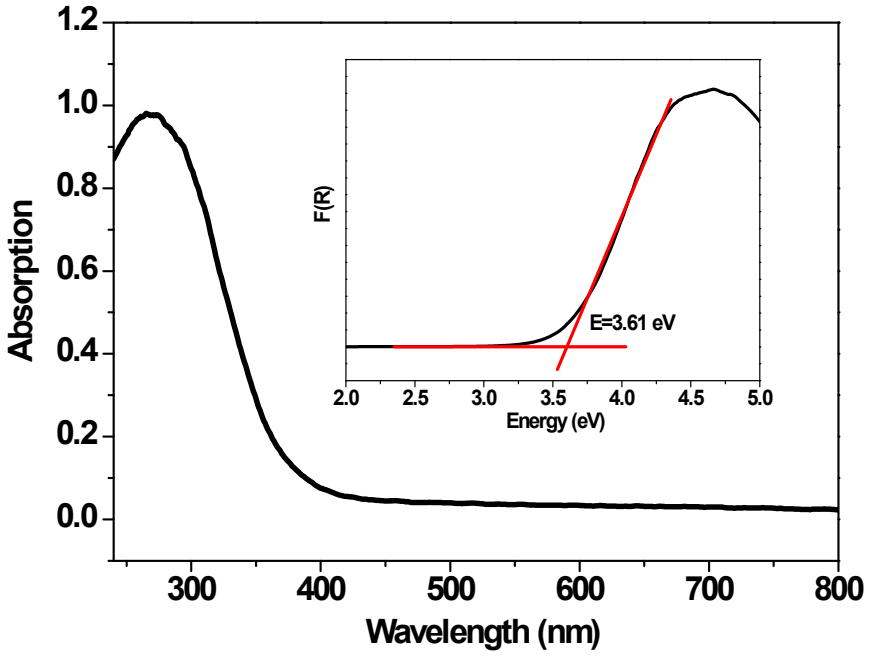

Fig. S15 UV/Vis spectrum for **2**

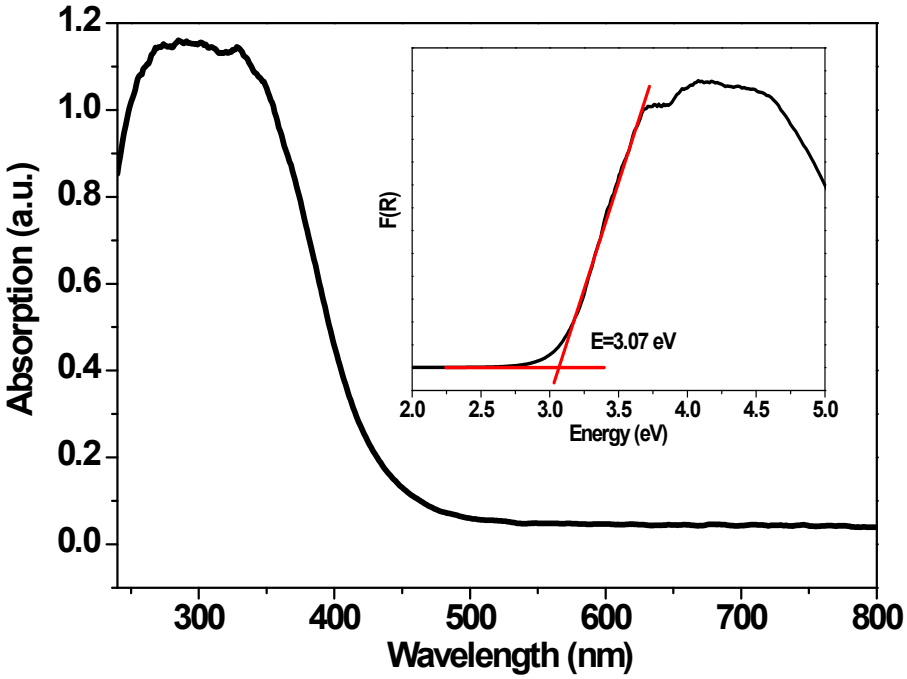

Fig. S16 UV/Vis spectrum for **3**

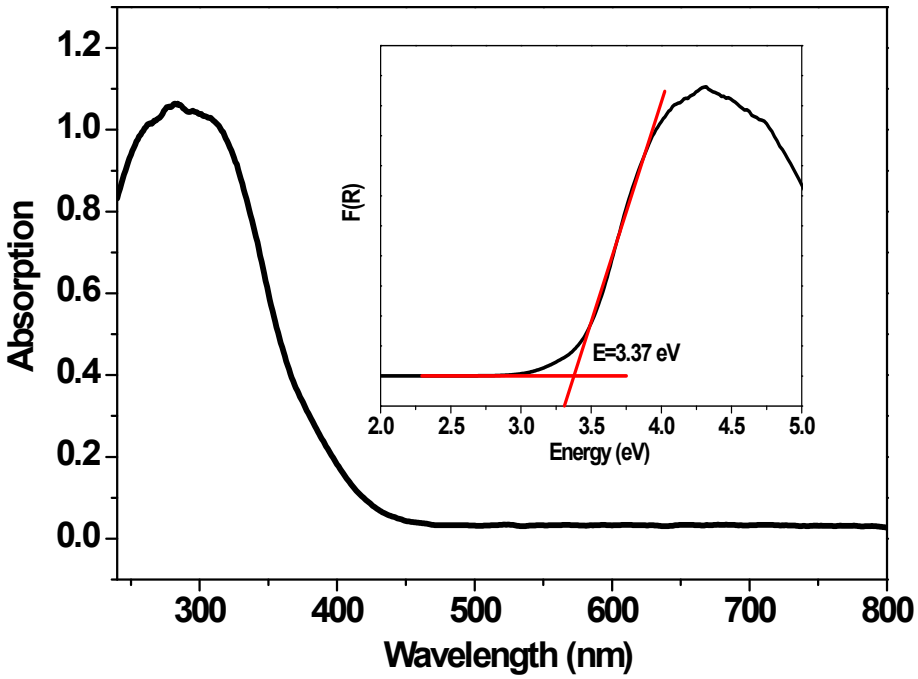

Fig. S17 UV/Vis spectrum for **4**

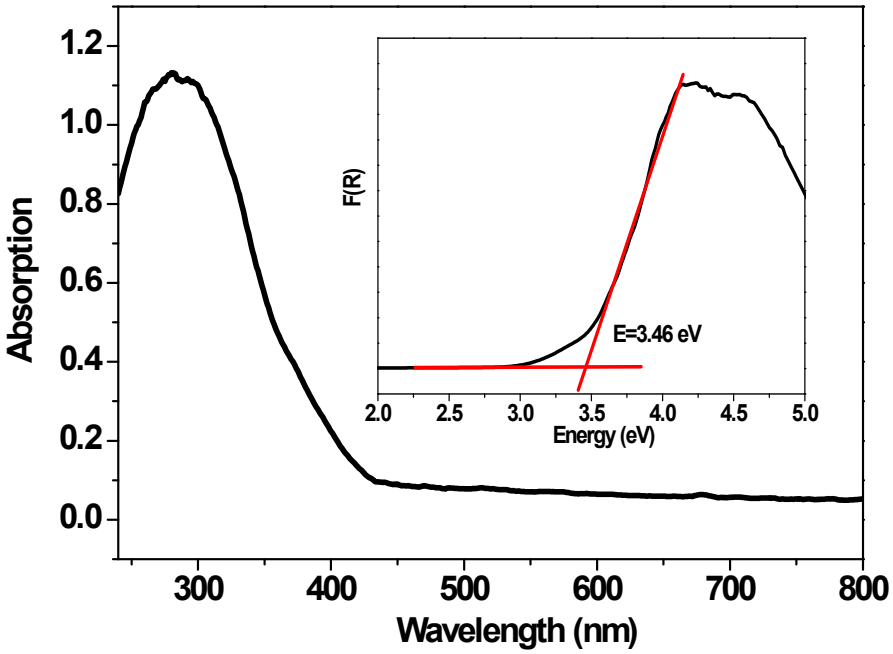

Fig. S18 UV/Vis spectrum for **5**

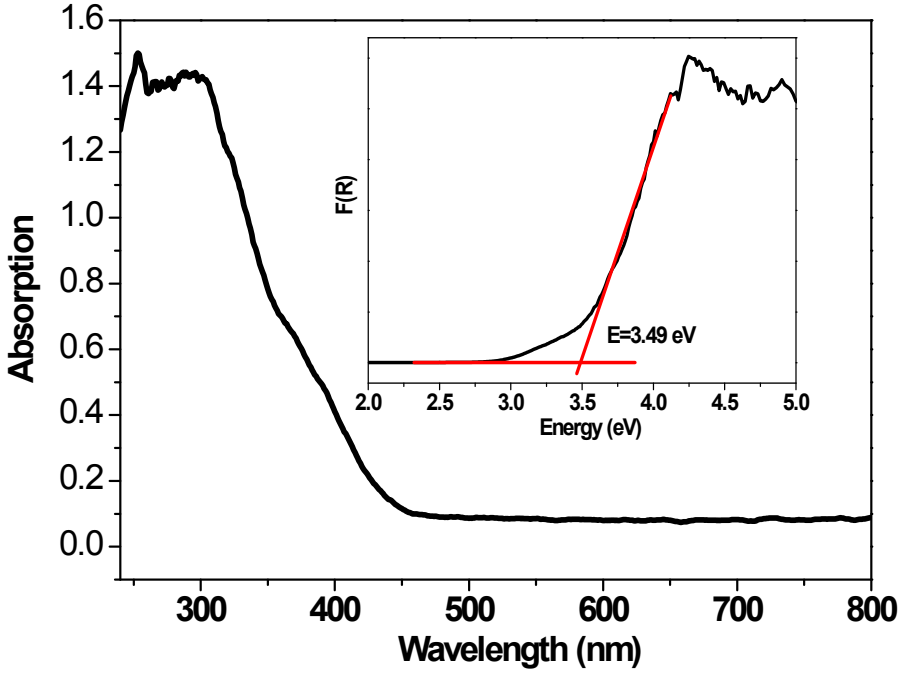

Fig. S19 UV/Vis spectrum for **6**

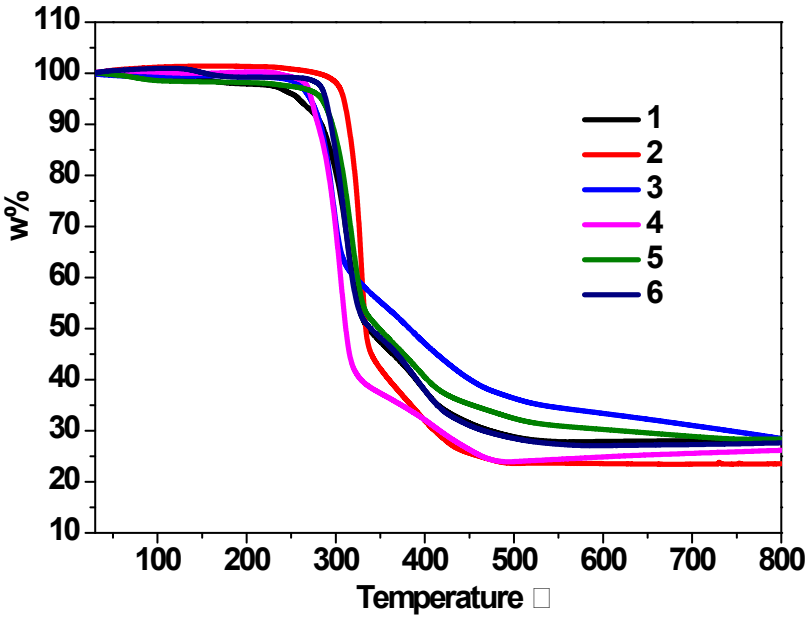

Fig. S20 TGA curves of **1-6**.

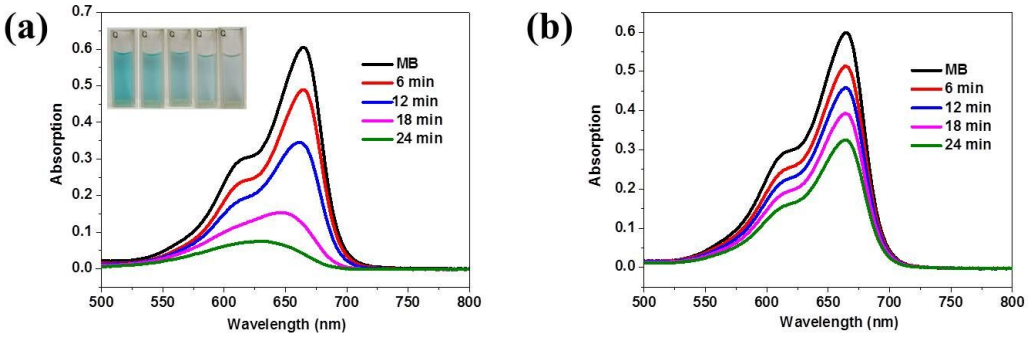

Fig. S21 Time-dependent absorption spectra for sunlight-driven photocatalytic MB degradation with (a) compound **1** and (b) blank.

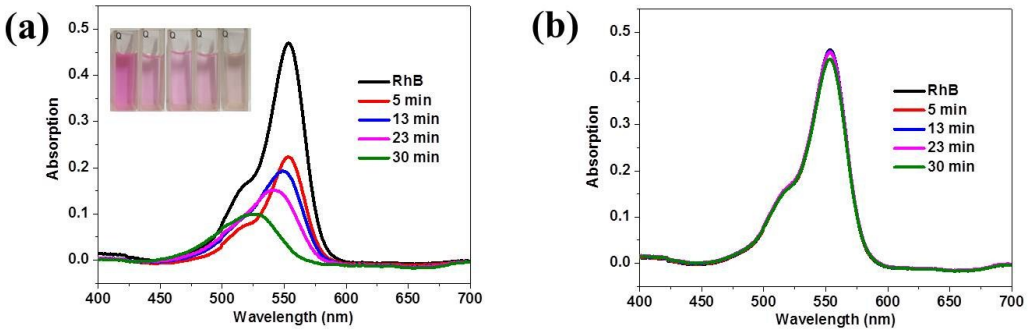

Fig. S22 Time-dependent absorption spectra for sunlight-driven photocatalytic RhB

degradation with (a) compound **1** and (b) blank.

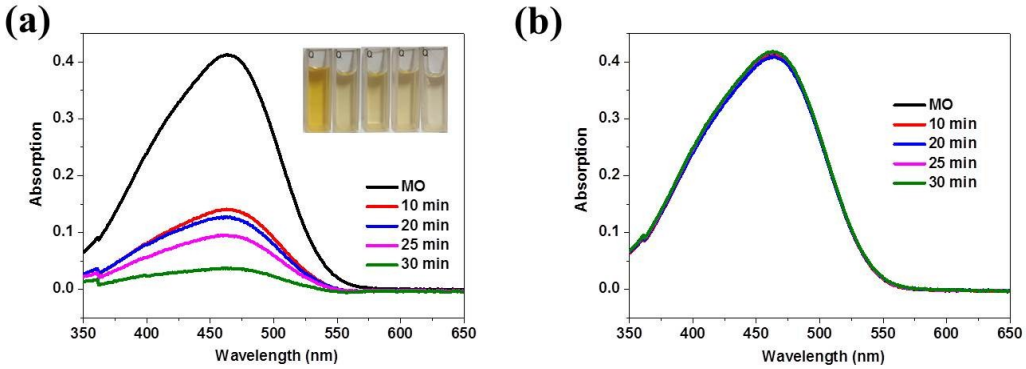

Fig. S23 Time-dependent absorption spectra for sunlight-driven photocatalytic MO degradation with (a) compound **1** and (b) blank.