Electronic Supplementary Information

Tetrahedral Geometry Induction of Stable Ag-Ti Nanoclusters by Flexible Trifurcate TiL_3 Metalloligand

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Table S1. Crystal data and structure refinement summary for **Metalloligand**, **PTC-85** and **PTC-86**.

	Metalloligand	**PTC-85**	**PTC-86**
CCDC No	2009555	1948724	1948725
Cryst. Formula	$C_{25}H_{28}N_2O_9Ti$	$C_{85}H_{56}Ag_8O_{41}Ti_4$	$Ag_{12}C_{102}O_{37}S_6Ti_4H_{94}$
Mr	548.39	2787.86	3590.17
Crystal system	monoclinic	triclinic	triclinic
Space group	*P*21/*n*	*P*-1	*P*-1
a [Å]	11.612(11)	15.3597(3)	18.0120(5)
b [Å]	14.308(14)	17.7343(3)	18.6507(6)
c [Å]	15.523(15)	19.7875(4)	20.1759(7)
α[°]	90	86.465(2)	91.220(3)
β[°]	92.40(2)	86.261(2)	90.204(2)
γ[°]	90	80.762(2)	96.282(2)
V [Å^3]	2577(4)	5301.58(17)	6735.5(4)
Z	4	2	2
T [K]	293(2)	293(2)	293(2)
ρ_c[gcm^{-3}]	1.414	1.746	1.77
μ[mm^{-1}]	0.388	1.806	2.084
reflns coll.	17118	85846	50893
unique reflns	4262	37843	23131
GOF	0.944	0.956	1.159
*R*1[I>2σ(I)][a]	0.0645	0.0943	0.1096
w*R*2[I>2σ(I)][b]	0.1331	0.3366	0.3511

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2. Crystal data and structure refinement summary for **PTC-87** and **PTC-89**.

	PTC-87	**PTC-88**	**PTC-89**
CCDC No	1948726	1948728	1948727
Cryst. Formula	$Ag_{22}C_{120}O_{40}S_{13}Ti_4H_{132}$	$C_{146}H_{206}Ag_{42}O_{60}S_{26}Ti_4$	$C_{156}O_{44}S_{26}Ti_4Ag_{36}F_{12}H_{204}$
Mr	5195.72	8476.81	7919.98
Crystal system	monoclinic	tetragonal	cubic
Space group	*P*2$_1$/*c*	*I*4$_1$/*a*	*P*23
a [Å]	30.868(6)	30.2914(3)	17.9700(17)
b [Å]	20.036(3)	30.2914(3)	17.9700(17)
c [Å]	31.917(6)	27.4844(3)	17.9700(17)
α[°]	90.000(2)	90	90
β[°]	117.639(2)	90	90

γ[°]	90.000(3)	90	90
V [Å^3]	17487(6)	25218.9(4)	5802.9(16)
Z	4	4	1
T [K]	293(2)	100.01(13)	292.51(10)
ρ_c[gcm^{-3}]	1.974	2.233	2.266
μ[mm^{-1}]	2.787	29.006	3.388
reflns coll.	136900	11649	5510
unique reflns	39978	11649	3115
GOF	1.052	1.069	1.048
$R1$[I>2σ(I)][a]	0.0681	0.0539	0.0868
w$R2$[I>2σ(I)][b]	0.2388	0.1492	0.2781

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S3. ICP data for **PTC-85**, **PTC-86**, **PTC-87** and **PTC-89**.

	Calculated (weight ratio of Ti:Ag)	Experimental (weight ratio of Ti:Ag)
PTC-85	0.2219	0.2308
PTC-86	0.1479	0.1416
PTC-87	0.0807	0.0808
PTC-89	0.0493	0.0512

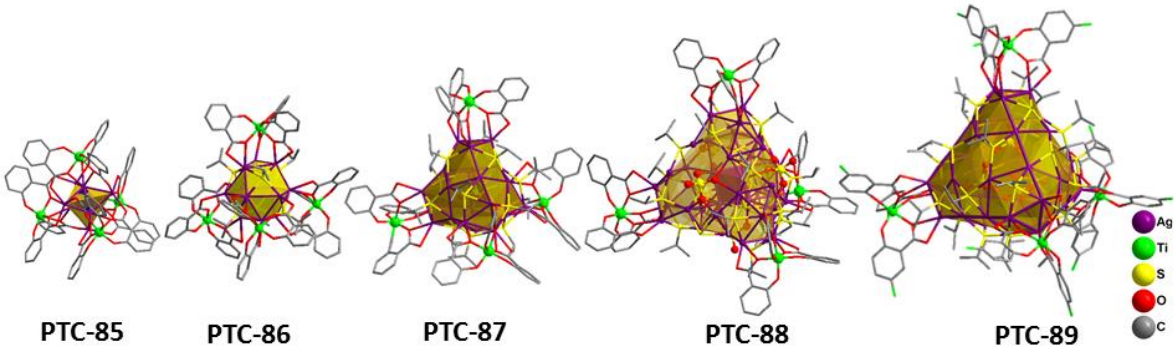

Figure S1. Molecular structures of **PTC-86** to **PTC-89.** H atoms have been omitted for clarity.

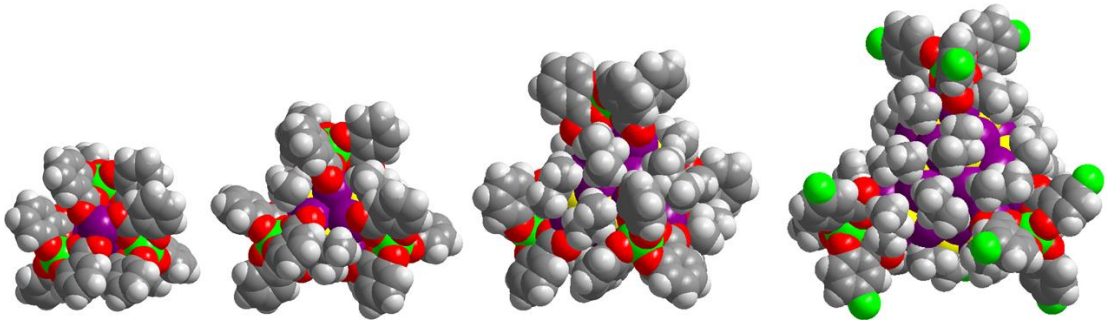

Figure S2. Space-filling representation of the molecular structures of **PTC-85, PTC-86, PTC-87** and **PTC-89.**

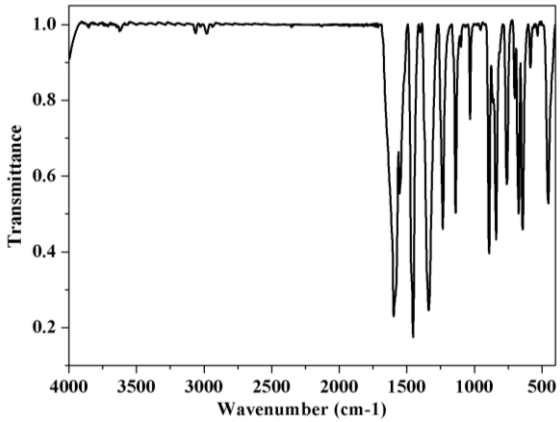

Figure S3. The FT-IR spectrum of **PTC-85.**

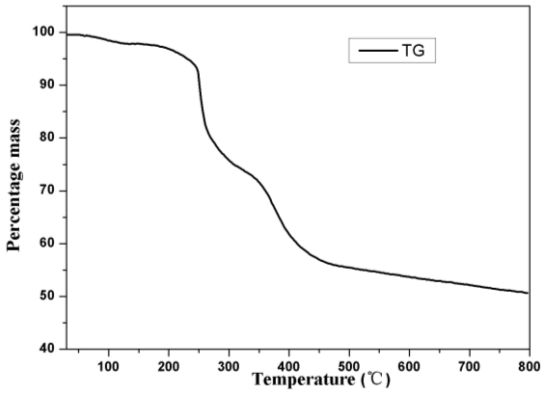

Figure S4. The TGA curve of **PTC-85.**

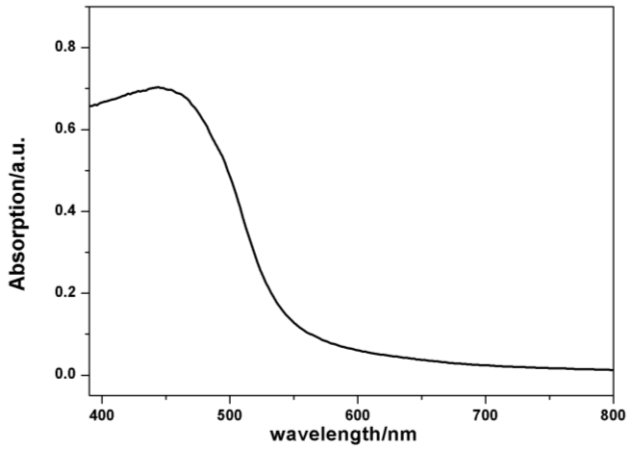

Figure S5. The solid state UV-vis absorption spectrum of **PTC-85**.

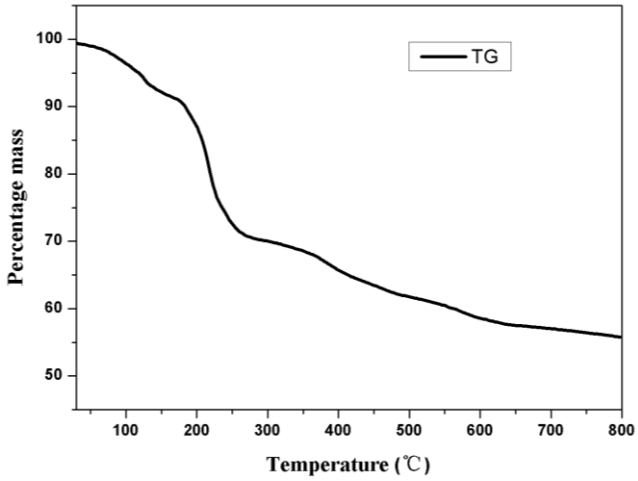

Figure S6. The TGA curve of **PTC-86.**

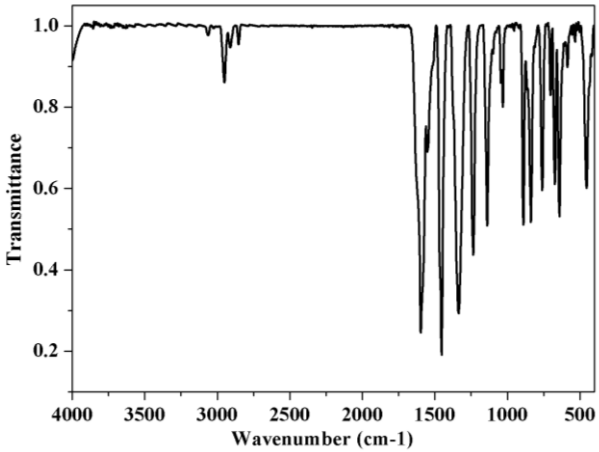

Figure S7. The FT-IR spectrum of **PTC-87.**

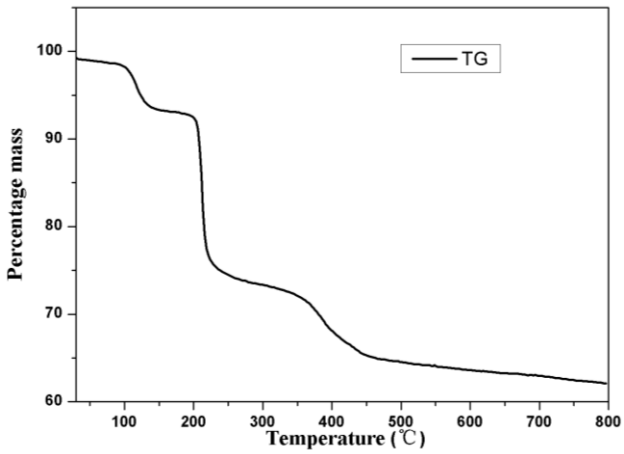

Figure S8. The TGA curve of **PTC-87.**

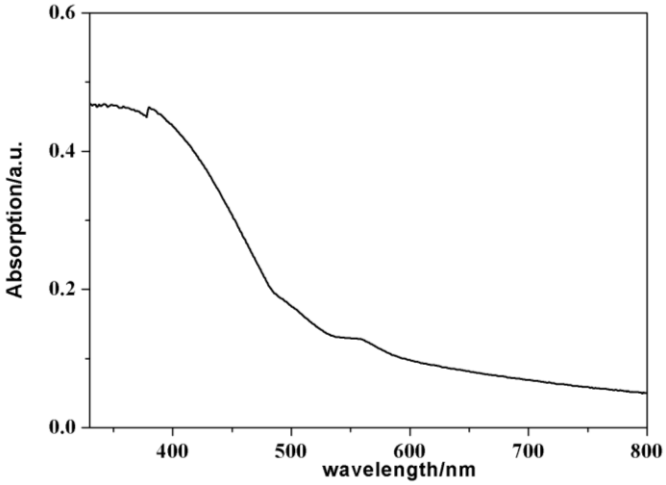

Figure S9. The solid state UV-vis absorption spectrum of **PTC-87**.

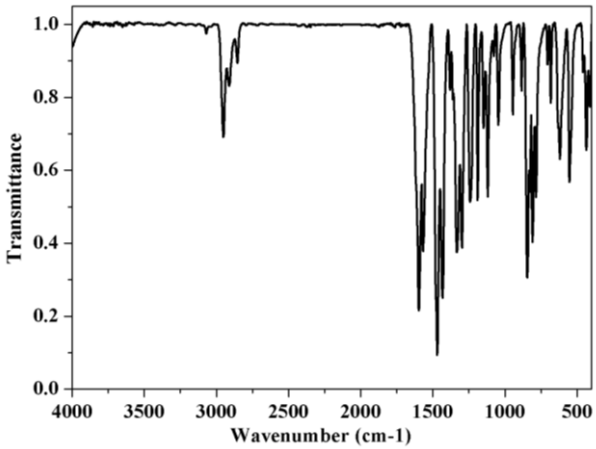

Figure S10. The FT-IR spectrum of **PTC-89.**

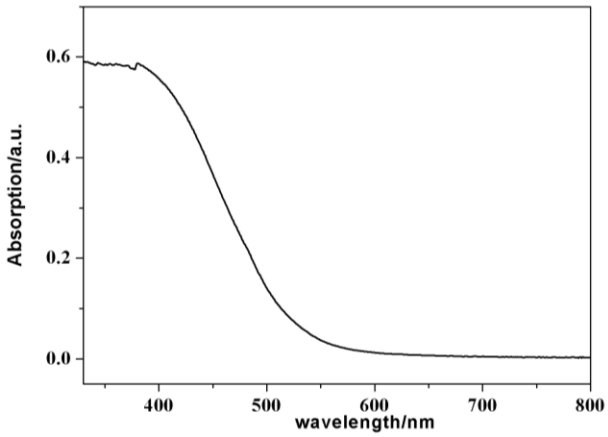

Figure S11. The solid state UV-vis absorption spectrum of **PTC-89**.

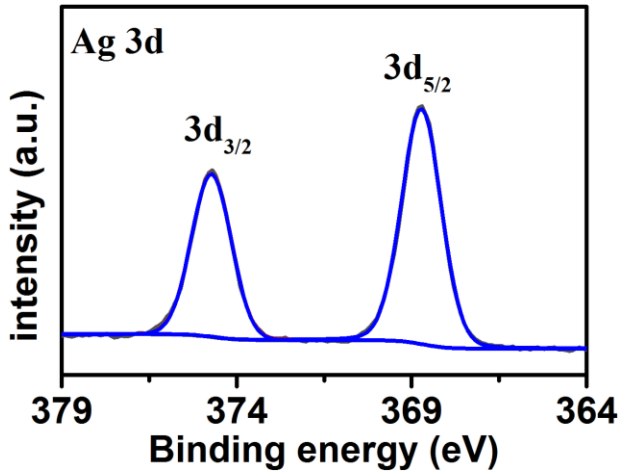

Figure S12. The Ag-3d high-resolution XPS spectrum of **PTC-85**.

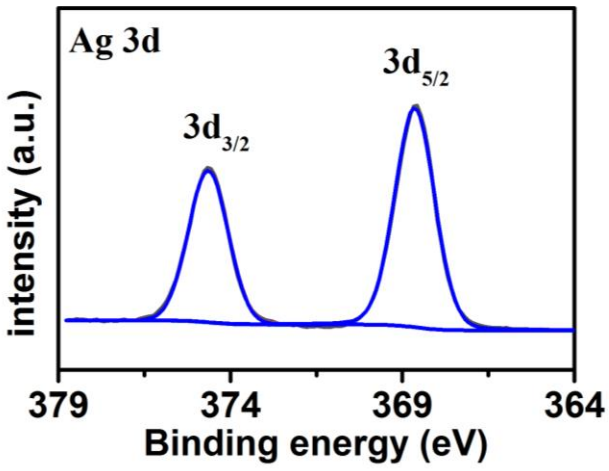

Figure S13. The Ag-3d high-resolution XPS spectrum of **PTC-87**.

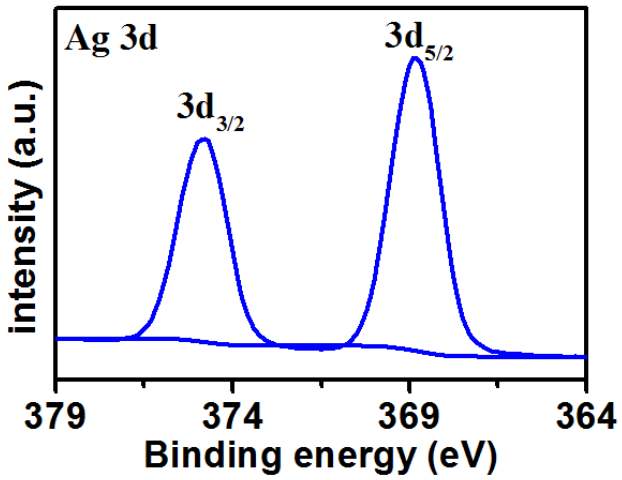

Figure S14. The Ag-3d high-resolution XPS spectrum of **PTC-89**.

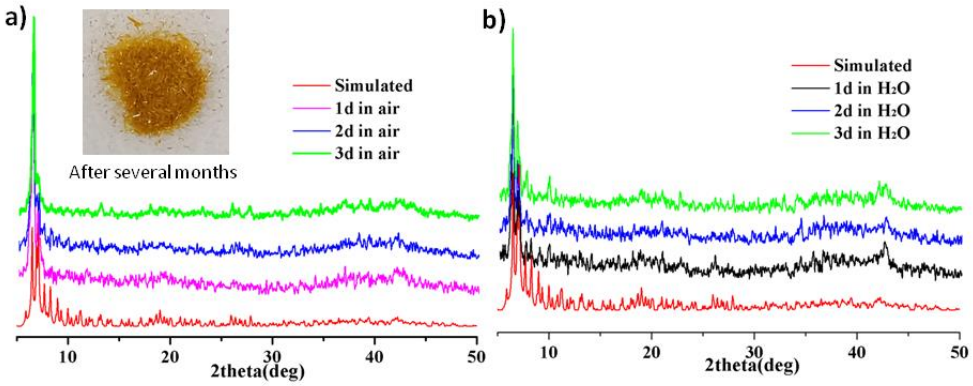

Figure S15. PXRD patterns for **PTC-85** in (a) air and (b) water. Inset: compound **PTC-85** in the air for several months.

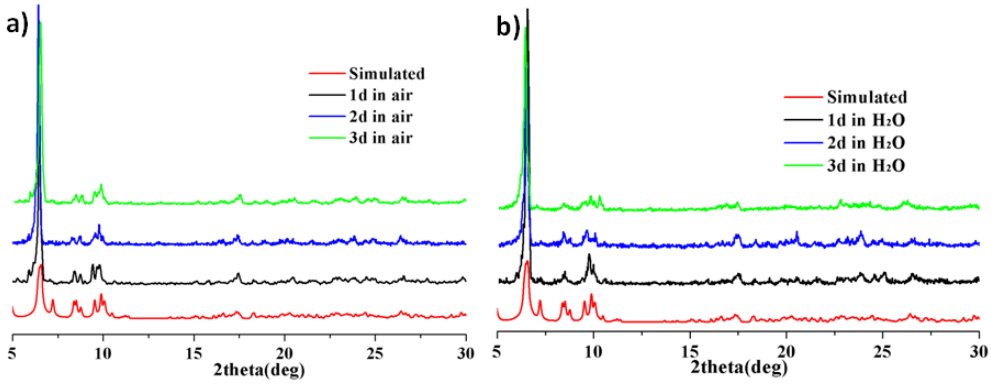

Figure S16. PXRD patterns for **PTC-86** in (a) air and (b) water.

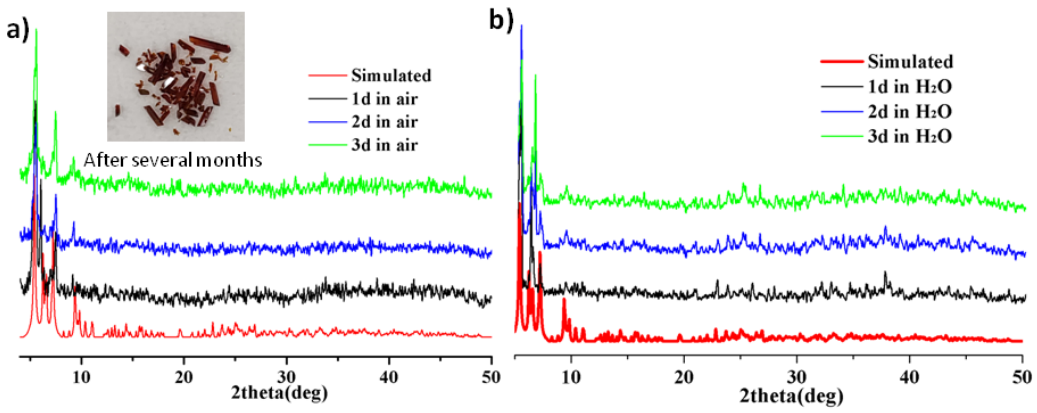

Figure S17. PXRD patterns for **PTC-87** in (a) air and (b) water. Inset: compound **PTC-87** in the air for several months.

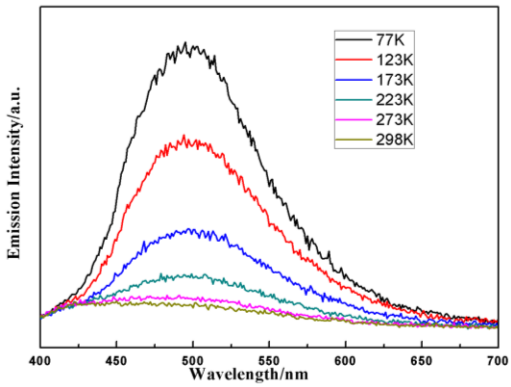

Figure S18. Luminescence spectra of **PTC-85** as a function of temperature from 77 to 298 K in the solid state for excitation at 340 nm.

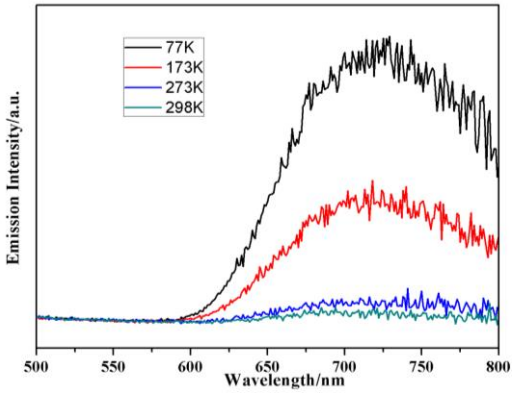

Figure S19. Luminescence spectra of **PTC-86** as a function of temperature from 77 to 298 K in the solid state for excitation at 365 nm.

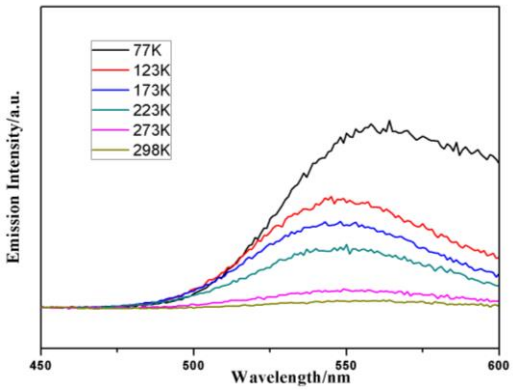

Figure S20. Luminescence spectra of **PTC-89** as a function of temperature from 77 to 298 K in the solid state for excitation at 350 nm.

Table S4. Selected bond distances (Å) for **PTC-85**.

Ag1	Ag2	2.7496(12)	Ag3	Ti4	3.277(2)
Ag1	Ag3	2.7609(12)	Ag3	O00S	2.425(8)
Ag1	Ag4	2.7478(13)	Ag3	O00T	2.496(8)
Ag1	Ag5	2.9579(13)	Ag3	O00V	2.433(7)
Ag1	Ag6	2.9764(13)	Ag4	Ag6	2.8945(13)
Ag1	Ag8	2.9450(13)	Ag4	Ag7	2.8935(14)
Ag1	Ti2	3.272(2)	Ag4	Ag8	2.9098(13)
Ag1	O00I	2.421(8)	Ag4	Ti3	3.297(2)
Ag1	O00L	2.442(7)	Ag4	O00K	2.475(7)
Ag1	O00N	2.451(7)	Ag4	O00M	2.469(8)
Ag2	Ag3	2.7601(11)	Ag4	O00Y	2.368(8)
Ag2	Ag4	2.7773(12)	Ag5	O00W	2.302(9)
Ag2	Ag5	2.9201(14)	Ag5	O010	2.282(8)
Ag2	Ag6	2.9212(13)	Ag5	O01E	2.290(9)
Ag2	Ag7	2.9230(14)	Ag6	O00X	2.264(9)
Ag2	Ti1	3.278(2)	Ag6	O011	2.267(8)
Ag2	O00F	2.471(7)	Ag6	O015	2.284(9)
Ag2	O00G	2.377(7)	Ag7	O00Z	2.316(9)
Ag2	O00O	2.527(7)	Ag7	O01A	2.318(8)
Ag3	Ag4	2.7529(12)	Ag7	O01J	2.359(11)
Ag3	Ag5	2.8908(13)	Ag8	O00U	2.346(9)

Ag3	Ag7	2.8705(14)	Ag8	O018	2.302(10)
Ag3	Ag8	2.8959(14)	Ag8	O019	2.313(9)

Table S5. Selected bond distances (Å) for **PTC-86**.

Ag1	Ag2	3.0765(15)	Ag6	S1	2.473(3)
Ag1	Ag4	3.1796(18)	Ag6	S4	2.477(4)
Ag1	Ag10	3.2553(19)	Ag6	O17	2.508(11)
Ag1	Ag12	3.150(2)	Ag7	Ag8	3.325(2)
Ag1	S2	2.444(3)	Ag7	Ag9	3.086(2)
Ag1	S3	2.422(3)	Ag7	Ag10	3.272(2)
Ag1	O8	2.509(9)	Ag7	S4	2.456(4)
Ag2	Ag3	3.0905(16)	Ag7	S6	2.467(4)
Ag2	Ag5	3.3143(18)	Ag7	O18	2.434(11)
Ag2	Ag12	3.183(2)	Ag8	Ag11	3.161(2)
Ag2	S2	2.448(3)	Ag8	S1	2.476(4)
Ag2	S5	2.475(4)	Ag8	S6	2.520(4)
Ag2	O26	2.317(11)	Ag8	O28	2.387(11)
Ag3	Ag5	3.2361(18)	Ag9	Ag10	3.316(2)
Ag3	Ag8	3.304(2)	Ag9	Ag11	3.319(2)
Ag3	Ag11	3.185(2)	Ag9	Ag12	3.261(2)
Ag3	S1	2.492(4)	Ag9	S3	2.443(4)
Ag3	S5	2.460(4)	Ag9	S6	2.481(4)
Ag3	O11	2.303(10)	Ag9	O7	2.558(9)
Ag4	Ag5	3.3664(17)	Ag9	O35	2.497(11)
Ag4	Ag6	3.0690(18)	Ag10	S3	2.510(4)
Ag4	S2	2.451(3)	Ag10	S4	2.468(4)
Ag4	S4	2.551(4)	Ag10	O3	2.310(12)
Ag4	O16	2.430(9)	Ag11	S5	2.537(4)
Ag5	Ag6	3.2905(18)	Ag11	S6	2.420(4)
Ag5	S1	2.497(3)	Ag11	O27	2.440(10)
Ag5	S2	2.553(3)	Ag12	S3	2.496(4)
Ag5	O30	2.350(12)	Ag12	S5	2.440(4)

Ag6	Ag7	3.1061(18)	Ag12	O31	2.375(13)
Ag6	Ag8	3.3621(19)			

Table S6. Selected bond distances (Å) for **PTC-87**.

Ag1	Ag6	2.9063(9)	Ag13	S4	2.634(2)
Ag1	Ag13	3.2309(10)	Ag13	S7	2.570(2)
Ag1	Ag17	3.2287(11)	Ag13	S13	2.596(2)
Ag1	Ag18	2.8539(10)	Ag14	Ag22	3.1277(11)
Ag1	S5	2.4157(19)	Ag14	S8	2.611(2)
Ag1	S7	2.4158(19)	Ag14	S9	2.5440(19)
Ag2	Ag3	2.8609(9)	Ag14	S12	2.582(2)
Ag2	Ag4	3.0752(10)	Ag15	S9	2.740(2)
Ag2	Ag6	3.1142(10)	Ag15	S10	2.447(2)
Ag2	S2	2.5048(18)	Ag15	O01B	2.430(4)
Ag2	S5	2.5509(19)	Ag15	O01N	2.430(6)
Ag2	O016	2.521(4)	Ag16	Ag20	3.0438(11)
Ag2	O01Q	2.393(6)	Ag16	S3	2.761(2)
Ag3	Ag8	3.1756(9)	Ag16	S8	2.469(2)
Ag3	Ag17	3.1809(11)	Ag16	O01P	2.411(5)
Ag3	Ag20	2.9109(10)	Ag16	O021	2.434(6)
Ag3	S2	2.4091(19)	Ag17	S5	2.571(2)
Ag3	S6	2.3983(19)	Ag17	S6	2.565(2)
Ag4	Ag6	3.0494(11)	Ag17	S11	2.615(2)
Ag4	Ag10	2.8704(9)	Ag18	Ag19	3.0498(11)
Ag4	S2	2.5697(19)	Ag18	Ag21	3.1339(13)
Ag4	S4	2.505(2)	Ag18	S7	2.771(2)
Ag4	O014	2.512(5)	Ag18	S11	2.437(2)
Ag4	O01Z	2.403(6)	Ag18	O01X	2.275(5)

Ag5	Ag8	3.1231(11)	Ag19	Ag21	3.1425(13)
Ag5	Ag14	3.3538(10)	Ag19	S11	2.618(2)
Ag5	Ag15	2.9151(10)	Ag19	S12	2.453(2)
Ag5	Ag16	2.8486(11)	Ag19	O019	2.562(5)
Ag5	S3	2.3998(19)	Ag19	O01T	2.371(6)
Ag5	S9	2.3856(19)	Ag20	S3	2.4173(19)
Ag6	S4	2.584(2)	Ag20	S6	2.853(2)
Ag6	S5	2.507(2)	Ag20	O023	2.258(6)
Ag6	O01V	2.344(5)	Ag21	Ag22	2.9265(11)
Ag7	Ag11	2.9549(10)	Ag21	S7	2.439(2)
Ag7	Ag14	3.1616(10)	Ag21	S12	2.651(2)
Ag7	Ag17	3.1922(10)	Ag21	O01C	2.547(5)
Ag7	Ag19	2.9510(10)	Ag21	O01O	2.357(6)
Ag7	S8	2.4055(18)	Ag22	S12	2.411(2)
Ag7	S11	2.4187(19)	Ag22	S13	2.446(2)
Ag8	Ag10	3.3015(11)	Ti1	O014	2.038(5)
Ag8	S2	2.5873(18)	Ti1	O016	2.006(5)
Ag8	S3	2.604(2)	Ti1	O018	2.036(5)
Ag8	S10	2.540(2)	Ti1	O01E	1.855(5)
Ag9	Ag12	3.0427(11)	Ti1	O01I	1.840(5)
Ag9	Ag15	3.0372(11)	Ti1	O01J	1.868(5)
Ag9	Ag22	2.8710(11)	Ti2	O01A	1.865(5)
Ag9	S9	2.473(2)	Ti2	O01B	2.059(5)
Ag9	S13	2.551(2)	Ti2	O01G	1.861(5)
Ag9	O01L	2.491(4)	Ti2	O01K	1.863(5)
Ag9	O01U	2.423(6)	Ti2	O01L	2.003(5)
Ag10	Ag12	3.0378(10)	Ti2	O01S	2.050(5)
Ag10	Ag13	3.0041(10)	Ti3	O015	2.019(5)

Ag10	S4	2.429(2)	Ti3	O019	2.040(5)
Ag10	S10	2.411(2)	Ti3	O01C	2.036(5)
Ag11	Ag16	3.0975(12)	Ti3	O01D	1.874(6)
Ag11	Ag20	3.1929(12)	Ti3	O01H	1.861(6)
Ag11	S6	2.4210(19)	Ti3	O01W	1.877(6)
Ag11	S8	2.738(2)	Ti4	O01F	2.024(6)
Ag11	O017	2.323(5)	Ti4	O01M	2.043(6)
Ag12	Ag15	3.0333(11)	Ti4	O01P	2.036(6)
Ag12	S10	2.682(2)	Ti4	O01R	1.882(6)
Ag12	S13	2.484(2)	Ti4	O020	1.878(7)
Ag12	O01Y	2.271(6)	Ti4	O026	1.852(7)
Ag13	Ag22	3.0959(11)			

Table S7. Selected bond distances (Å) for **PTC-88**.

Ag1	Ag2	2.8447(8)	Ag6	S20	2.544(3)
Ag1	Ag2[1]	3.1057(8)	Ag6	S22	2.521(3)
Ag1	Ag2[2]	2.8447(8)	Ag6	O26[3]	2.477(7)
Ag1	Ag2[3]	3.1057(8)	Ag7	Ag8	3.0179(12)
Ag1	Ag10	2.9267(17)	Ag7	S14	2.457(2)
Ag1	Ag10[2]	2.9267(17)	Ag7	S20	2.524(2)
Ag1	Ag12[2]	3.0646(17)	Ag7	O46	2.579(7)
Ag1	Ag12	3.0647(17)	Ag7	O45	2.411(9)
Ag1	S19[2]	2.474(2)	Ag8	S14	2.441(2)
Ag1	S19	2.474(2)	Ag8	S22	2.475(2)
Ag1	Ag0A	3.348(2)	Ag9	S20	2.427(3)
Ag1	Ag0A[2]	3.347(2)	Ag9	S22[1]	2.473(3)
Ag2	Ag1[3]	3.1057(8)	Ag10	Ag11	2.961(2)
Ag2	Ag2[1]	2.9313(10)	Ag10	Ag12	2.798(3)
Ag2	Ag2[3]	2.9313(10)	Ag10	S14	2.523(3)

Ag2	Ag5[1]	2.8876(9)	Ag10	S19[2]	2.720(2)
Ag2	Ag6[2]	2.9757(11)	Ag10	S21	2.542(2)
Ag2	S19	2.541(2)	Ag10	O27[2]	2.288(11)
Ag2	S19[3]	2.502(2)	Ag11	Ag12	1.338(2)
Ag2	O25	2.461(8)	Ag11	S18	2.520(3)
Ag3	Ag4	3.0993(9)	Ag11	S21	2.3783(14)
Ag3	Ag7	3.0273(10)	Ag11	Ag0A	2.892(3)
Ag3	Ag10	3.1916(17)	Ag12	S18	2.459(3)
Ag3	Ag11	3.0107(16)	Ag12	S21	2.666(2)
Ag3	S14	2.556(2)	Ag12	O27	1.919(12)
Ag3	S18	2.447(2)	Ag12	Ag0A	2.953(3)
Ag3	O36	2.407(6)	Ti13	O35	2.019(7)
Ag3	Ag0A	3.053(2)	Ti13	O47	1.877(7)
Ag4	Ag5	3.1275(10)	Ti13	O46	2.027(8)
Ag4	Ag7	3.0702(12)	Ti13	O54	2.015(7)
Ag4	Ag9	3.0346(9)	Ti13	O56	1.869(9)
Ag4	S18	2.512(2)	Ti13	O37	1.855(7)
Ag4	S20	2.450(2)	S14	Ag0A	2.402(3)
Ag4	O48	2.434(8)	S19	Ag2[1]	2.502(2)
Ag4	O54	2.587(6)	S19	Ag5[2]	2.648(2)
Ag5	Ag2[3]	2.8875(9)	S19	Ag6[2]	2.639(2)
Ag5	Ag6[1]	3.3652(9)	S19	Ag10[2]	2.720(2)
Ag5	Ag9	2.9634(12)	S21	Ag10[2]	2.542(2)
Ag5	Ag12	2.8593(16)	S21	Ag11[2]	2.3783(14)
Ag5	S18	2.5470(19)	S21	Ag12[2]	2.666(2)
Ag5	S19[2]	2.648(2)	S21	Ag0A	2.421(2)
Ag5	S22[1]	2.541(2)	S21	Ag0A[2]	2.421(2)
Ag5	O26	2.492(8)	S22	Ag5[3]	2.540(2)
Ag6	Ag2[2]	2.9757(11)	S22	Ag9[3]	2.473(3)
Ag6	Ag5[3]	3.3651(9)	O26	Ag6[1]	2.477(7)
Ag6	Ag7	3.1660(10)	O27	Ag10[2]	2.288(11)
Ag6	Ag8	3.0438(12)	O27	Ag0A[2]	2.447(11)

Ag6	S19[2]	2.639(2)	Ag0A	O27[2]	2.447(11)
[1]3/4-Y,-1/4+X,7/4-Z; [2]1-X,1/2-Y,+Z; [3]1/4+Y,3/4-X,7/4-Z					

Table S8. Selected bond distances (Å) for **PTC-89**.

Ag1	Ag1[1]	3.030(5)	Ag3	Ag3[4]	3.183(9)
Ag1	Ag1[2]	3.030(5)	Ag3	S1	2.364(9)
Ag1	Ag3[2]	3.050(5)	Ag3	S2	2.396(11)
Ag1	S1	2.502(9)	Ti1	O2[2]	2.06(2)
Ag1	S1[2]	2.483(9)	Ti1	O2[1]	2.06(2)
Ag1	O1	2.37(2)	Ti1	O2	2.06(2)
Ag2	Ag3[1]	3.340(6)	Ti1	O3	1.825(19)
Ag2	Ag3	3.366(6)	Ti1	O3[1]	1.825(19)
Ag2	S1[1]	2.633(10)	Ti1	O3[2]	1.825(19)
Ag2	S2[3]	2.585(9)	S1	Ag1[1]	2.483(9)
Ag2	S2	2.437(9)	S1	Ag2[2]	2.633(10)
Ag3	Ag1[1]	3.050(5)	S2	Ag2[5]	2.585(9)
Ag3	Ag2[2]	3.340(6)			
[1]+Z,1-X,1-Y; [2]1-Y,1-Z,+X; [3]1-Z,+X,1-Y; [4]1-X,+Y,1-Z; [5]+Y,1-Z,1-X					

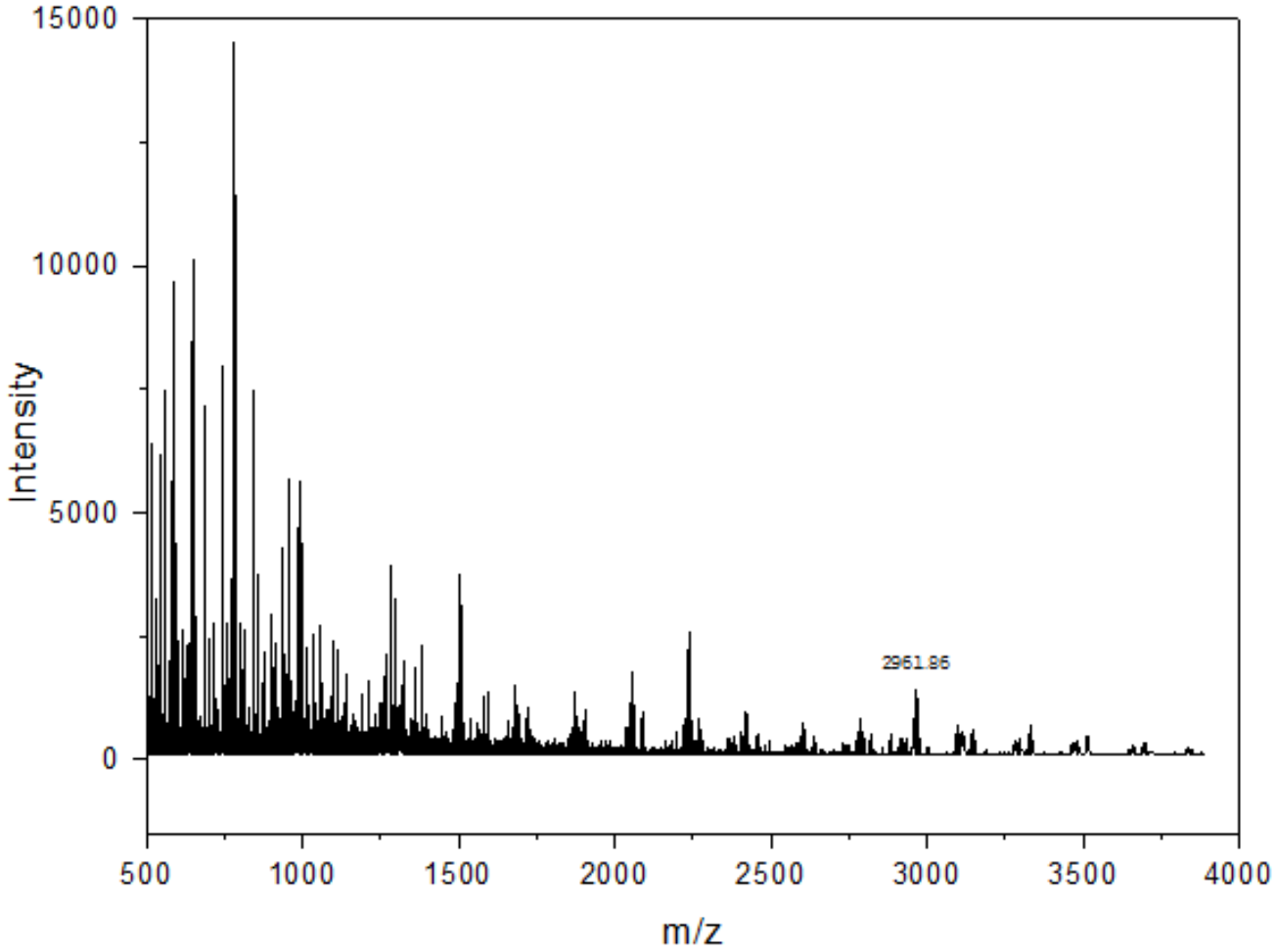

Figure S21. Negative -mode ESI-MS spectra of **PTC-85** (solution: DMF).

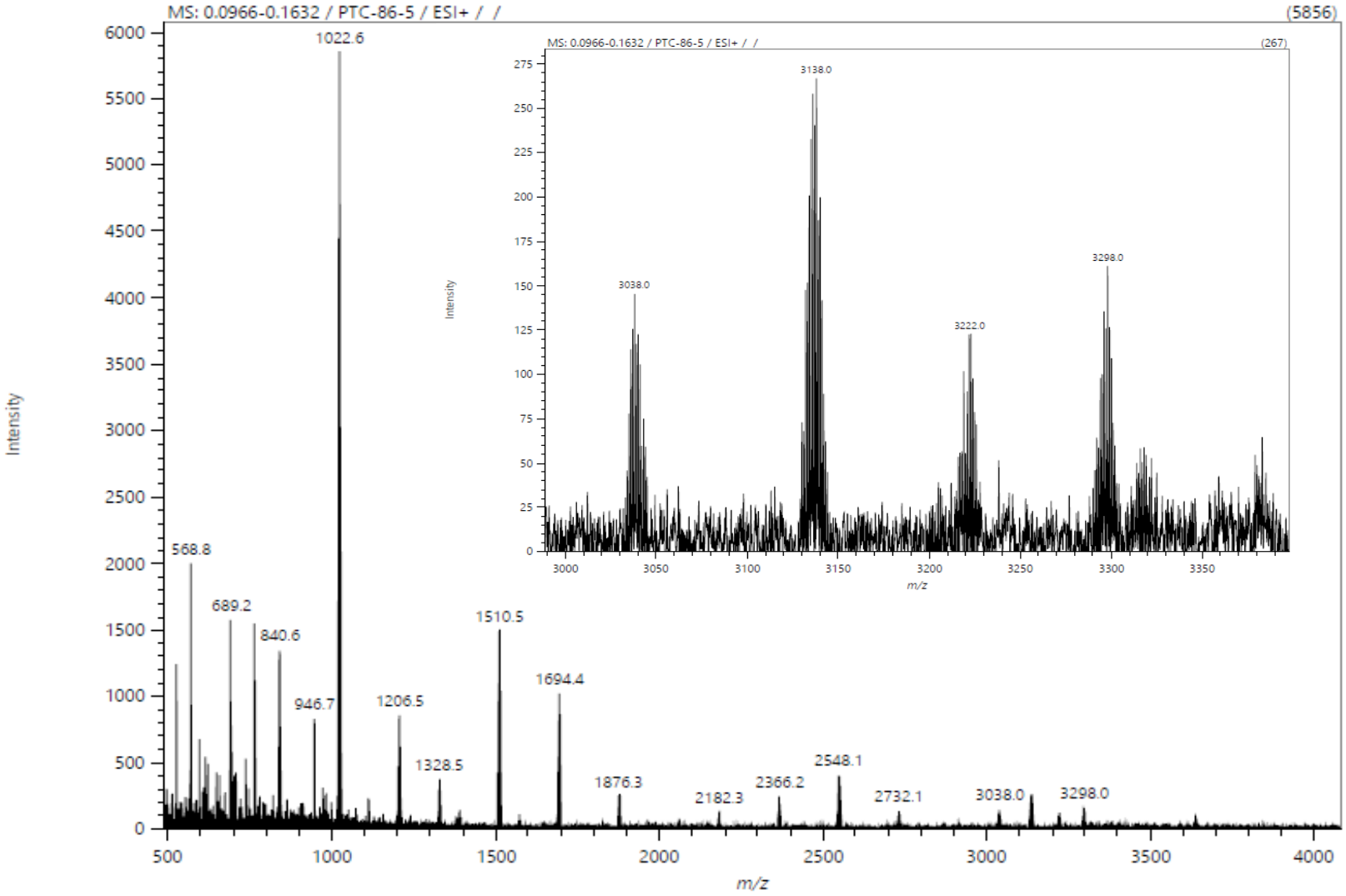

Figure S22. Positive-mode ESI-MS spectra of **PTC-86** (solution: DMF).