Electronic Supplementary Material (ESI) for CrystEngComm.

Synthesis and Characterization of Polyoxometalate-based Silver(I) Phenylethynide Compounds with Antibacterial and Antifungal Activities

Supporting Information

Table S1. X-ray crystal data and structure refinement parameters.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{37}H_{32}Ag_5F_3O_5S_3$	$C_{24}H_{53}Ag_4O_{48}PS_8W_{12}$	$C_{24}H_{53}Ag_4Mo_{12}O_{48}PS_8$	$C_{28}H_{65}Ag_5O_{50}S_{10}SiW_{12}$	$C_{84}H_{100}Ag_{12}O_{50}S_{10}SiW_{12}$	$C_{144}H_{132}Ag_{19}O_{50}PS_8W_{12}$
Formula weight	1249.16	4034.79	2979.87	4296.04	5758.97	7205.68
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	*P*-1 (No. 2)	*C*2/*c* (No. 15)	*P*-1 (No. 2)
a [Å]	33.174(4)	17.0815(6)	16.9657(8)	13.5633(6)	20.6616(12)	13.6613(15)
b [Å]	8.3649(5)	17.3104(5)	17.2724(8)	15.5962(6)	22.0358(12)	18.0152(9)
c [Å]	32.717(4)	25.7879(9)	25.7174(12)	18.8084(9)	30.4391(18)	18.7774(6)
α [°]	90	90	90	86.273(4)	90	93.702(3)
β [°]	114.198(14)	106.596(4)	106.578(5)	85.954(4)	105.960(6)	101.547(6)
γ [°]	90	90	90	85.935(4)	90	101.388(7)

V[Å^3]	8281.1(15)	7307.5(4)	7222.9(6)	3951.5(3)	13324.6(13)	4412.5(6)
Z	8	4	4	2	4	1
D_{calc}(g/cm3)	2.004	3.667	2.74	3.611	2.871	2.712
μ(Mo-Kα)(mm^{-1})	2.527	20.186	3.41	18.961	12.266	10.009
F(000)	4832	7200	5664	3860	10520	3320
Reflections collected	15821	20072	14762	27649	23962	42160
Independent reflections	7273	6438	6351	13878	11713	15225
Observed reflections [I>2s(I)]	4323	5619	5702	8789	7275	10780
Parameters	1467	470	468	1021	772	1074
Goodness-of-fit	1.193	1.219	1.127	1.091	1.204	0.956
R_1[I>2s(I)][a]	0.061	0.103	0.166	0.073	0.057	0.036
wR_2(all data)[b]	0.074	0.222	0.314	0.082	0.089	0.078

[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. Selected bond lengths **(**Å**)** for **1−6**.

1					
C1≡C2	1.194(1)	C9≡C10	1.210(9)	C17≡C18	1.181(9)
C25≡C26	1.208(1)	Ag1-C1	2.074(8)	Ag4-C1#1	2.531(7)
Ag2-C1	2.412(7)	Ag3-C9	2.066(8)	Ag2-C9	2.364(9)
Ag5-C9#4	2.374(7)	Ag3-C17	2.091(8)	Ag4-C17	2.481(7)
Ag5-C17#1	2.572(9)	Ag2-C17#2	2.531(7)	Ag5-C25	2.337(7)
Ag1-C25	2.045(8)	Ag4-C25	2.380(8)	Ag1···Ag4#1	2.969(1)
Ag1···Ag2	2.996(8)	Ag1···Ag5#1	3.118(10)	Ag1···Ag5	3.132(9)
Ag1···Ag4	3.013(1)	Ag1···Ag3	3.158(8)	Ag2···Ag3#2	2.943(9)
Ag2···Ag5#3	3.252(1)	Ag3···Ag2	3.058(1)	Ag3···Ag4	2.979(8)
Ag3···Ag5#1	2.979(1)	Ag5···Ag3#1	2.979(1)	Ag4-O2	2.311(6)
Ag5···Ag3#4	3.140(9)	Ag2-O1	2.318(6)		
2					
C7≡C8	1.220(7)	Ag2···Ag1#1	2.905(6)	Ag1-O1	2.500(3)
Ag1-C8	2.320(1)	Ag2···Ag2#1	2.907(7)	Ag1-O21	2.270(3)
Ag2-C8	2.130(4)	Ag1···Ag2	2.898(6)	Ag2-O22	2.110(3)
Ag2-O23	2.450(3)	Ag1-O24	2.440(3)		
3					
C1≡C2	1.180(6)	Ag1-C1	2.323(10)	Ag2-C1	2.150(3)
Ag1···Ag2	2.894(4)	Ag2···Ag2#1	2.907(6)	Ag1···Ag2#1	2.908(5)
Ag2-O1	2.440(3)	Ag2-O2	2.130(3)	Ag1-O3	2.440(3)
Ag1-O4	2.240(3)	Ag1-O5	2.520(2)		
4					
C1≡C2	1.200(2)	Ag3···Ag5	2.885(2)	Ag2-O42	2.572(1)

Ag2-C1	2.380(2)	Ag4···Ag5	2.879(3)	Ag3-O46	2.177(1)
Ag3-C1	2.173(2)	Ag1-O43	2.220(1)	Ag3-O43	2.462(1)
Ag4-C1	2.250(2)	Ag1-O42	2.242(1)	Ag4-O48	2.219(1)
Ag5-C1	2.242(2)	Ag1-O41	2.301(2)	Ag4-O47	2.260(2)
Ag2-C2	2.390(2)	Ag1-O37	2.534(1)	Ag5-O50	2.253(1)
Ag2···Ag3	3.002(2)	Ag2-O45	2.256(1)	Ag5-O49	2.310(1)
Ag3···Ag4	2.809(3)	Ag2-O44	2.370(2)		
5					
C1≡C2	1.176(2)	Ag6-C17	2.111(2)	Ag3···Ag6	3.062(2)
C9≡C10	1.180(2)	Ag7-C17	2.431(1)	Ag3···Ag2#1	3.223(2)
C17≡C18	1.192(2)	Ag7-C18	2.644(1)	Ag4···Ag5	2.925(2)
C25≡C26	1.166(2)	Ag4-C25	2.094(2)	Ag4···Ag7#1	2.960(2)
Ag2-C1	2.404(2)	Ag5-C25	2.313(2)	Ag4···Ag6	3.161(1)
Ag3-C1	2.288(2)	Ag7-C25#1	2.305(2)	Ag5···Ag6	3.074(2)
Ag4-C1	2.082(2)	Ag1···Ag3	2.893(2)	Ag6···Ag7	3.164(2)
Ag2-C2	2.705(2)	Ag1···Ag2	3.010(2)	Ag2-O2	2.406(1)
Ag1-C9	2.180(2)	Ag2···Ag6	3.154(2)	Ag3-O5	2.284(1)
Ag2-C9	2.393(2)	Ag2···Ag3#1	3.223(2)	Ag5-O1	2.347(1)
Ag3-C9#1	2.293(2)	Ag2···Ag4	3.307(2)	Ag5-O4	2.393(1)
Ag2-C17	2.573(1)	Ag2···Ag3	3.320(2)	Ag7-O3	2.319(1)
Ag5-C17	2.440(1)	Ag3···Ag4	3.010(2)	Ag7-O4	2.464(1)
6					
C1≡C2	1.218(1)	Ag8-C33	2.114(9)	Ag2···Ag5	3.097(1)
C9≡C10	1.232(1)	Ag9-C33#2	2.420(9)	Ag2···Ag3	3.103(1)
C17≡C18	1.173(1)	Ag10-C33	2.520(9)	Ag2···Ag7	3.112(1)
C25≡C26	1.245(1)	Ag5-C34	2.656(8)	Ag3···Ag4	2.836(7)

C33≡C34	1.227(1)	Ag6-C41	2.056(9)	Ag3···Ag6	3.203(1)
C41≡C42	1.217(1)	Ag10-C41	2.438(1)	Ag5···Ag7	2.981(9)
C49≡C50	1.223(1)	Ag1-C42#1	2.643(9)	Ag5···Ag6	2.991(1)
C57≡C58	1.215(1)	Ag7-C49	2.078(9)	Ag5···Ag8	3.225(1)
Ag1-C1	2.203(9)	Ag9-C49	2.545(9)	Ag6···Ag10	3.074(1)
Ag2-C1	2.220(1)	Ag10-C49	2.657(8)	Ag7 ···Ag8	3.070(1)
Ag3-C1	2.278(9)	Ag1-C49#1	2.592(9)	Ag7···Ag9	3.079(1)
Ag2-C9	2.281(8)	Ag8-C57	2.114(9)	Ag7···Ag10	3.120(1)
Ag5-C9	2.337(9)	Ag9-C57	2.401(9)	Ag8···Ag9#2	2.922(1)
Ag7-C9	2.114(8)	Ag10-C57#2	2.299(8)	Ag8···Ag9	2.992(9)
Ag3-C17	2.521(9)	Ag1···Ag3	2.899(1)	Ag8···Ag10	3.111(1)
Ag5-C17	2.415(10)	Ag1···Ag4	2.918(9)	Ag8···Ag10#2	3.165(1)
Ag6-C17	2.103(9)	Ag1···Ag6#1	3.134(1)	Ag9···Ag10#2	3.086(1)
Ag4-C25	2.108(9)	Ag1···Ag2	3.138(1)	Ag3-O1W	2.396(7)
Ag3-C25#1	2.450(8)	Ag1···Ag10#1	3.367(1)	Ag9-O23	2.300(6)
Ag5-C33	2.499(9)	Ag2···Ag4	3.024(9)	Ag5-O24	2.395(7)

[a] Symmetry transformations used to generate equivalent atoms:

For **1**: #1 $-x + 0.5, -y + 1.5, -z + 2$; #2 $-x + 0.5, -y + 2.5, -z + 2$; #3 $x, y + 1, z$; #4 $x, y -1, z$.

For **2**: #1 $-x + 1, y, -z + 1.5$.

For **3**: #1 $-x + 1, y, -z + 1.5$.

For **5**: #1 $-x, y, -z + 1.5$.

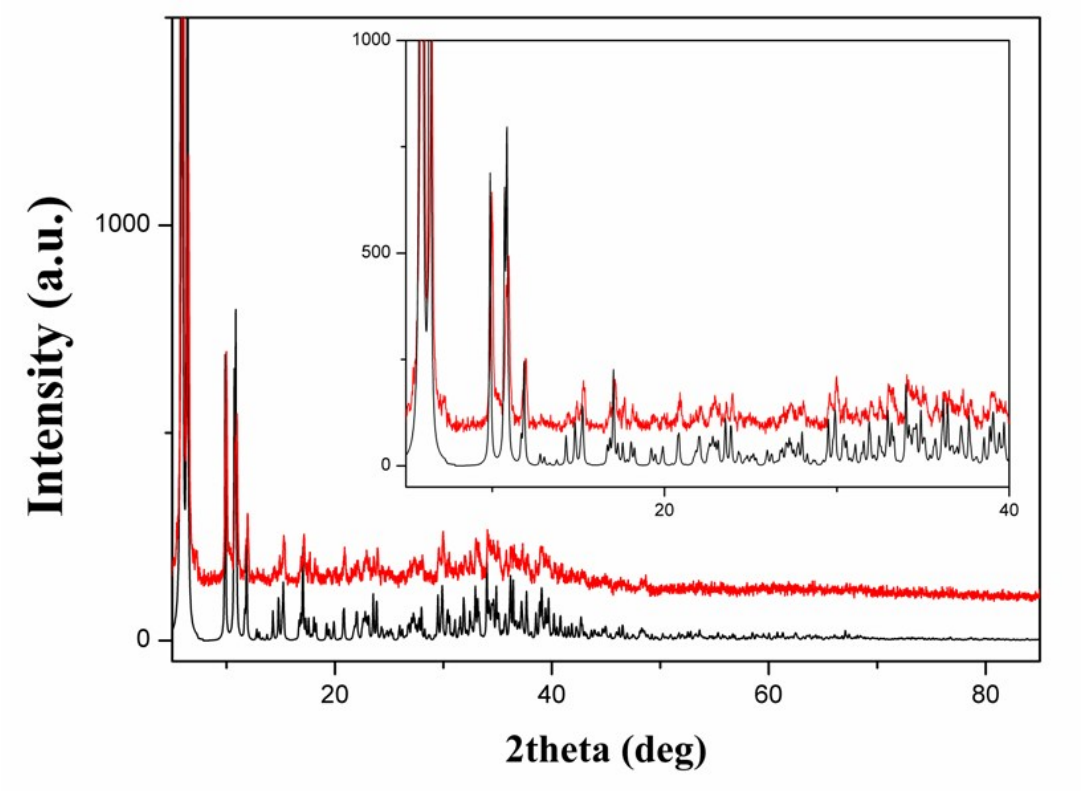
For **6**: #1 $-x + 1, -y + 2, -z + 1$; #2 $-x + 2, -y + 2, -z + 1$.

Table S3. Antibacterial and antifungal activities of **1-5** compared with gentamicin or amphotericin B.

The diameters of antibacterial or antifungal laps (mm)						
Bacterial species	**1**	**2**	**3**	**4**	**5**	Gentamicin
B. pumilus	11.5 ±0.5	11	11.7 ± 0.6	9.3 ± 0.6	12.3 ± 0.6	27 ± 1
B. subtilis	11.3 ± 0.6	10.3 ± 0.6	9.3 ± 0.6	9.2 ± 0.3	11.7 ± 0.6	26.8 ± 0.3
S. aureus	15.7 ± 0.6	13.3 ± 0.6	12.7 ± 0.63	13.3 ± 0.6	16.5 ± 0.5	15.2 ± 0.3
E. coli	17.7 ± 0.6	12.7 ± 0.6	14.5 ± 0.5	15.7 ± 1.2	18.8 ± 0.3	15.7 ± 0.6
Fungi species	**1**	**2**	**3**	**4**	**5**	Amphotericin B
A. niger	9.3 ± 0.6	8.8 ± 0.8	9.7 ± 0.6	8.7 ± 0.6	10.2 ± 0.3	12.3 ± 0.3
C. albicans	15.7 ± 1.2	15.8 ± 0.8	14.5 ± 0.5	12.7 ± 1.2	16.5 ± 1.5	16 ± 0.5

Gentamicin and amphotericin B are used as standards. The experiments are repeated three times, and the averages of inhibition zone values are taken.

Figure S1. Experimental (red) and simulated (black) X-ray powder diffraction patterns for **1**-**5**.



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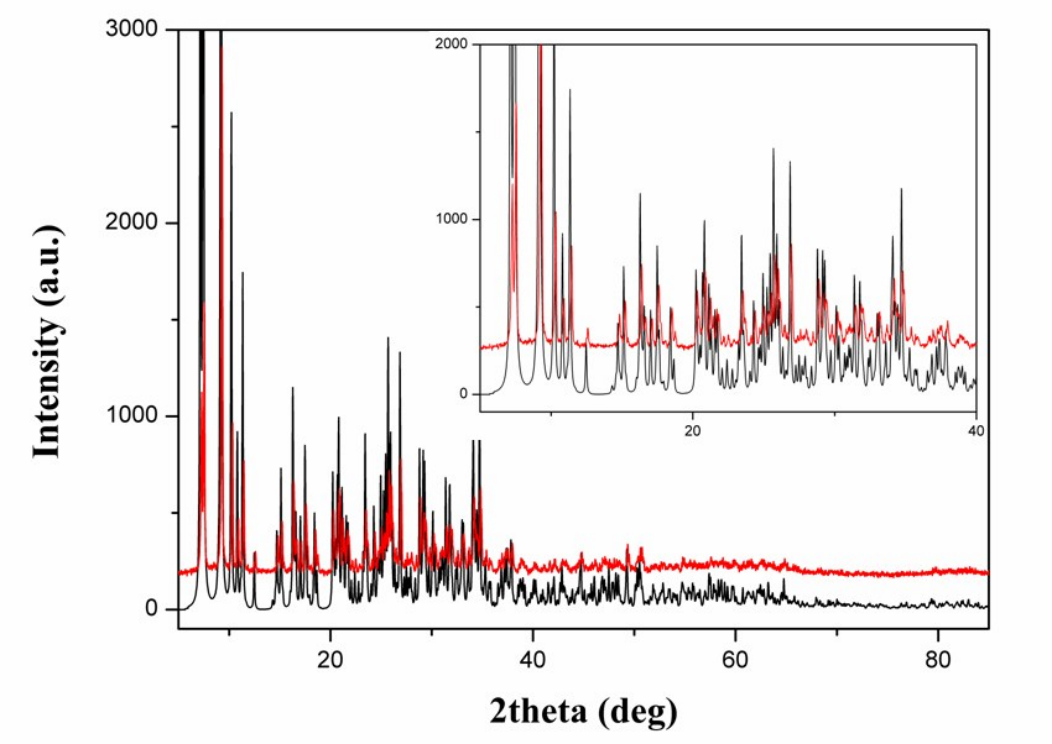
Intensity (a.u.)
2theta (deg)
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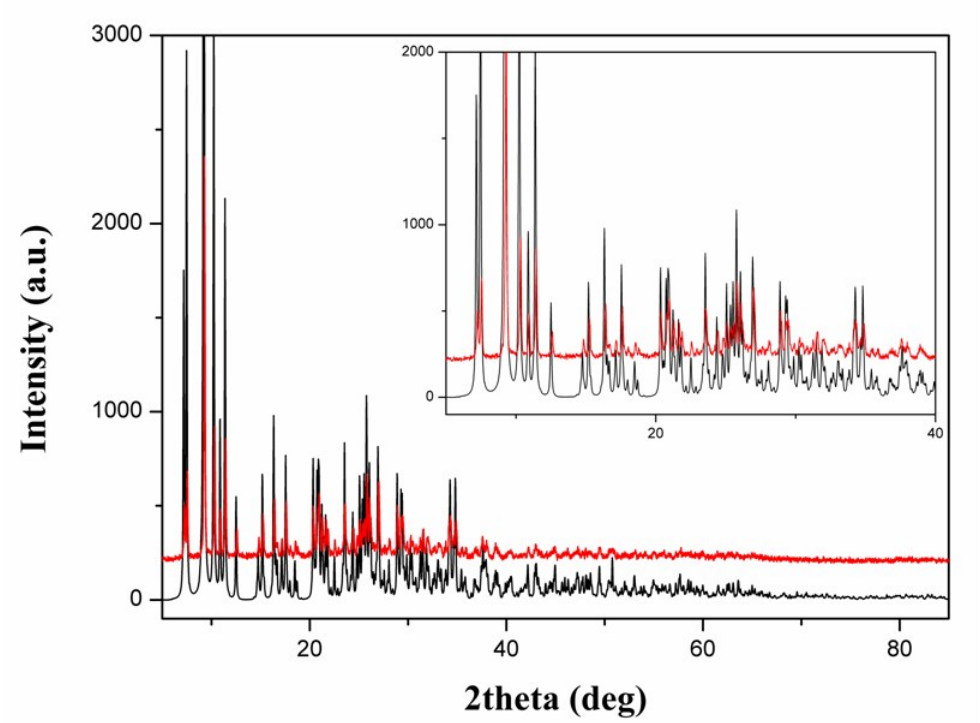
2000
1000
0
20
40
60
80

(**2**)


Intensity (a.u.)
2theta (deg)
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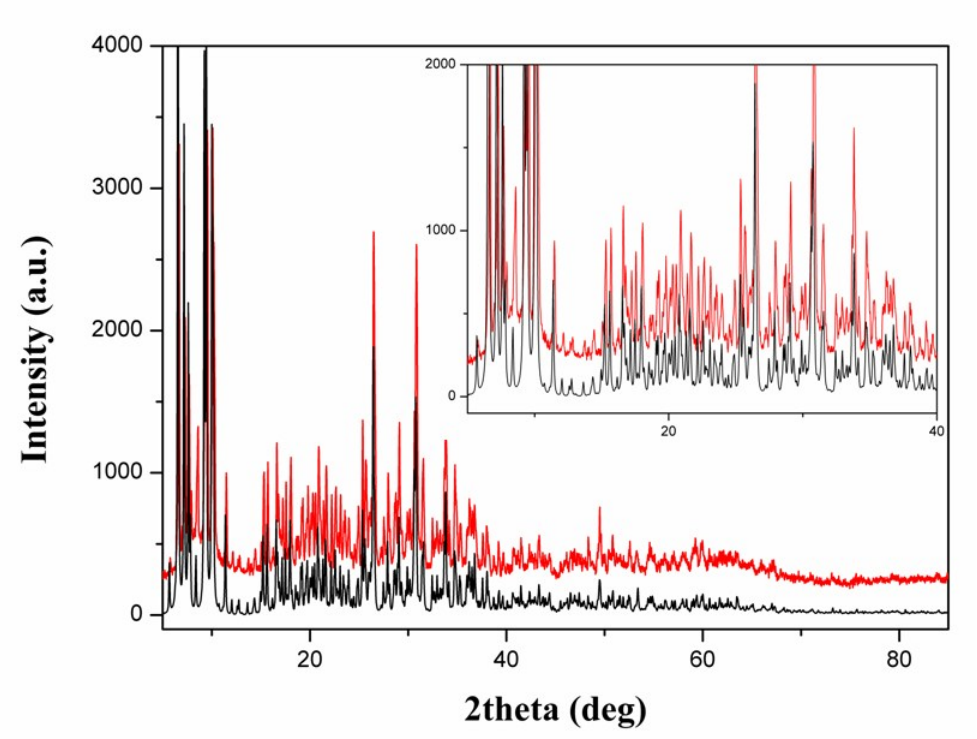
2000
1000
0
20
40
60
80

(**3**)


Intensity (a.u.)
2theta (deg)
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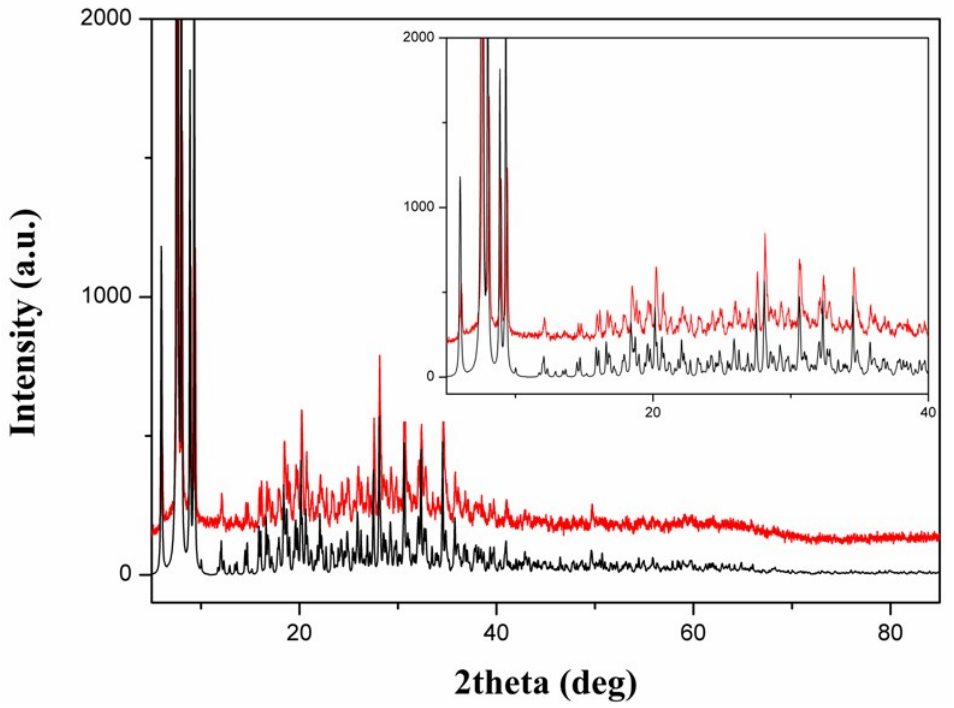
3000
2000
1000
0
20
40
60
80
2000
1000
0
20
40

(**4**)


Intensity (a.u.)
2theta (deg)
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1000
0
20
40
60
80
2000
1000
0
20
40

(**5**)

Figure S2. TGA curves for **1**-**5**.

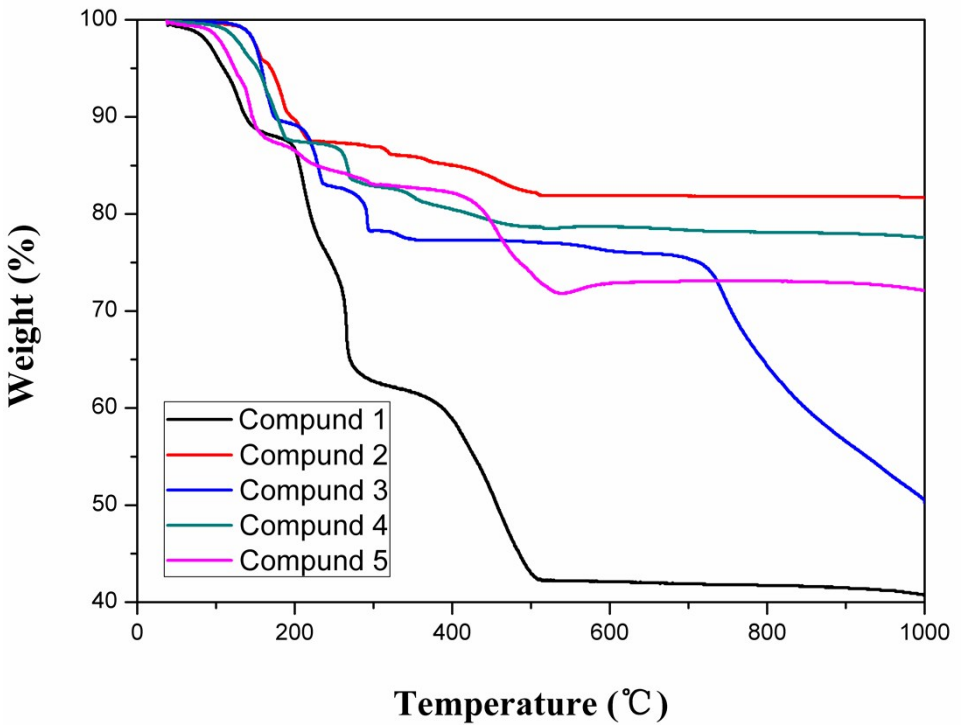
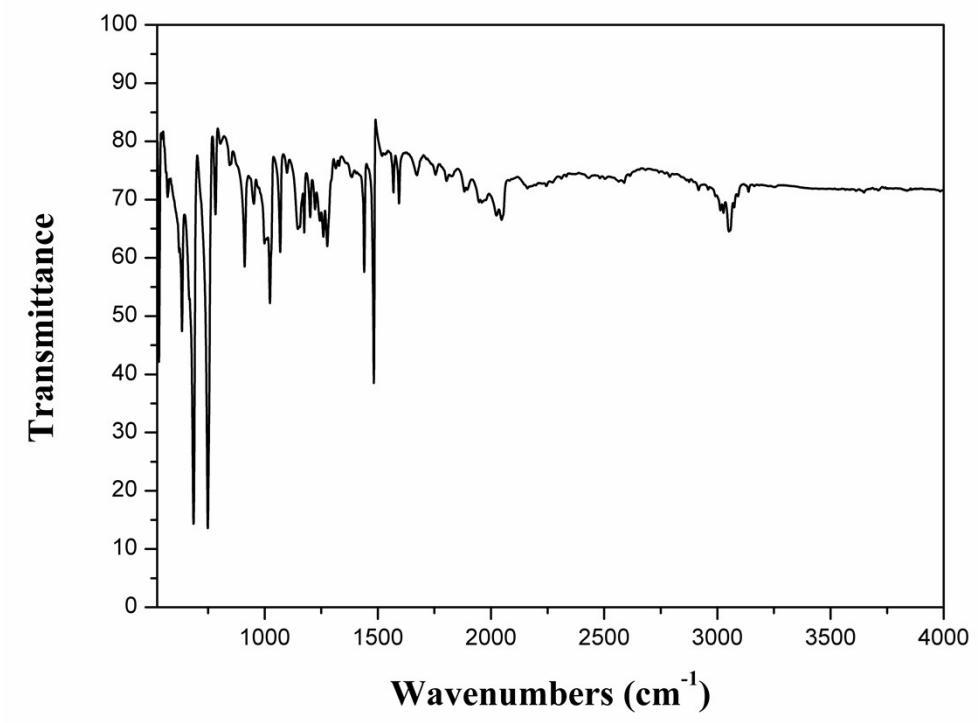
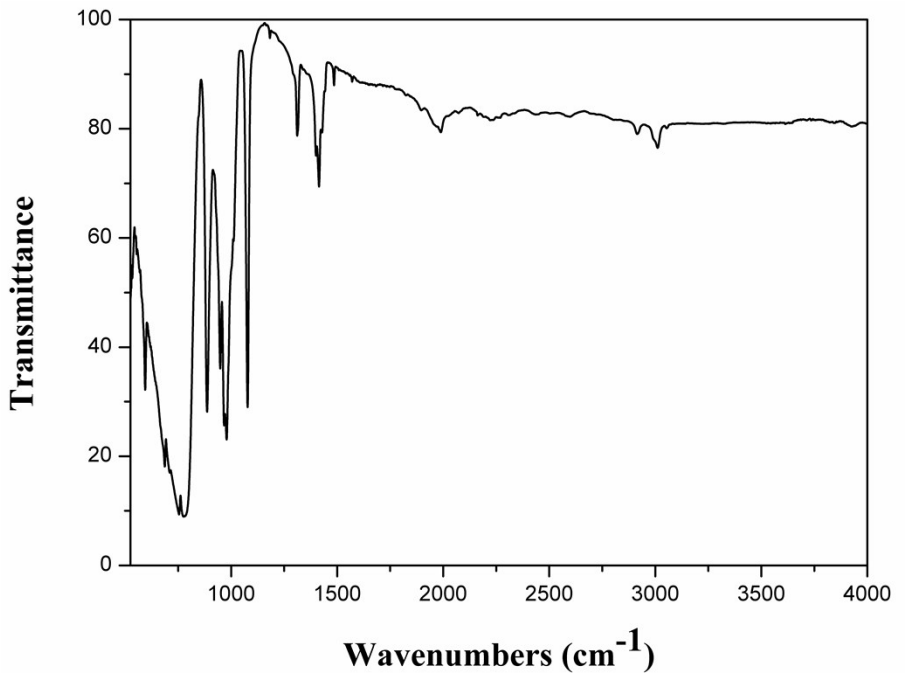


Figure S3. The infrared spectra of **1**-**5**.



(**1**)



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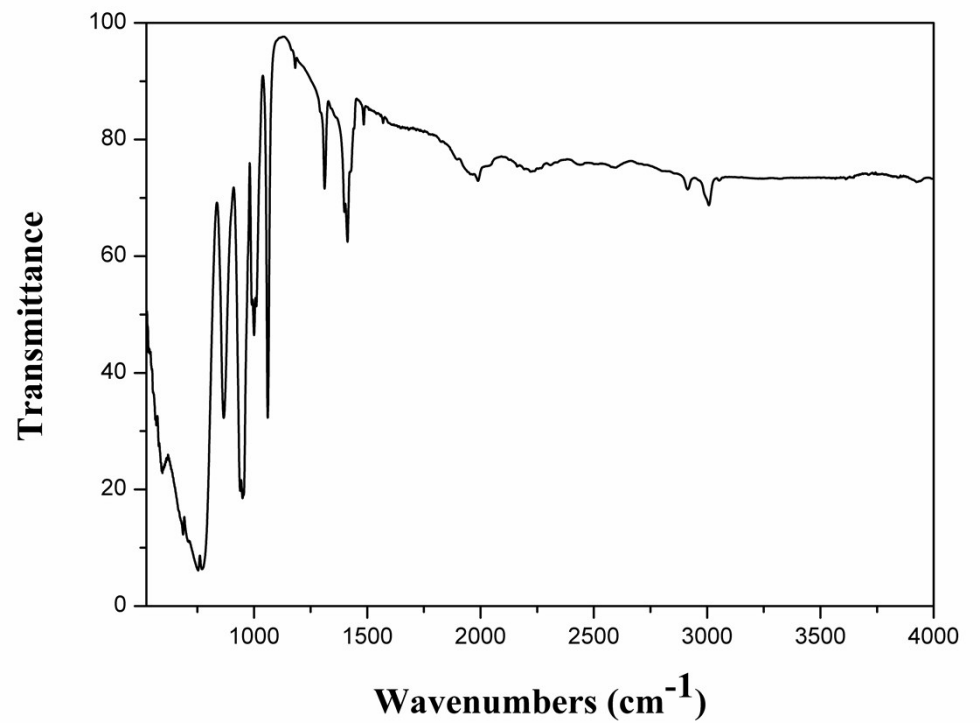
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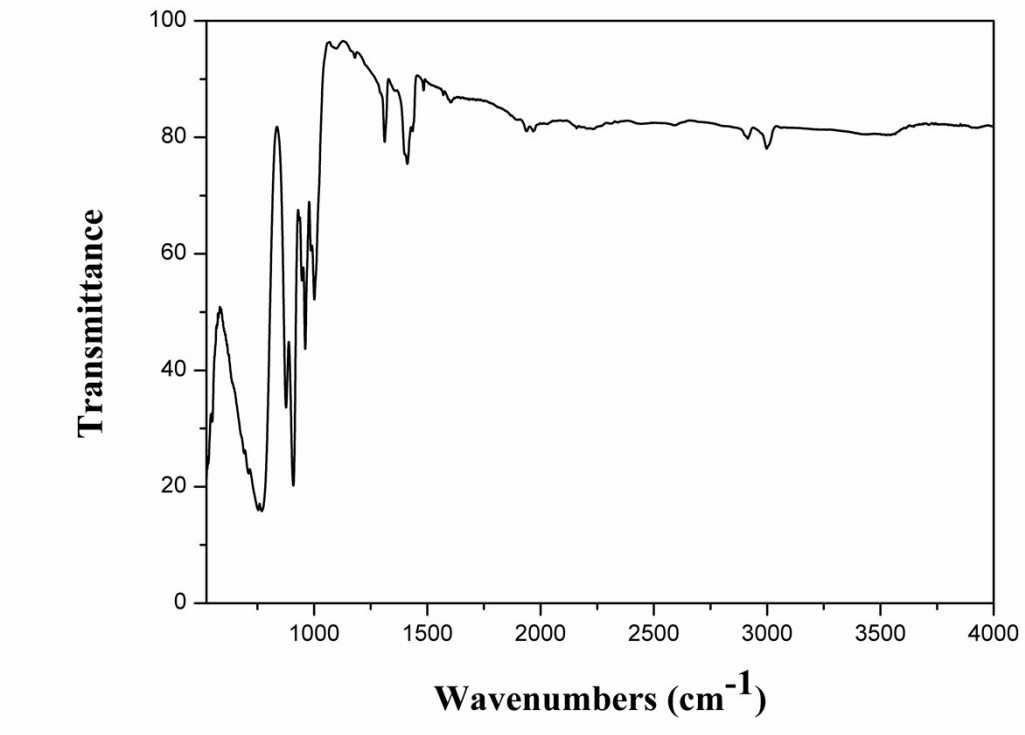
80
60
40
20
0
1000
1500
2000
2500
3000
3500
4000
Wavenumbers (cm-1)

(3)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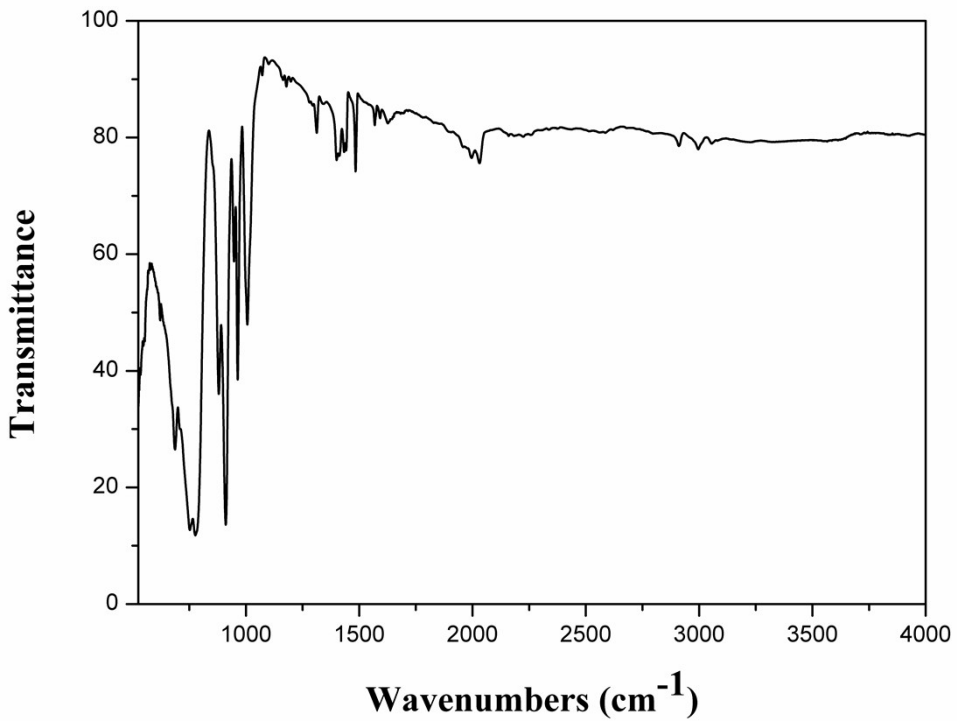
20
0
1000
1500
2000
2500
3000
3500
4000
Wavenumbers (cm-1)

(4)


Transmittance
100
80
60
40
20
0
1000
1500
2000
2500
3000
3500
4000
Wavenumbers (cm-1)

(**5**)

Figure S4. UV-visible absorption spectra of **1**-**5**.

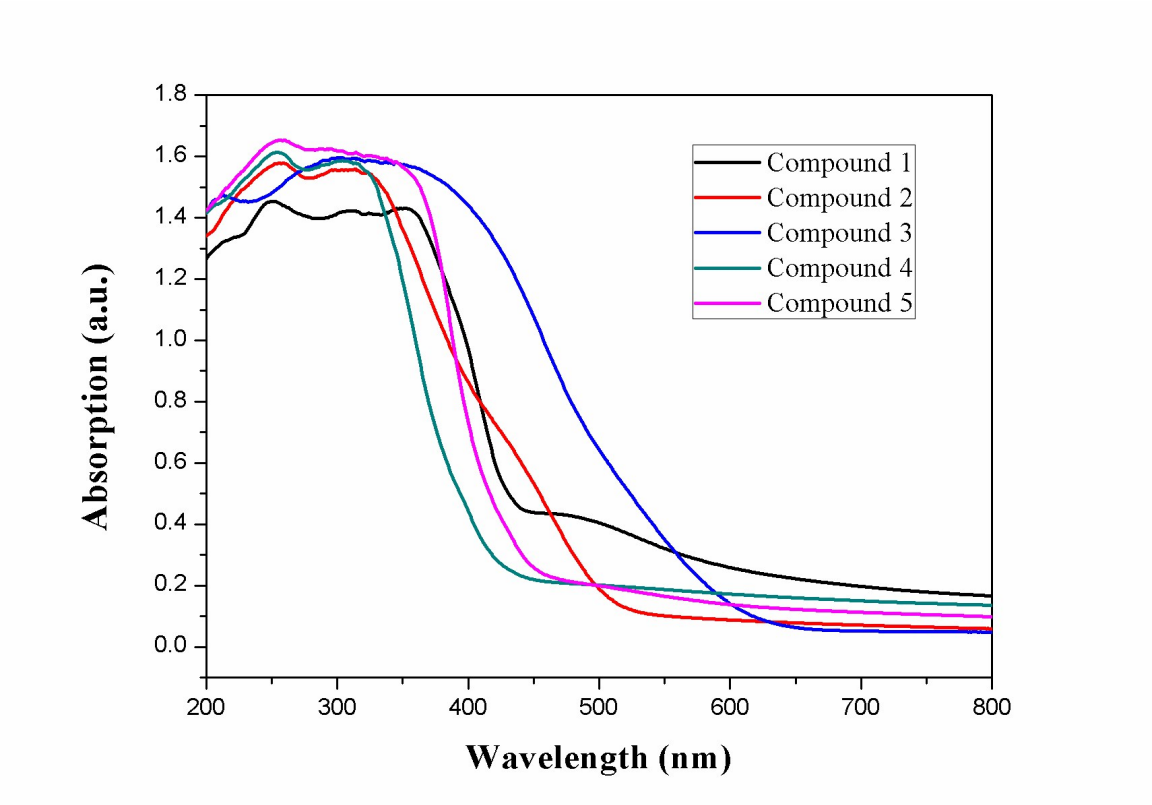
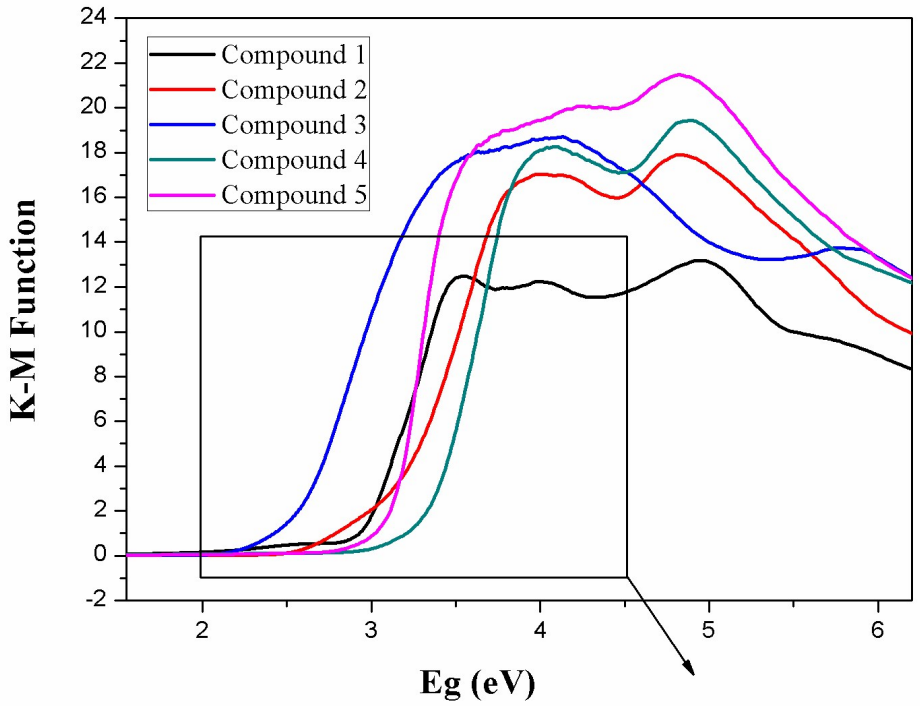
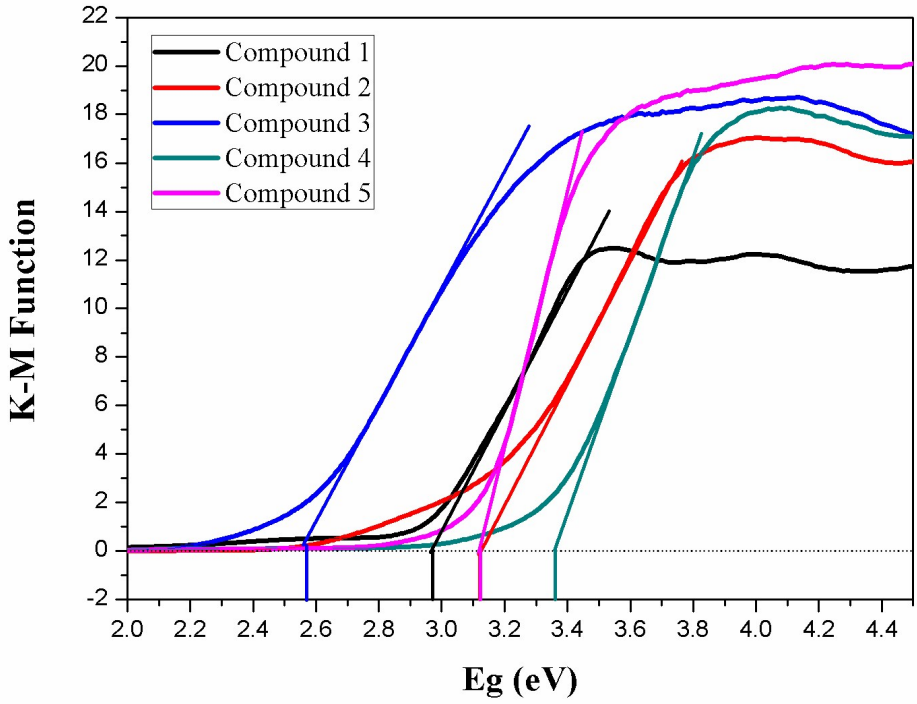


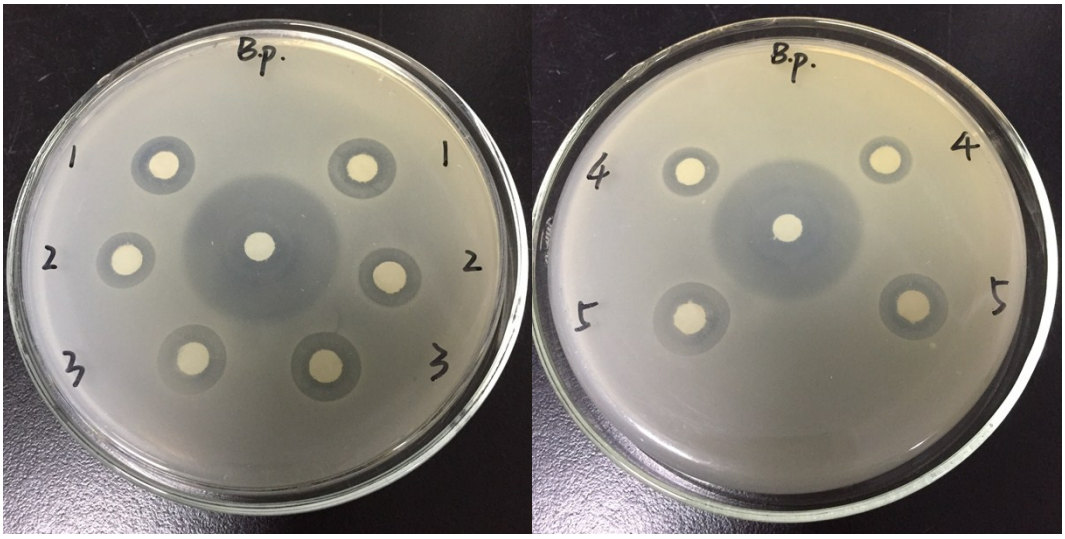
Figure S5. UV-visible diffuse reflectance spectra and optical band gaps of compounds **1**-**5**.



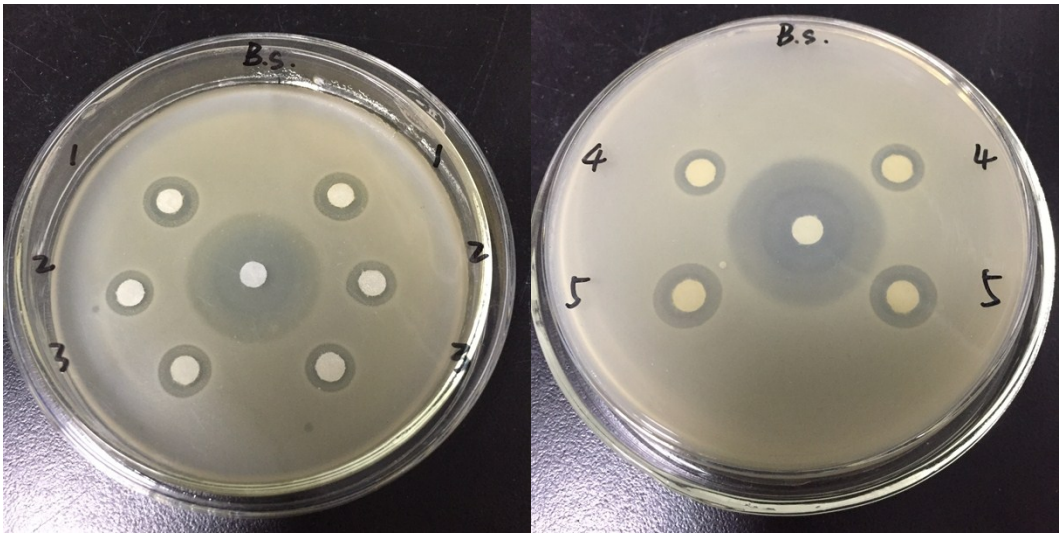


	Compound **1**	Compound **2**	Compound **3**	Compound **4**	Compound **5**
Band gap (eV)	2.96	3.12	2.56	3.36	3.12

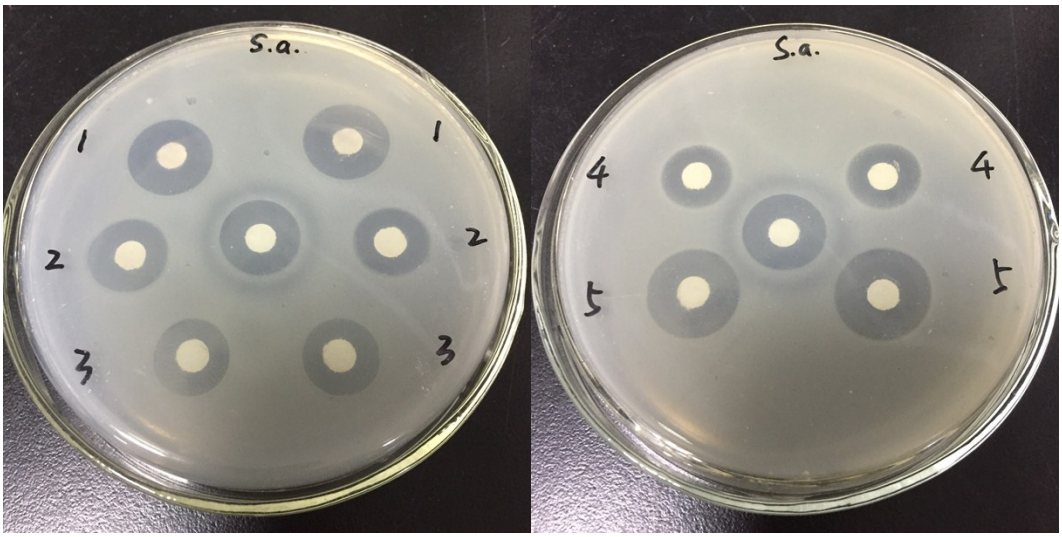
Figure S6. Optical photograph of antibacterial and antifungal tests of **1**-**5**, (a) *Bacillus pumilus*; (b) *Bacillus subtilis*; (c) *Staphylococcus aureus*; (d) *Escherichia coli*; (e) *Aspergillus niger*; (f) *Canidia albicans*.



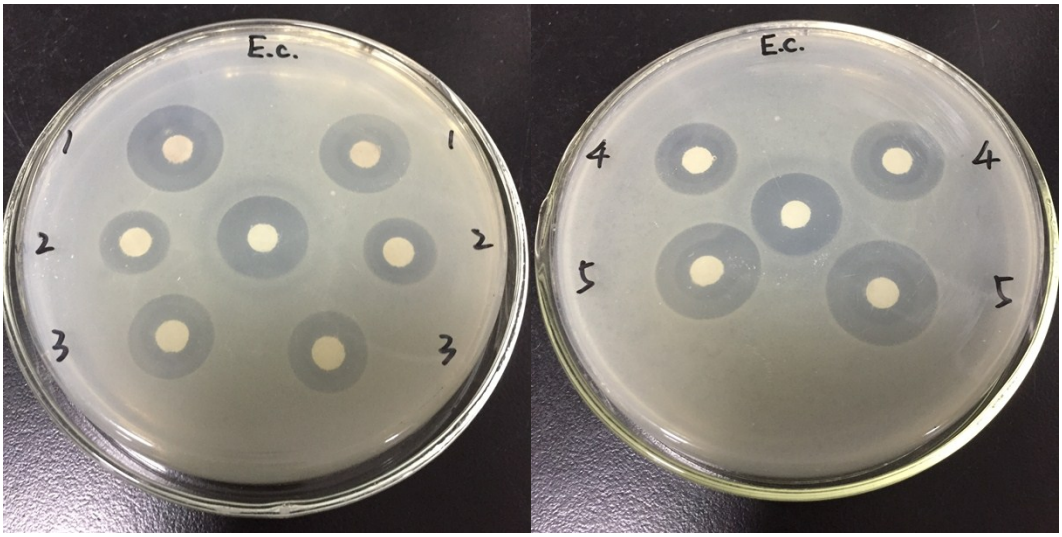
(a)



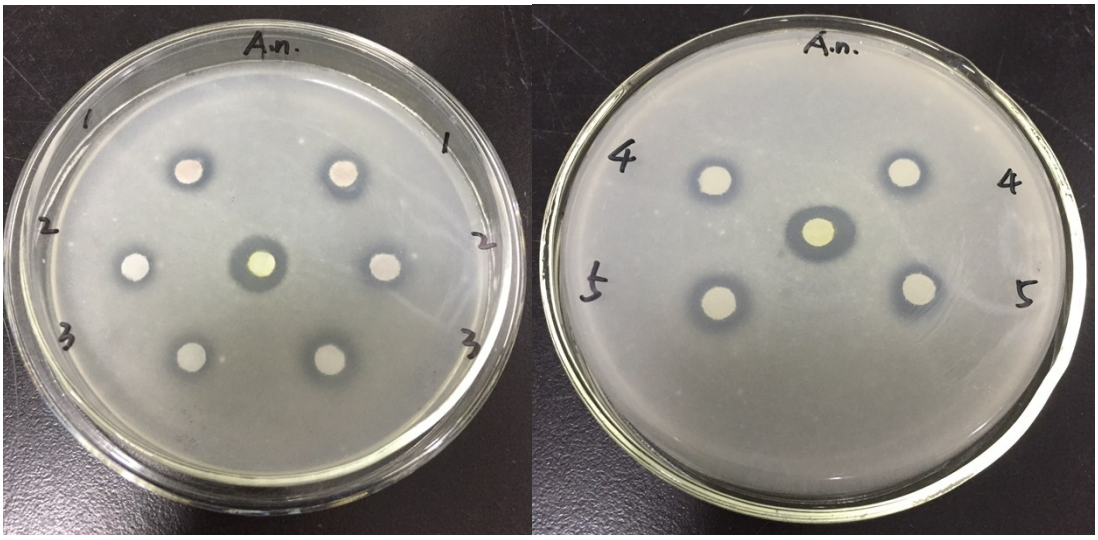
(b)



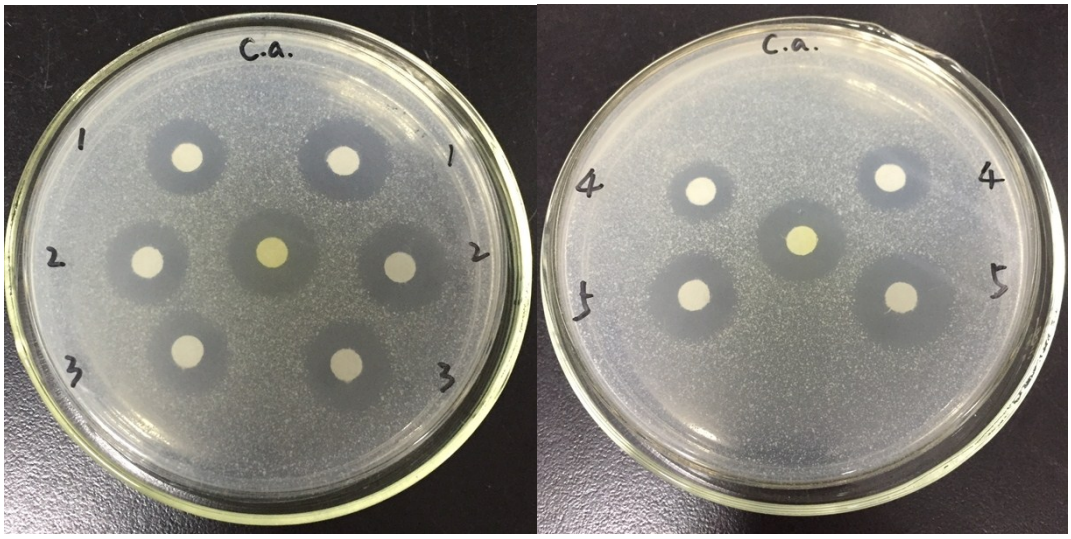
(c)



(d)

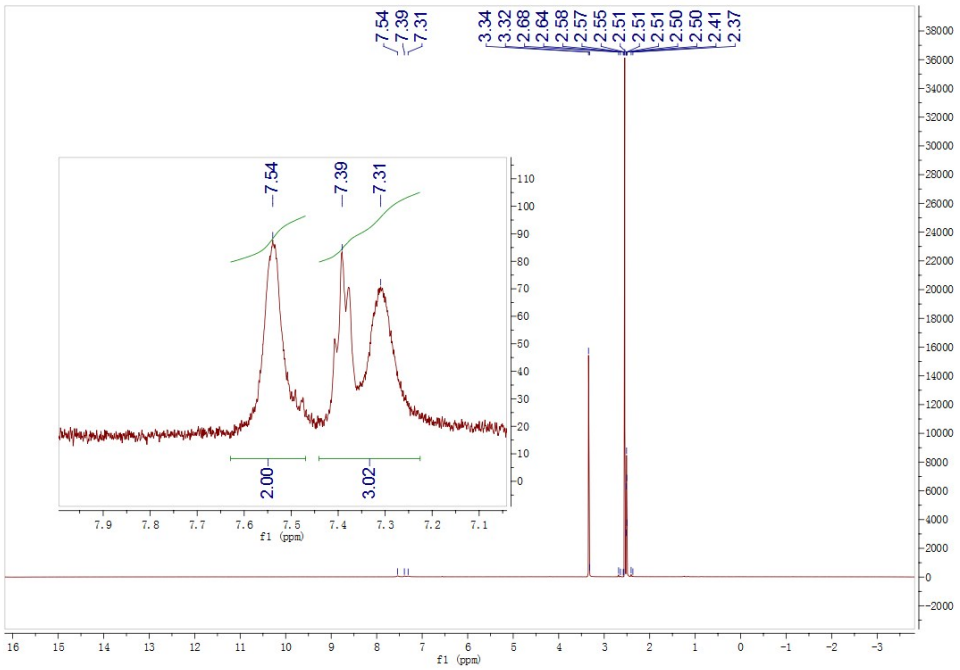


(e)

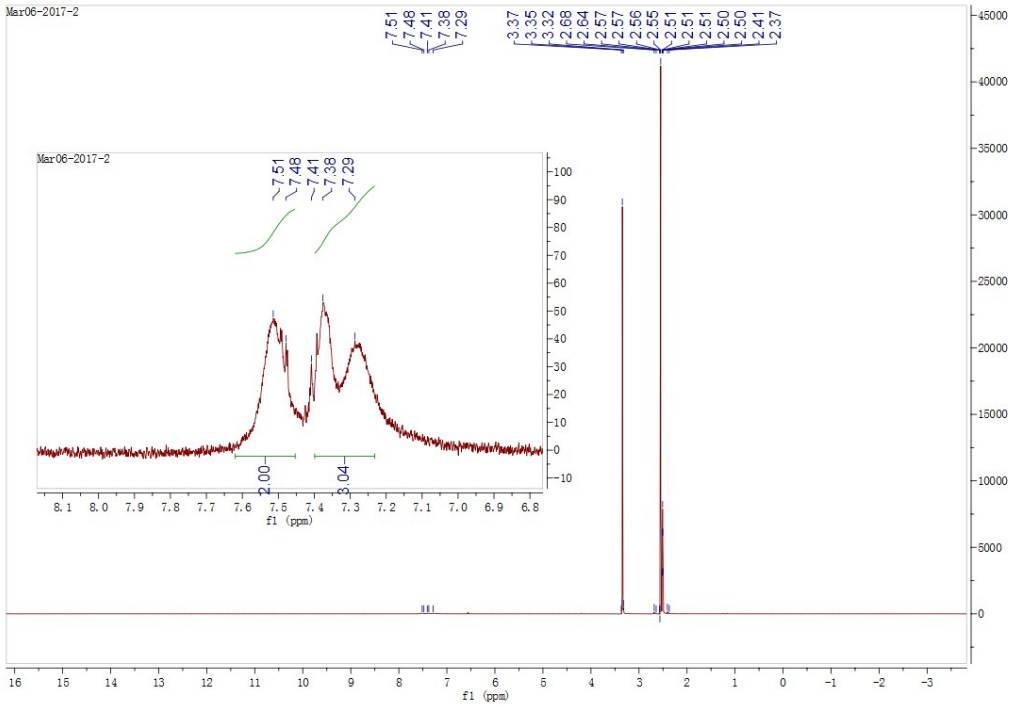


(f)

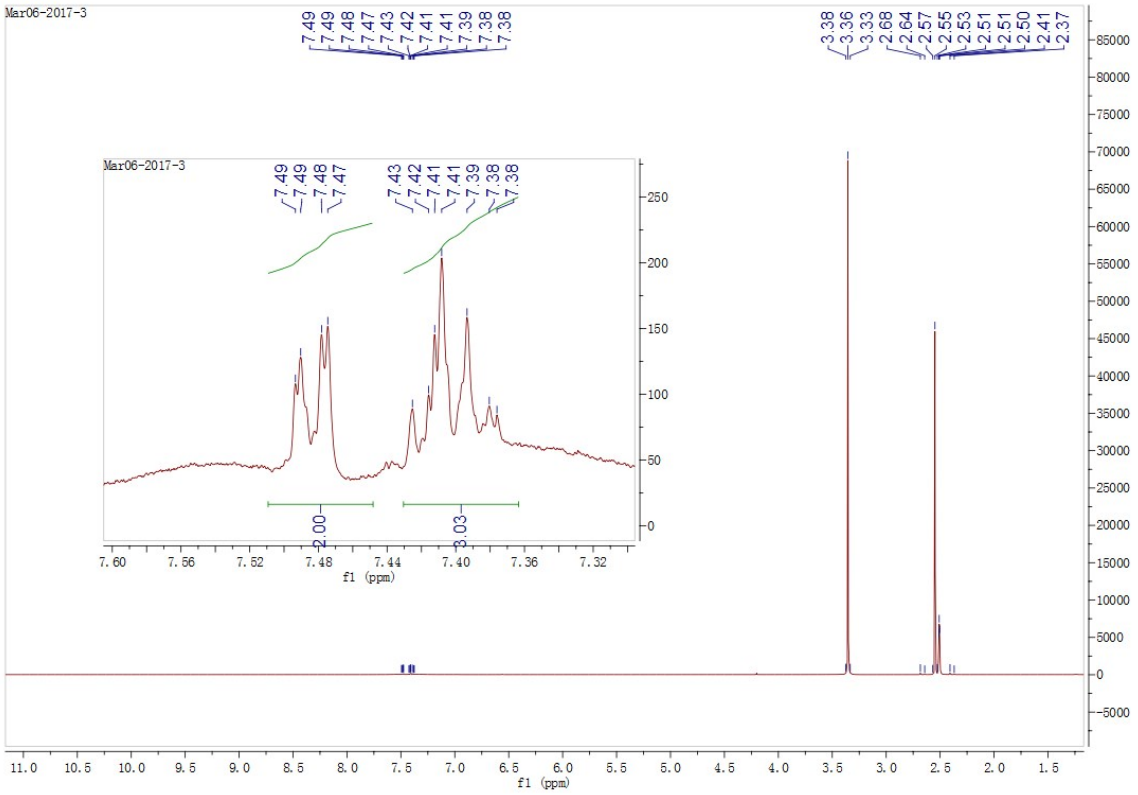
Figure S7. [1] H NMR spectra of compounds **1-5**.



(**1**)



(**2**)


Mar06-2017-3
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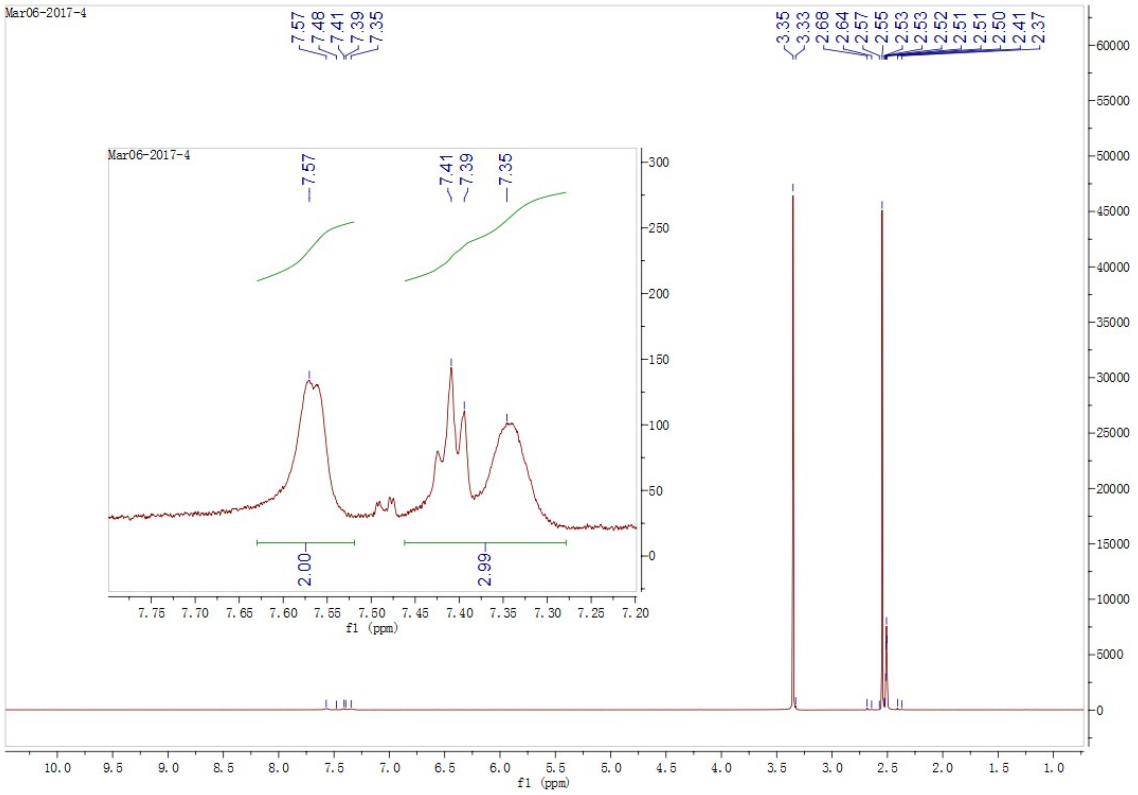
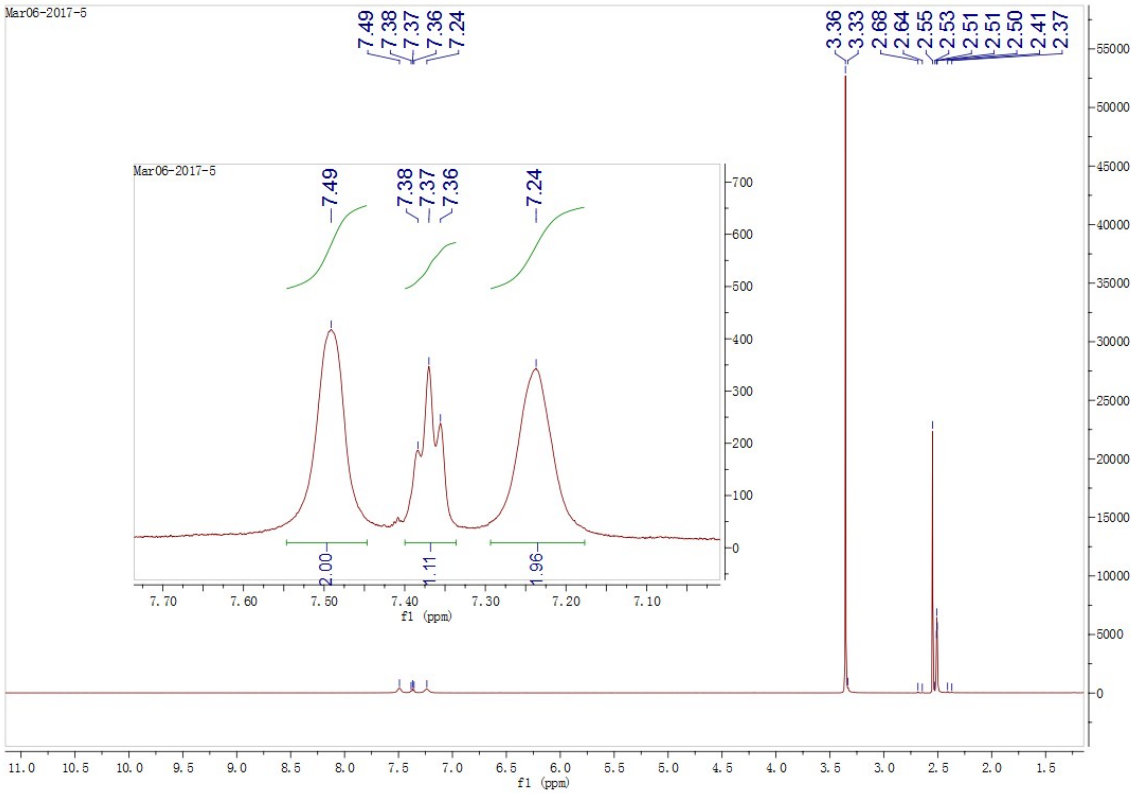
7.49
7.48
7.47
7.43
7.42
7.41
7.41
7.39
7.38
7.38
3.38
3.36
3.33
2.68
2.64
2.57
2.55
2.53
2.51
2.51
2.50
2.41
2.37
2.00
3.03
f1 (ppm)

(**3**)


Mar06-2017-4
7.57
7.48
7.41
7.39
7.35
3.35
3.33
2.68
2.64
2.57
2.55
2.53
2.53
2.52
2.51
2.51
2.50
2.41
2.37
Mar06-2017-4
7.57
7.41
7.39
7.35
2.00
2.99
f1 (ppm)
f1 (ppm)

(4)


Mar06-2017-5
7.49
7.38
7.37
7.36
7.24
3.36
3.33
2.68
2.64
2.55
2.53
2.51
2.51
2.50
2.41
2.37
2.00
1.11
1.96
f1 (ppm)

(**5**)