Electronic Supplementary Material (ESI) for Analytical Methods.

In-situ quantification of volatile ethanol content in complex components based on colorimetric sensor array

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Table S1 Reference measurement of ethanol in calibration and prediction sets.

Subsets	Units (%)	Sample number	Range	Mean	Standard deviation
Calibration set	v/v	40	18.03-53.94	34.59	10.45
Prediction set	v/v	20	19.73-49.57	33.57	9.52

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Table S2 The name and abbreviation of porphyrins

Number of compounds	Name	Abbreviation
1	5,10,15,20-Tetraphenyl-21H,23H-porphyine	TPP
2	5,10,15,20-Tetraphenyl-21H,23H-porphyine manganese	TPP-Mn
3	5,10,15,20-Tetraphenyl-21H,23H-porphyine zinc	TPP-Zn
4	5,10,15,20-Tetraphenyl-21H,23H-porphine cobalt(II)	TPP-Co
5	5,10,15,20-Tetraphenyl-21H,23H-porphyine nickel	TPP-Ni
6	5,10,15,20-Tetraphenyl-21H,23H-porphine copper(II)	TPP-Cu
7	5,10,15,20-Tetraphenyl-21H,23H-porphine palladium (II)	TPP-Pd
8	5,10,15,20-Tetraphenyl-21H,23H-porphyine manganese(III) Chloride	TPP-Cl- Mn
9	5,10,15,20-Tetrakis(4-fluorophenyl)-21H,23H-porphyine manganese(II)	TPP-F -Mn
10	Octaethyl-21H,23H-porphyine manganese(III) chloride	OEP-Cl- Mn
11	5,10,15,20-Tetrakis(4-methoxyphenyl)-21H,23H-porphyine manganese(II)	CH3O-TPPMn
12	6,13,20,21-tetratolyl[14]tribenzotriphyrin(2.1.1) Manganse(I) Tricarbonyl	CH3-Trip-Mn

Table S3 Response values of the red, green, and blue (RGB) component with different porphyrins after exposure to 60% ethanol at 35℃.The data (repeated four times) displaced in the table are in the type of mean ± standard deviation.

Porphyrins	R component	G component	B component
TPP	1.73±1.40	2.42±0.67	7.66±3.91
TPP-Mn	17.05±4.73	9.14±2.86	36.90±8.35
TPP-Zn	6.61±1.19	1.79±0.92	22.15±1.20
TPP-Co	2.72±0.59	2.19±0.62	4.59±0.45
TPP-Ni	5.71±0.35	3.94±1.62	0.63±0.79
TPP-Cu	3.26±0.81	2.33±0.79	5.67±1.70
TPP-Pd	2.66±0.50	1.53±0.40	2.91±0.48

Q band of porphyrins existing in the visible region related to optical property for light harvesting in the molecular reaction of VOCs and porphyrins. Furthermore, it has been reported that the Q bands formation of porphyrins mainly arise from the electron transition from the HOMO and HOMO-1 to the LUMO and LUMO+1 orbitals. Therefore, it is important to understand the energy level of four orbitals (HOMO, HOMO-1, LUMO and LUMO+1). In this study, TD-DFT was used to treat the changes in energy of four orbitals energy levels before and after binding to ethanol, resulted in Table S4.

Table S4. Orbital energy level and geometry structure changes after porphyrins binding with ethanol

Porphyrins	Value(B)	Coefficient of variation (B)	HOMO-LUMO	HOMO-1 -LUMO+1	Distance
TPP	7.66	0.5104	2.7152	3.0177	0
TPP-Mn	36.9	0.2263	2.5045	2.8770	0.136
TPP-Zn	22.15	0.0542	2.8030	3.0079	0.268
TPP-Co	4.59	0.0980	2.7375	2.9157	0.079
TPP-Ni	0.63	1.2540	2.9720	3.0594	0
TPP-Cu	5.67	0.2998	2.8820	3.0158	0.042
TPP-Pd	2.91	0.1649	3.0098	3.0977	0.001

Since there are no metal atoms in the center of TPP, it was set to zero by default. Fig. 3(a) showed the distance of Mn out of planarity before and after TPP-Mn binding to ethanol. Before exposure to ethanol, the distance of Mn out of planarity was 0, and the value was 0.136 after binding to ethanol. Fig. 3(b) showed the charges of TPP-Mn before and after binding to ethanol. Prior to the TPP-Mn binding to ethanol, the charges of four N atoms were -0.614, -0.608, -0.643, -0.593 respectively. While after TPP-Mn binding to ethanol, charges of four N atoms changed to -0.570, -0.584, -0.588, -0.568.

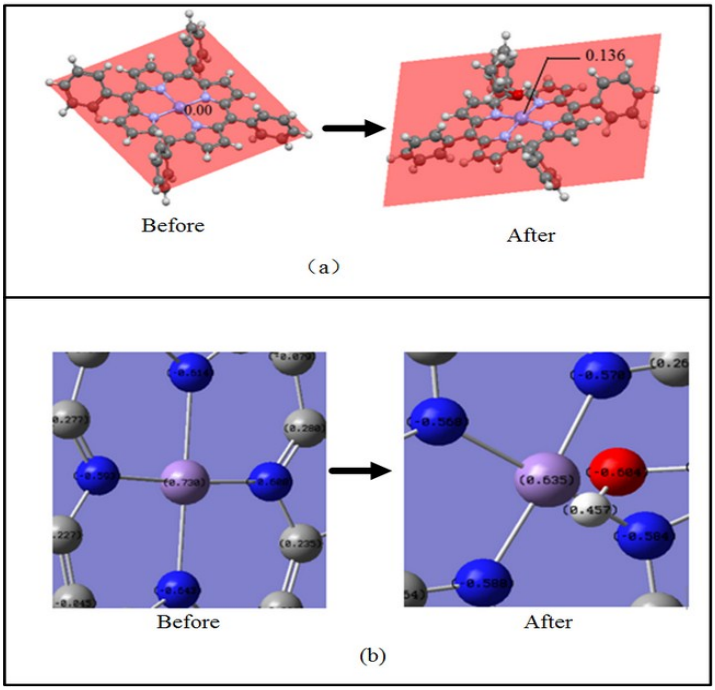

Fig. S1 Changes of TPP-Mn after binding with ethanol in geometry structure changes (a) and charge distribution (b)

Table S5 Changes of the charge distribution in the process of ethanol binding to porphyrins

Porphyrins	Value (B)	Coefficient of variation (B)	Charge distribution						
			Metals	N1	N2	N3	N4	N	Total
TPP	7.66	0.5104	-	-0.038	0	0.001	0	-0.037	-0.037
TPP-Mn	36.9	0.2263	-0.095	0.025	0.044	0.055	0.024	0.148	0.053
TPP-Zn	22.15	0.0542	-0.022	0.029	0.020	0.020	0.036	0.105	0.083
TPP-Co	4.59	0.0980	-0.115	-0.026	-0.037	-0.034	-0.029	-0.126	-0.241
TPP-Ni	0.63	1.2540	-0.043	-0.007	0.009	0.01	0.009	0.021	-0.022

TPP-Cu	5.67	0.2998	-0.051	0.010	0.013	0.012	-0.002	0.033	-0.018
TPP-Pd	2.91	0.1649	-0.141	-0.003	0	-0.001	-0.007	-0.011	-0.130

Table S6 Quantum chemistry calculation results of different porphyrin binding with ethanol

Porphyrins	Value(B)	Coefficient of variation (B)	HOMO-LUMO	HOMO-1 -LUMO+1	Dipole (before reaction)	Dipole (after reaction)	Total N charge	Distance
TPP	7.66	0.5104	2.7152	3.0177	0.001	1.3911	-0.037	-0.037
TPP-Mn	36.9	0.2263	2.5045	2.8770	0.599	2.3990	0.148	0.053
TPP-Zn	22.15	0.0542	2.8030	3.0079	0.017	3.8693	0.105	0.083
TPP-Co	4.59	0.0980	2.7375	2.9157	0.063	2.7635	-0.126	-0.241
TPP-Ni	0.63	1.2540	2.9720	3.0594	0.003	1.6789	0.021	-0.022
TPP-Cu	5.67	0.2998	2.8820	3.0158	0.011	0.9689	0.033	-0.018
TPP-Pd	2.91	0.1649	3.0098	3.0977	0.010	1.441	-0.011	-0.130

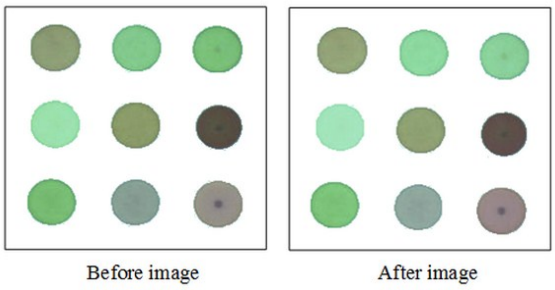

Fig. S2 The before and after image of colorimetric sensor array

In the process of variable selection, the data origin from the response value after exposure to ethanol constituted a 60 x 27 independent variable matrix X (60 samples and 27 variables), the actual ethanol content of samples were termed as Y. The

parameters of genetic algorithm were set as follows: population size is 60; cross rate is 0.8; mutation probability is 0.01; and frequency of hybridization is 100. The definition of fitness function as:

$$F = \frac{1}{1 + RMSECV}$$

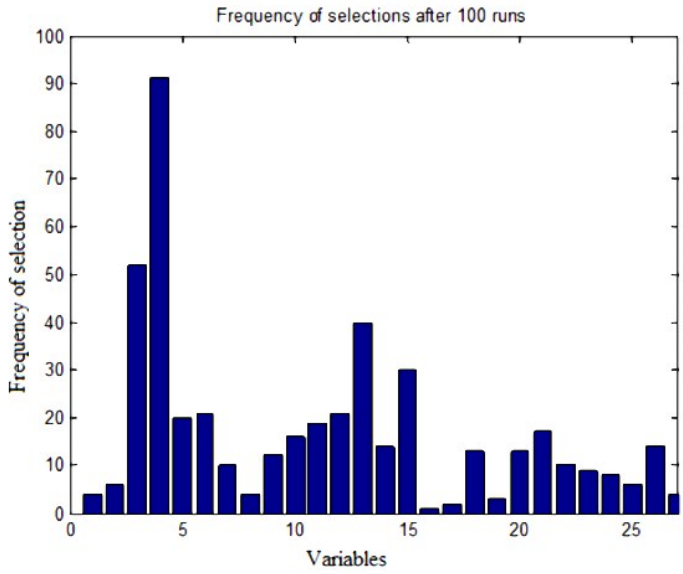

Fig. S3 The histogram of frequency selection of each variable

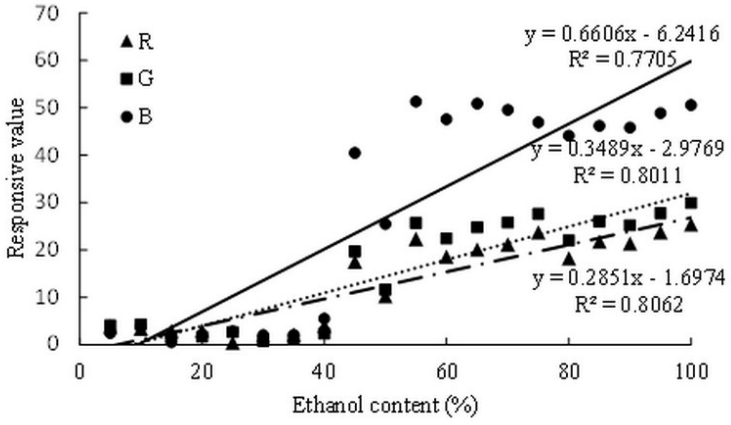

Fig. S4 Responsive values of TPP-Cl-Mn in the red, green, and blue (RGB) component after exposure to pure ethanol/water solution at various concentrations (5%-100%). Linear regression analysis and equations were also included.

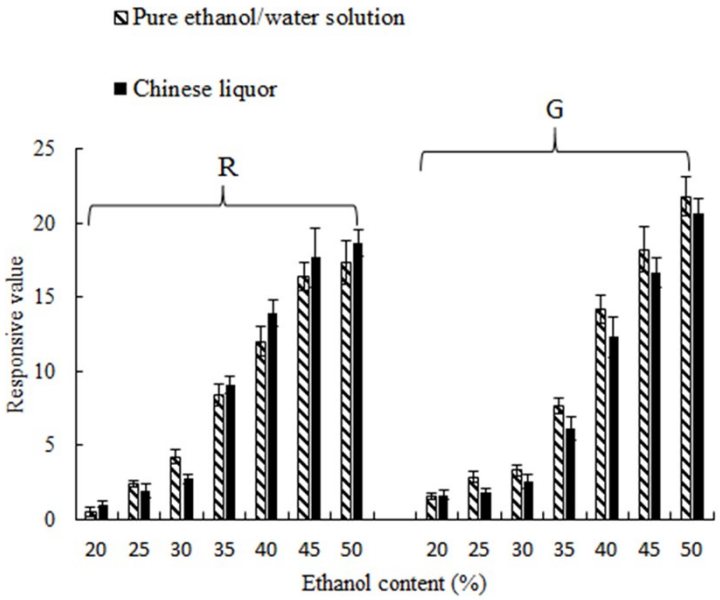

Fig. S5 Comparative analysis of TPP-Cl-Mn after exposure to pure ethanol/water solution and Chinese liquor in red and green components

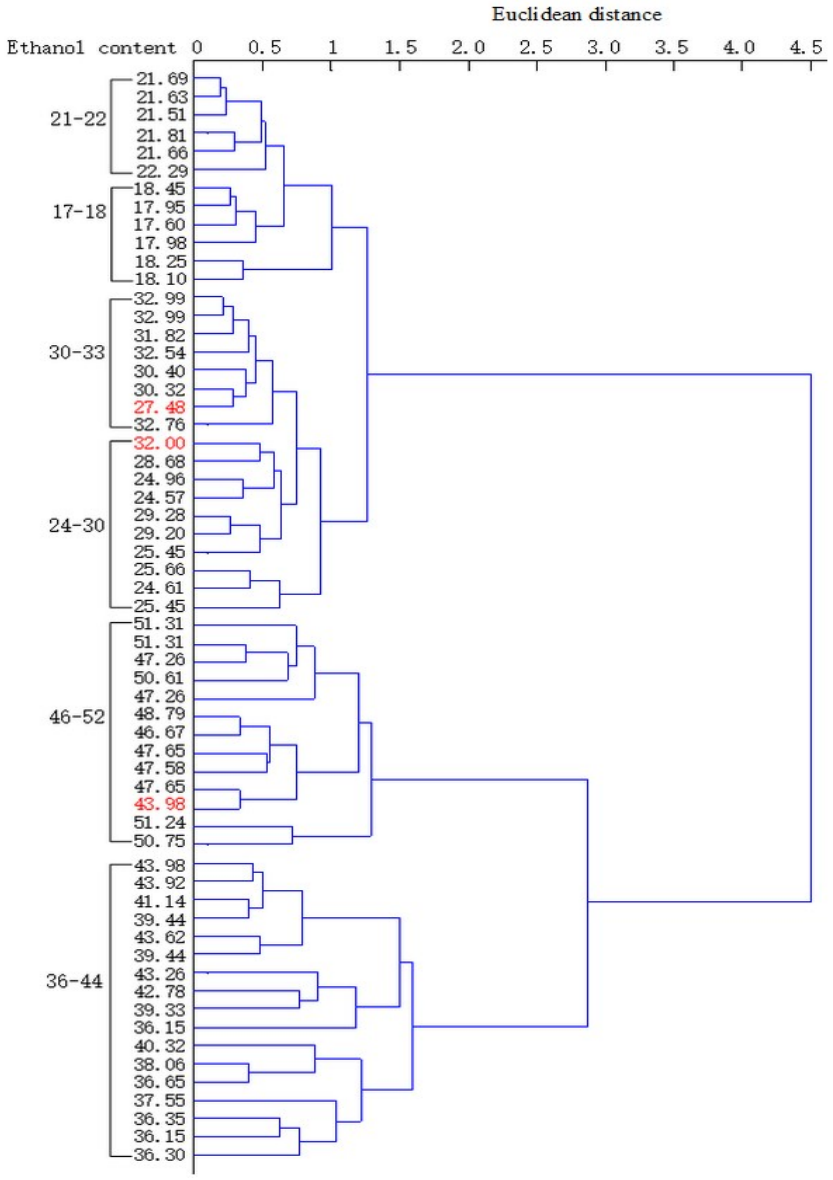

Fig. S6 Hierarchical cluster analysis (HCA) dendrogram of the six variables for 60 Chinese liquor with different ethanol.