Electronic Supplementary Information

Splicing oxygen-rich multidentate ligand and characteristic metals to construct flame colorants: abundant structures and attractive colors

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1. The method of synthesized tetranitroethane and dipotassium tetranitroethide

Dipotassium Tetranitroethide (EP-3). Tetraiodoethylene powder (20.0 g, 0.04 mol) was added to 50 ml of 96% HNO_3 in 0°C, with stirring. Then the solution heated quickly to 70°C. After 20 min, the mixture was poured onto 200 g of ice, and extracted with dichloromethane (100 mL). The solution was washed with $NaHSO_3$ solution (50 mL), brine (100 mL) and dried ($MgSO_4$). Removal of solvent gave 1,1-diiododinitroethylene, 8 g (50%) of a yellow solid. The solution of 1,1-diiododinitroethylene (8.0 g) in 50 mL of 60% aqueous methanol was added to a solution of KNO_2 (8.0 g) in 50 mL of 60% aqueous methanol. After 18h, the product, 5.5 g (90%), was gave by filtered and washed with methanol. Dipotassium tetranitroethide is a bright yellow solid, mp. 280°C.IR (KBr, cm^{-1}): 3446, 1534, 1472, 1385, 1349, 1261, 1197, 1141, 1007, 851, 796, 774, 727, 626 cm^{-1}. EA ($K_2C_2N_4O_8$, 286.24, %): calcd C, 8.39; N, 19.57. found: C, 8.35; N, 19.58.

Tetranitroethane (TNE). Concentrated sulfuric acid (10 mL) was added to a suspension of dipotassium tetranitroethide (4 mmol, 1.1 g) dichloromethane (30 mL) at -40°C and stirred for 1 h. Then the mixture was treated by a quick separation using a separating funnel, which gave the solution of tetranitroethane in dichloromethane.

2. The combustion reactions for calculated the heat of formation ($\Delta_f H_m$)

The combustion reaction equation of the compounds EP-1-EP-9 might be as follows:

$Li_2C_2N_4O_8{\cdot}2H_2O_{(s)} \rightarrow Li_2CO_{3\,(s)} + CO_{2\,(g)} + 2H_2O_{(l)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-1)**

$Na_2C_2N_4O_{8\,(s)} \rightarrow Na_2CO_{3\,(s)} + CO_{2\,(g)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-2)**

$K_2C_2N_4O_{8\,(s)} \rightarrow K_2CO_{3\,(s)} + CO_{2\,(g)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-3)**

$Rb_2C_2N_4O_{8\,(s)} \rightarrow Rb_2CO_{3\,(s)} + CO_{2\,(g)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-4)**

$Cs_2C_2N_4O_{8\,(s)} \rightarrow Cs_2CO_{3\,(s)} + CO_{2\,(g)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-5)**

$MgC_2N_4O_8{\cdot}6H_2O_{(s)} \rightarrow MgCO_{3\,(s)} + CO_{2\,(g)} + 6H_2O_{(l)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-6)**

$CaC_2N_4O_8{\cdot}4H_2O_{(s)} \rightarrow CaCO_{3\,(s)} + CO_{2\,(g)} + 4H_2O_{(l)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-7)**

$SrC_2N_4O_8{\cdot}_{(s)} \rightarrow SrCO_{3\,(s)} + CO_{2\,(g)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-8)**

$BaC_2N_4O_8{\cdot}2H_2O_{(s)} \rightarrow BaCO_{3\,(s)} + CO_{2\,(g)} + 2H_2O_{(l)} + 2N_{2\,(g)} + 3/2O_{2\,(g)}$ **(EP-9)**

3. The crystallographic data

Table S1 Crystallographic data and structure determination details for **EP-1**, **EP-2** and **EP-5**.

Compound	EP-1	EP-2	EP-5
Chemical formula	$Li_2C_2H_4N_4O_{10}$	$Na_2C_2N_4O_8$	$Cs_2C_2N_4O_8$
Formula weight	258	254	474
Crystal size [mm^3]	0.48×0.45×0.30	0.13×0.12×0.10	0.40×0.38×0.36
Temperature [K]	298(2)	298(2)	298(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*C*2/*c*	$P2_1/c$
a [Å]	7.5837(7)	13.0719(14)	8.3059(8)
b [Å]	8.1831(8)	7.6830(7)	12.8210(11)
c [Å]	8.5391(8)	9.0648(9)	9.6371(9)
α [º]	67.151(2)	90	90
β [º]	67.994(3)	107.017(3)	97.877(2)
γ [º]	87.638(4)	90	90
Volume [Å]^3	449.38(7)	870.53(15)	1016.57(16)
Z	2	4	4
ρ [$g \cdot cm^{-3}$]	1.907	1.938	3.096
F(000)	260	504	856
μ [mm^{-1}]	0.193	0.273	7.209
θ range (º)	2.72-28.85	2.35-28.44	2.66-28.59
Reflections collected	2196 (R_{int}=0.0315)	2035 (R_{int}=0.0420)	4970 (R_{int}=0.0413)
Independent reflections	1530	762	1785
parameters	168	73	146
S	1.090	1.244	1.069
Index ranges	-7≤h≤9 -9≤k≤9 -10≤l≤9	-15≤h≤15 -5≤k≤9 -10≤l≤9	-9≤h≤9 -11≤k≤15 -11≤l≤11
Final R indexes [I>2σ(I)]	R_1=0.0434 wR_2=0.1261	R_1=0.0520 wR_2=0.1633	R_1=0.0285 wR_2=0.0660
Final R indexes (all data)	R_1=0.0471 wR_2=0.1287	R_1=0.0575 wR_2=0.1670	R_1=0.0342 wR_2=0.0680
CCDC number	2087207	2093580	2102271

Table S2 Crystallographic data and structure determination details for EP-6-EP-9.

Compound	EP-6	EP-7	EP-8	EP-9
Chemical formula	$MgC_2H_{12}N_4O_{14}$	$CaC_2H_8N_4O_{12}$	$SrC_2N_4O_8$	$BaC_2H_4N_4O_{10}$
Formula weight	340	320	296	382
Crystal size [mm^3]	0.45×0.30×0.14	0.45×0.36×0.30	0.20×0.18×0.13	0.40×0.38×0.30
Temperature [K]	298(2)	153(3)	298(2)	298(2)
Crystal system	Triclinic	Tetragonal	Cubic	Monoclinic
Space group	*P*-1	$I4_1/a$	*Pn*-3*m*	$P2_1/c$
a [Å]	7.4376(7)	10.6341(9)	11.3702(4)	7.1144(7)
b [Å]	7.5291(8)	10.6341(9)	11.3702(4)	8.3556(8)
c [Å]	11.9971(11)	9.4640(8)	11.3702(4)	15.7942(14)
α [º]	94.007(10)	90	90	90
β [º]	106.366(3)	90	90	91.225(2)
γ [º]	94.166(2)	90	90	90
Volume [Å]^3	640.02(11)	1070.23(16)	1469.96(9)	938.67(15)
Z	2	4	2	2
ρ [$g \cdot cm^{-3}$]	1.767	1.987	1.806	2.699
F(000)	352	656	776	720
μ [mm^{-1}]	0.228	0.668	3.739	4.295
θ range (º)	2.765-28.279	2.709-28.342	4.366-24.754	2.580-29.018
Reflections collected	3146 (R_{int}=0.0322)	2366 (R_{int}=0.0473)	1253 (R_{int}=0.0391)	4308 (R_{int}=0.0451)
Independent reflections	2198	473	287	1655
parameters	193	44	25	155
S	1.079	1.090	1.096	1.153
Index ranges	-6≤h≤8 -8≤k≤8 -14≤l≤14	-12≤h≤5 -12≤k≤12 -11≤l≤10	-8≤h≤7 -7≤k≤13 -13≤l≤7	-5≤h≤8 -9≤k≤9 -15≤l≤18
Final R indexes [I>2σ(I)]	R_1=0.0560 wR_2=0.1650	R_1=0.0304 wR_2=0.0810	R_1=0.0354 wR_2=0.0947	R_1=0.0312 wR_2=0.0764
Final R indexes (all data)	R_1=0.0657 wR_2=0.1743	R_1=0.0322 wR_2=0.0798	R_1=0.0543 wR_2=0.1093	R_1=0.0343 wR_2=0.0778
CCDC number	2093662	2093741	2094065	2093792

4. The FT-IR spectra.

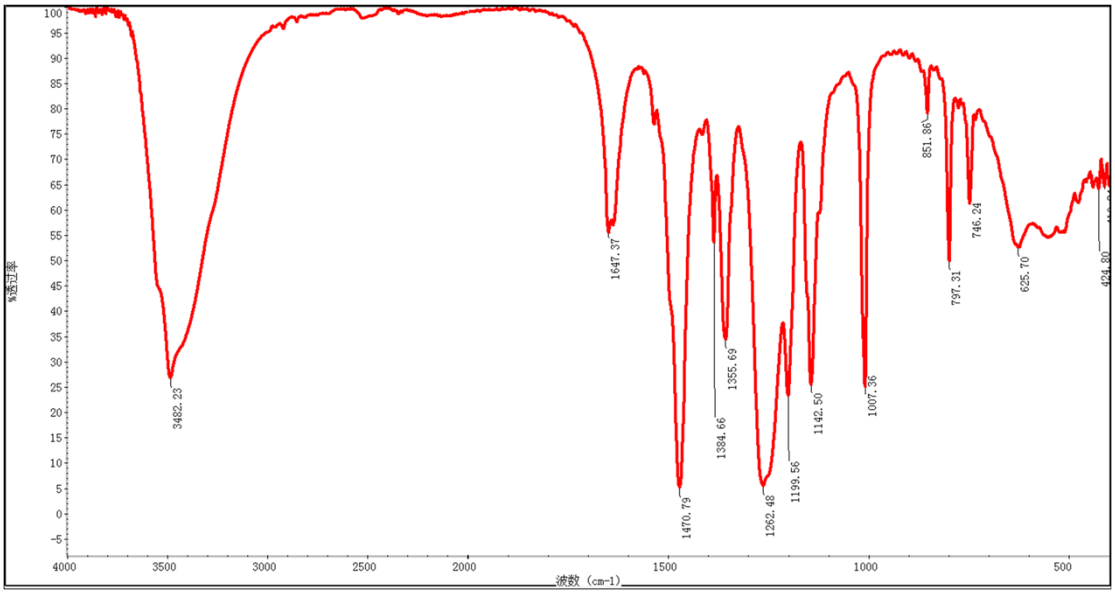

Figure S1 FT-IR spectra of salts **EP-1**.

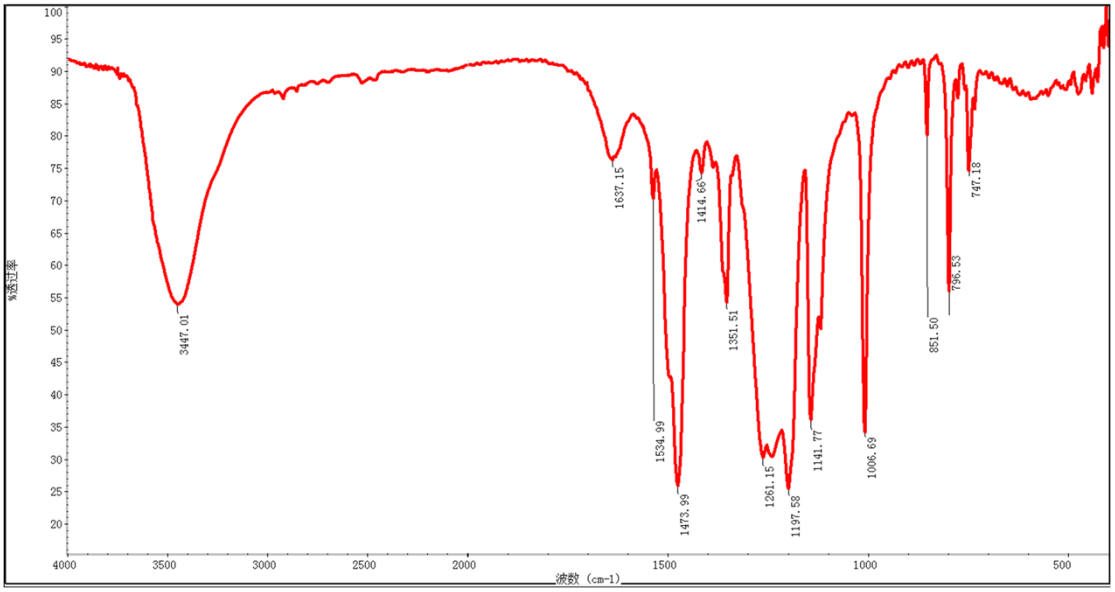

Figure S2 FT-IR spectra of salts **EP-2**.

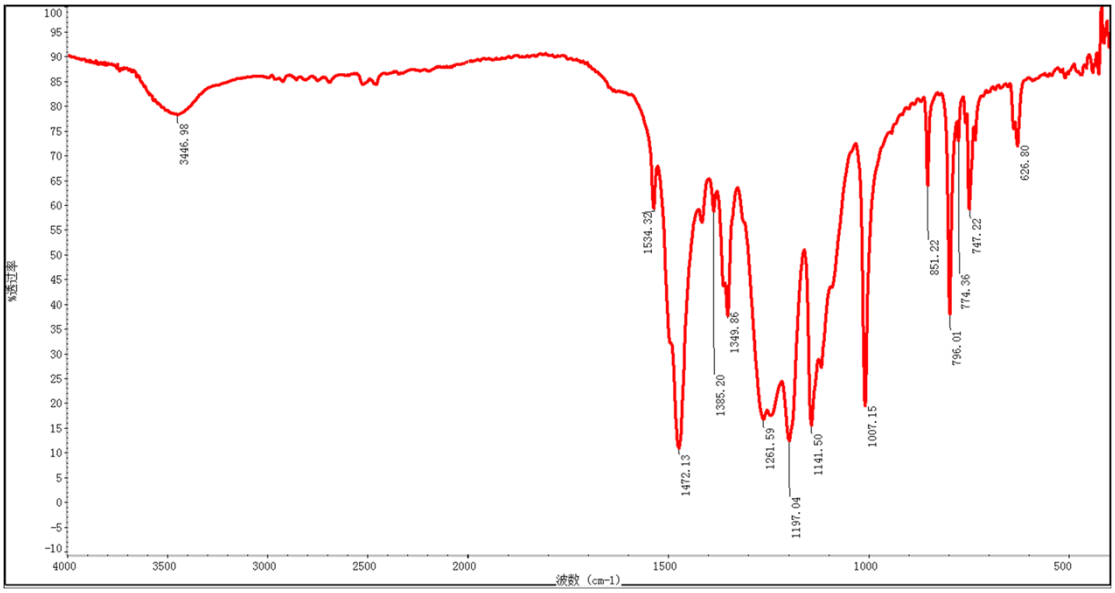

Figure S3 FT-IR spectra of **EP-3**.

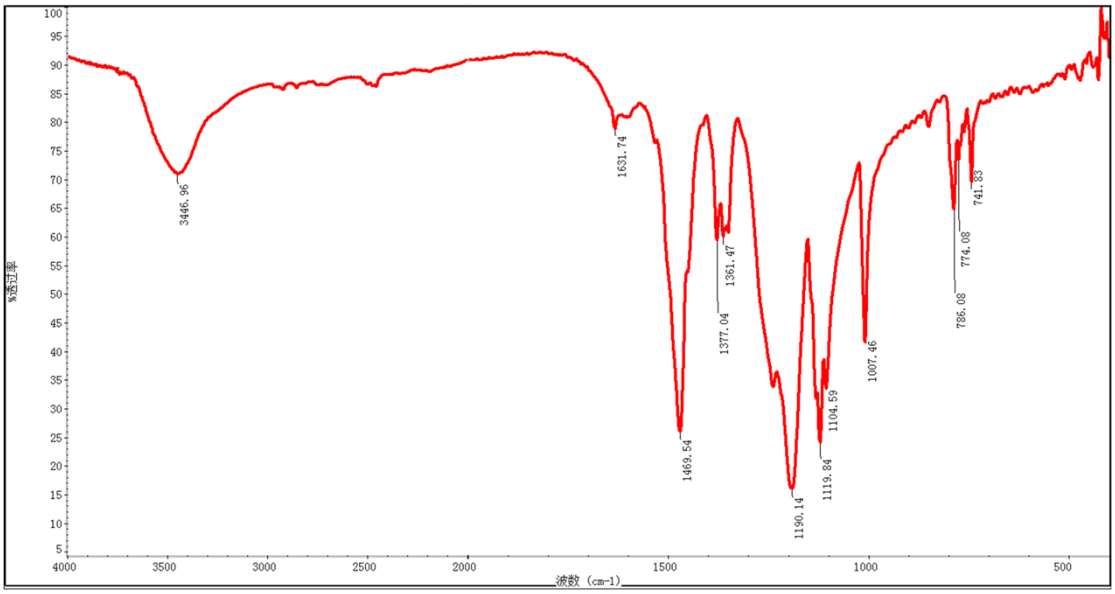

Figure S4 FT-IR spectra of salts **EP-4**.

Figure S5 FT-IR spectra of salts **EP-5**.

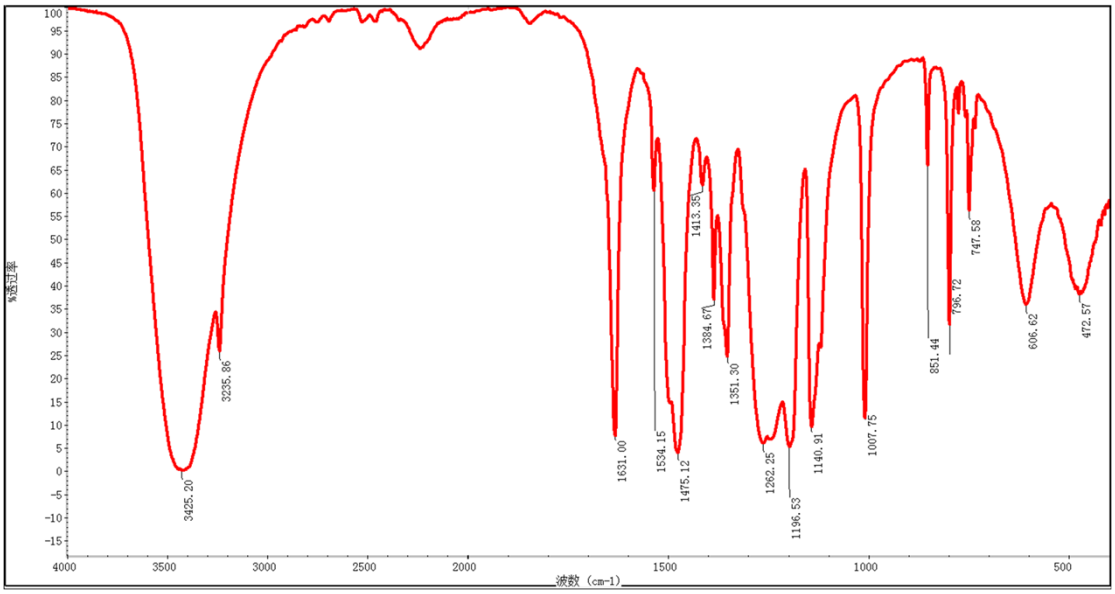

Figure S6 FT-IR spectra of **EP-6**.

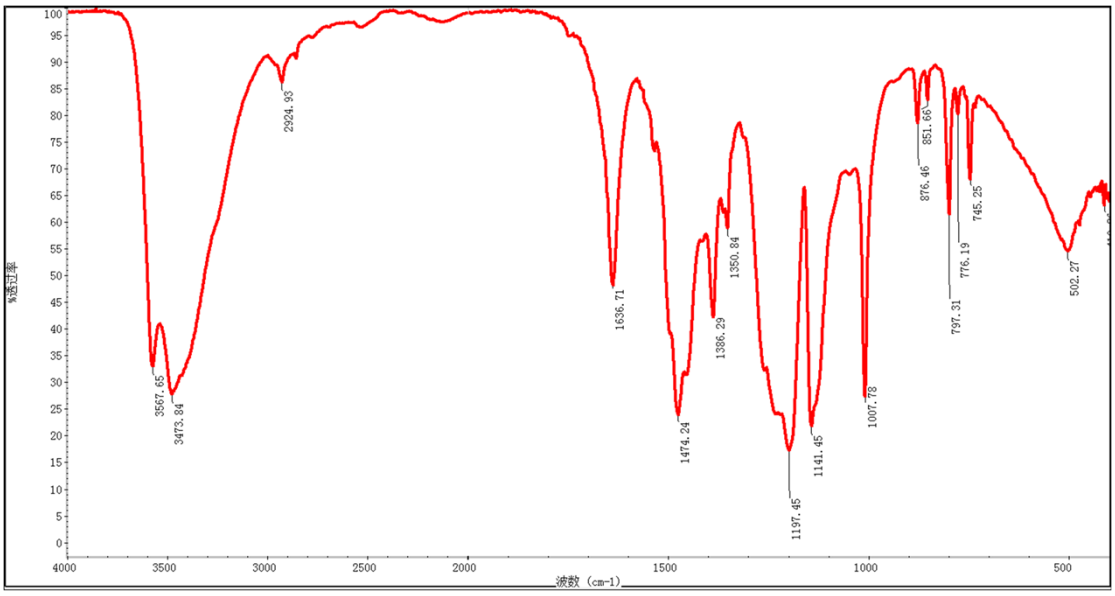

Figure S7 FT-IR spectra of **EP-7**.

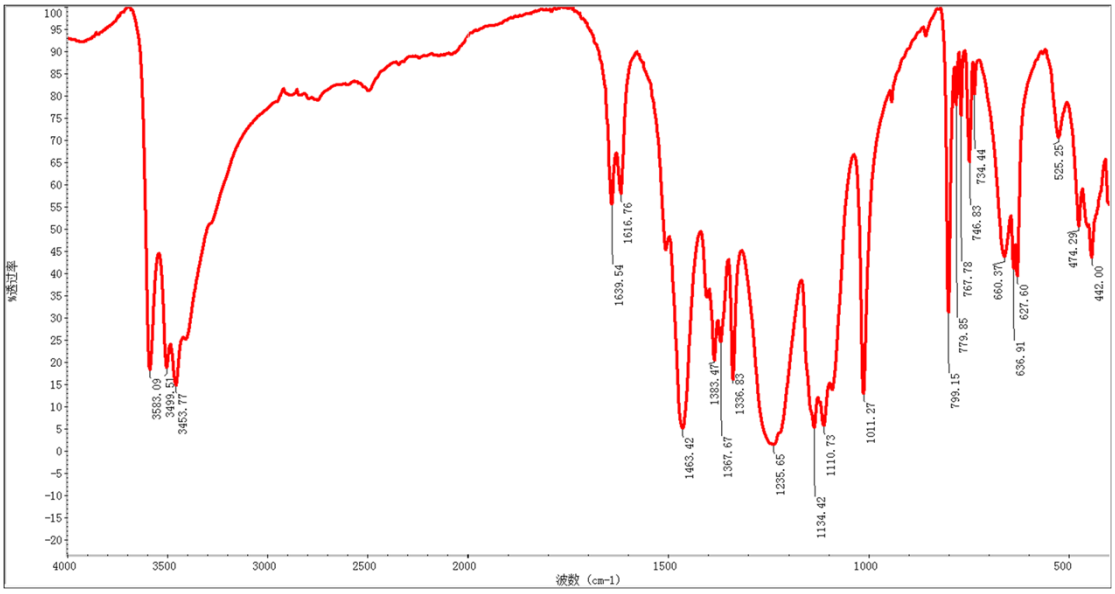

Figure S8 FT-IR spectra of **EP-8**.

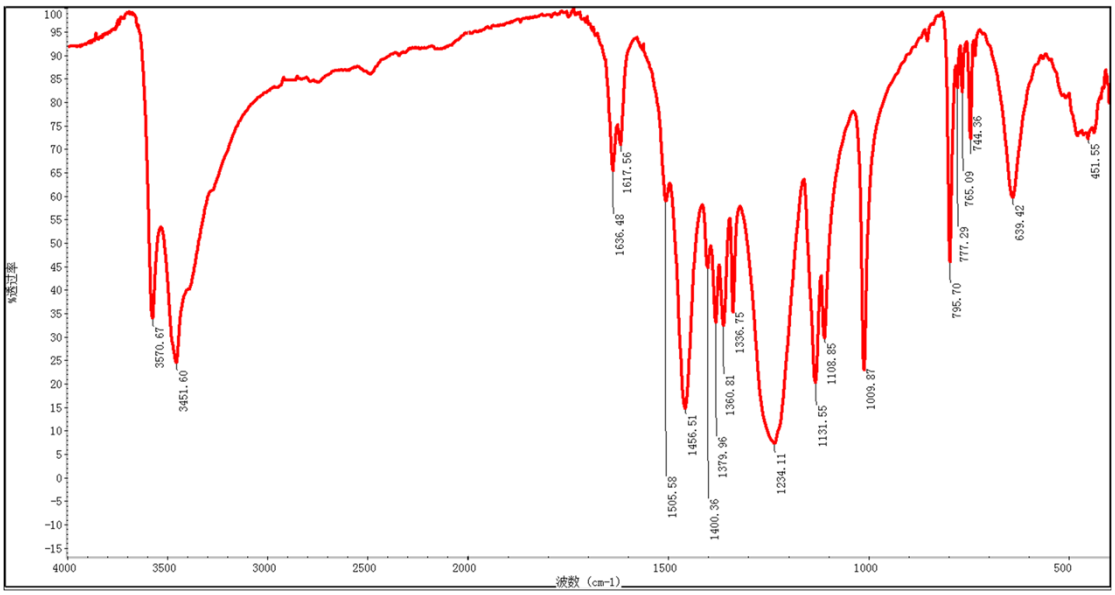

Figure S9 FT-IR spectra of **EP-9**.