

**Enhancement of smoke and toxic gas suppression during combustion,
and improvement of the mechanical properties of epoxy resin by
incorporation of a modified MOF material containing
phosphoheterophene group**

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Supporting Information

EXPERIMENTAL SECTION

Materials

EP, E-44, Bisphenol A diglycidyl ether, supplied by China Nantong Xingchen Synthetic Materials Co., Ltd. Terephthalic acid (H₂BDC), itaconic acid (ITA), DOPO, FeCl₃·6H₂O and 4,4-diaminodiphenylmethane (DDM) were provided by Wuhan Geao Chemical Technology Co., Ltd.

Characterization

¹H NMR spectrum of DOPI was tested using the AVANCE AV 400 Bruker spectrometer. The morphology was observed using FE-SEM (GeminiSEM 300, Carl Zeiss AG, Germany). The characteristic functional groups of the compounds were tested on a Thermo Nicolet 5700 FTIR spectrometer. The crystal structure was evaluated using X-ray diffractometer (D8 ADVANCE, Bruker). N₂ adsorption-desorption was measured at Micromeritics, ASAP 2020. The binding energies of elements were obtained using X-ray photoelectron spectroscopy (ESCALAB XI+). In N₂ atmosphere and heating rate of 10 °C/min, the thermogravimetric analysis was conducted on STA449F3 and TG-IR (STA-2500-IS50) was used to heat samples smaller than 3 mm × 3 mm × 3 mm. The Raman spectrum was measured with the Laser Micro-Raman Spectrometer. The LOI value of sample with the size of 130 mm × 6.5 mm × 3.2 mm was tested using a HC-2C Oxygen Index Tester. UL 94 combustion was tested according to ASTM D3801 with a sample size of 130 mm × 13 mm × 3.2 mm. Cone calorimeter test (CC) (FTT0007, UK) was conducted according to ISO 5660 with a sample dimension of 100 mm × 100 mm × 3.2 mm. To recognize the pyrolysis fragments of MIL-53(Fe)-DOPI, a gas chromatography-mass spectrometer (TRACE1310 GC and ISQ mass spectrometer) with an EGA/PY3030D thermal pyrolyzer was used for the tests under helium gas flow. The pyrolytic products were characterized based on the NIST MS spectroscopic

library. The three-point bending and impact tests were carried out on an 80 mm × 10 mm × 4 mm sample, and tensile test was carried out on a 75 mm × 4 mm × 2 mm sample.

Synthesis of DOPI

DOPO (54 g, 0.25 mol) and ITA (32.81 g, 0.252 mol) were added into a 250 mL three-neck flask. Under N₂ protection, the reactant was conducted at 160 °C for 6 h under mechanical stirring. After cooling to about 50 °C, the obtained crude product was treated by adding appropriate amount of tetrahydrofuran, the solids were then collected after filtration and dried in a vacuum oven at 90 °C for 24 h. The purified product is denoted as DOPI and its yield is 78.5% (68.1 g).

Synthesis of MIL-53(Fe)

H₂BDC (2.492 g, 15 mmol), FeCl₃·6H₂O (4.055 g, 15 mmol) and 150 mL DMF were added into a three-necked flask and stirred at room temperature until the reactants are entirely dissolved. Then, the clear solution was transferred to the polytetrafluoroethylene lining and hydrothermal reacted at 150 °C for 12 h. At the end of the reaction, the solid is centrifuged with fresh DMF three times. Subsequently, the solid was transferred to a single-mouthed flask and 100 mL of ethanol was added and stirred for 24 h to remove residual DMF molecules in the channel. After the solvent exchange, the solids were collected and dried for 24 h at 100 °C in a vacuum drying oven to obtain MIL-53(Fe).

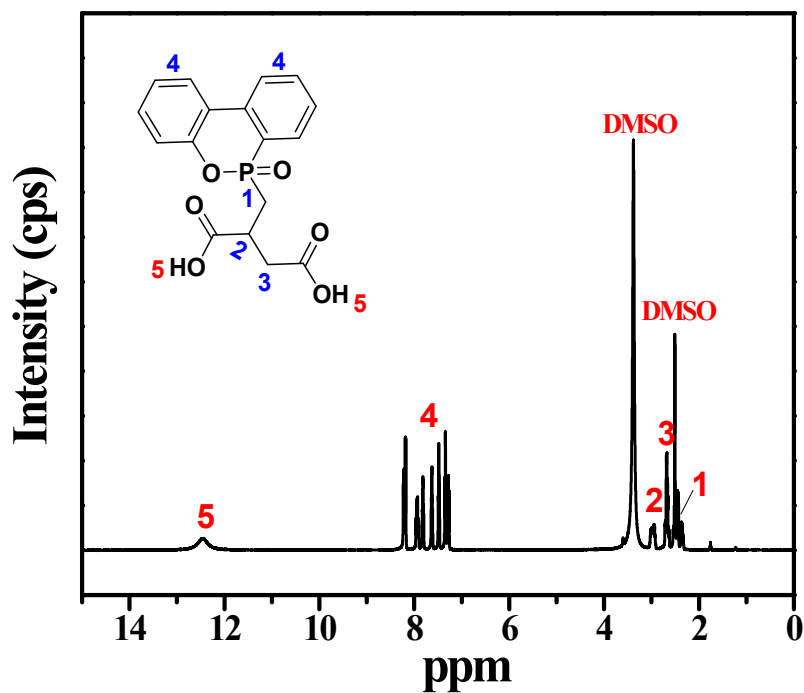


Fig. S1 ^1H NMR spectrum of DOPI.

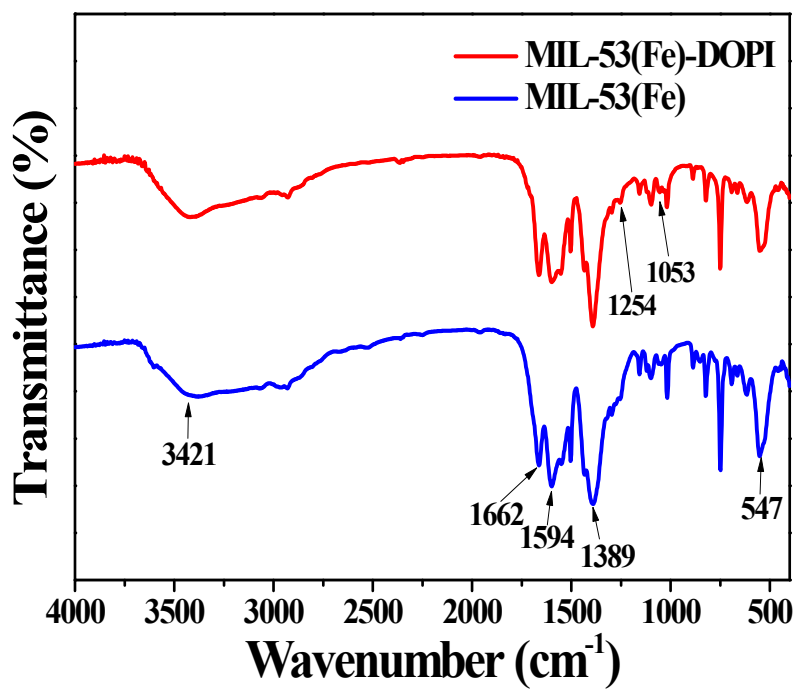


Fig. S2 FTIR spectra of MIL-53(Fe) and MIL-53(Fe)-DOPI.

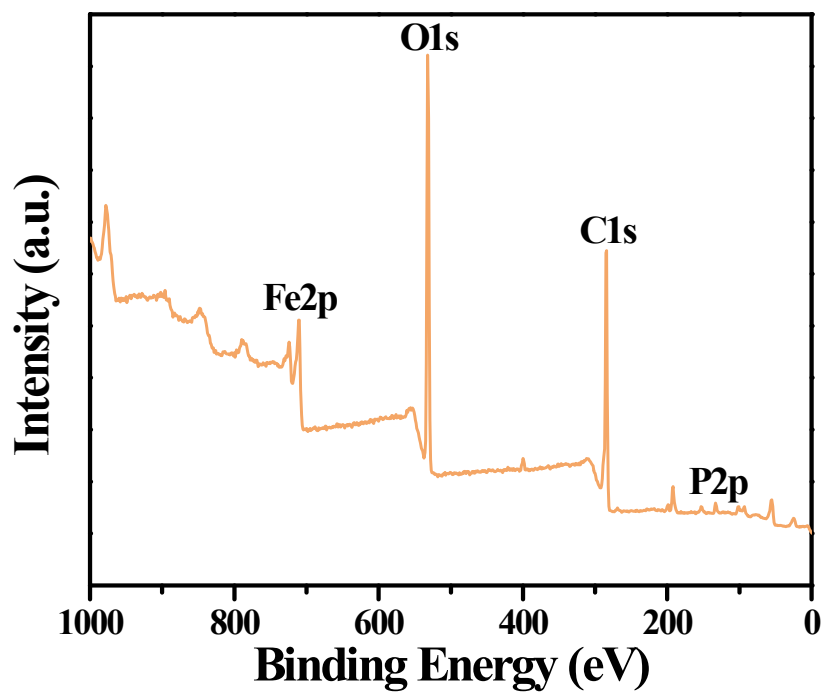


Fig. S3 XPS full spectrum of MIL-53(Fe)-DOPI.

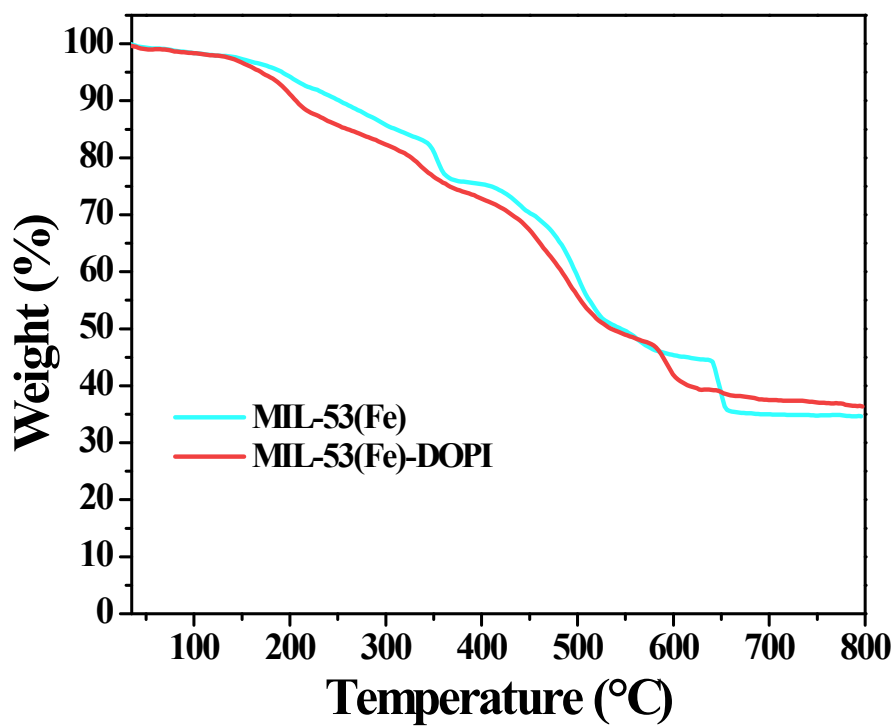


Fig. S4 TGA curves of MIL-53(Fe) and MIL-53(Fe)-DOPI.

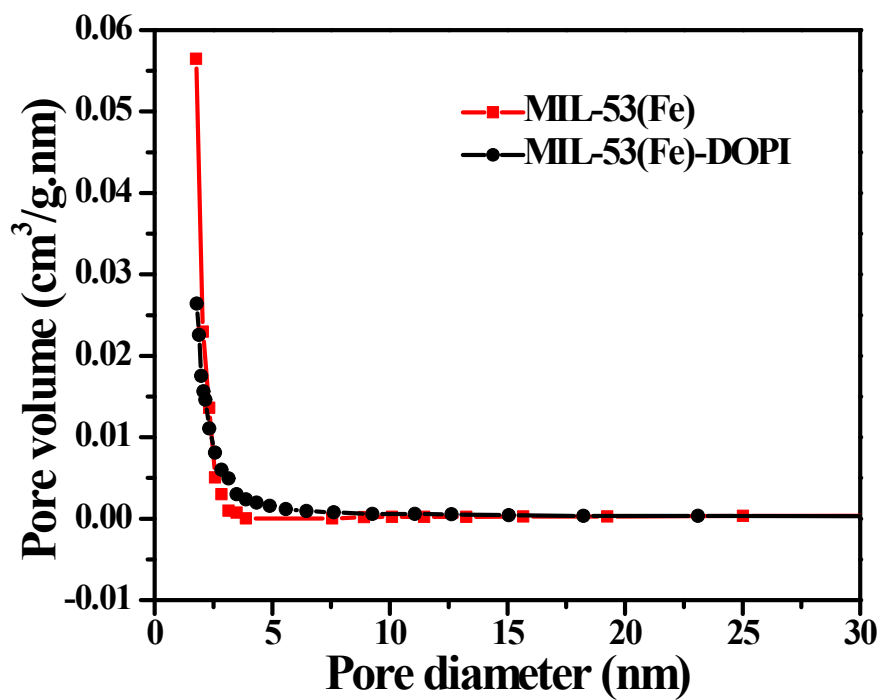


Fig. S5 Pore size distribution of MIL-53(Fe) and MIL-53(Fe)-DOPI.

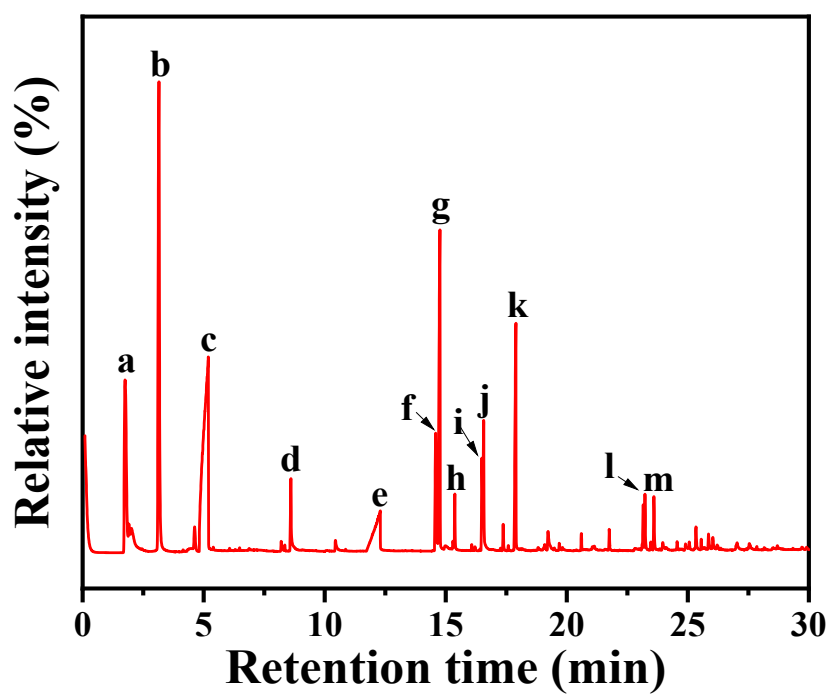


Fig. S6 Pyrolysis products of MIL-53(Fe)-DOPI at different retention time.

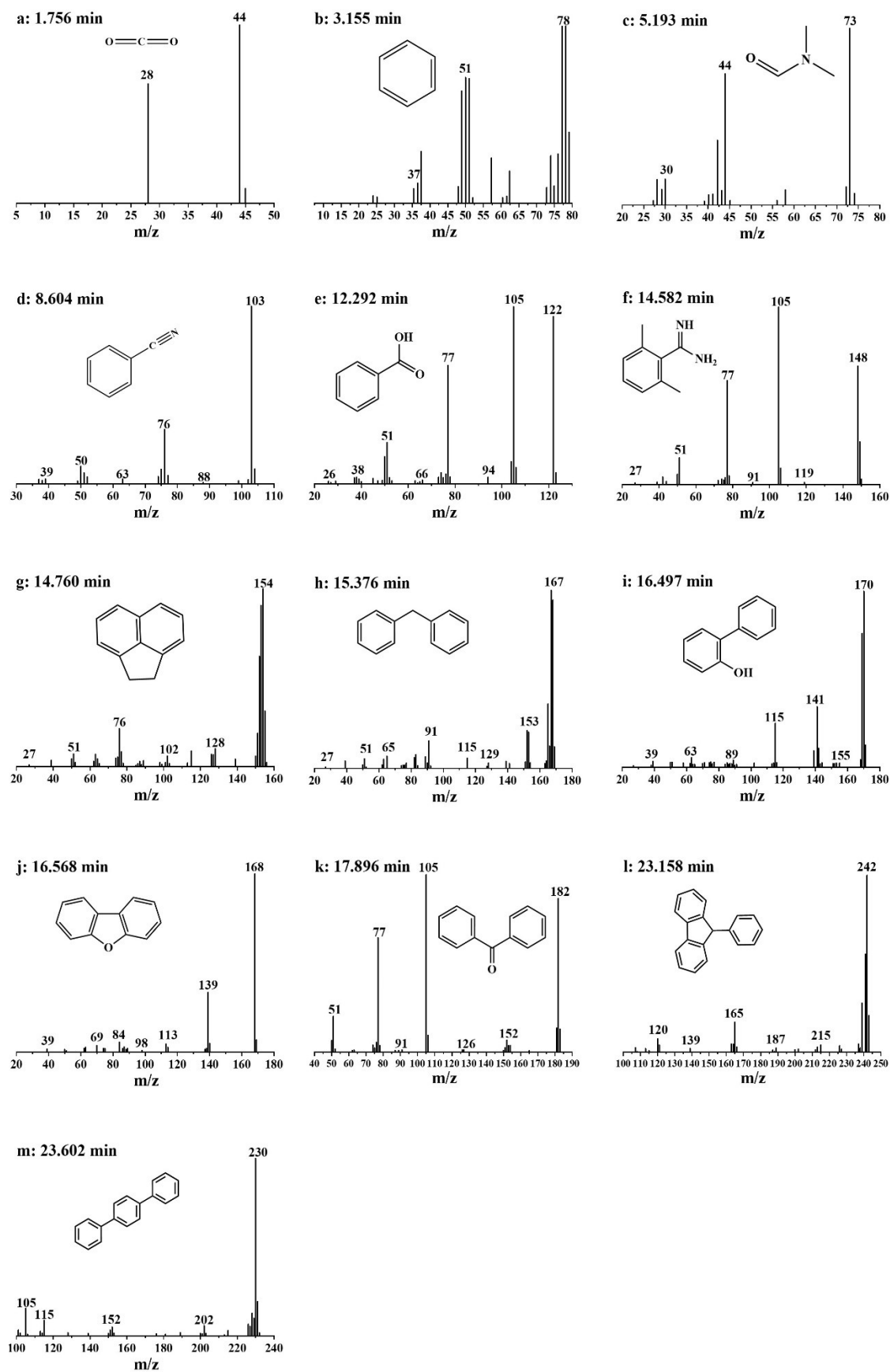


Fig. S7 Mass spectra of pyrolysis products of MIL-53(Fe)-DOPI at different retention time.

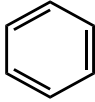
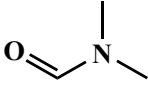
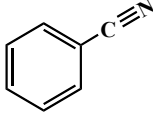
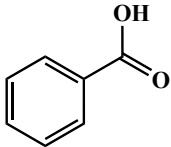
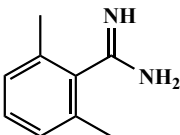
Table S1 Formulas of the EP containing different flame retardants.

Blends	EP (g)	DDM (g)	MIL-53(Fe)-DOPI (g)
Pure EP	25	6.5	0
1 wt% MIL-53(Fe)-DOPI/EP	25	6.5	0.32
2 wt% MIL-53(Fe)-DOPI/EP	25	6.5	0.64
3 wt% MIL-53(Fe)-DOPI/EP	25	6.5	0.97
4 wt% MIL-53(Fe)-DOPI/EP	25	6.5	1.31
5 wt% MIL-53(Fe)-DOPI/EP	25	6.5	1.66

Table S2 Specific surface area, pore size and total pore volume of MIL-53(Fe) and MIL-53(Fe)-DOPI.

Materials	Specific surface area (m ² /g)	Pore size (nm)	Total pore volume (cm ³ /g)
MIL-53(Fe)	270.554	6.41	0.086
MIL-53(Fe)-DOPI	166.244	7.55	0.078

Table S3 Attribution of pyrolysis products of MIL-53(Fe)-DOPI.

No.	m/z	Assigned structure
a	44	O=C=O
b	78	
c	73	
d	103	
e	122	
f	148	

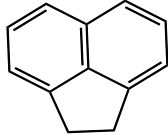
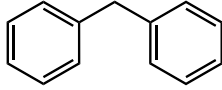
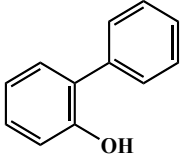
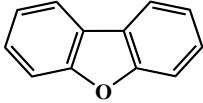
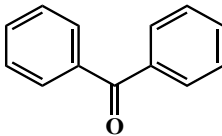
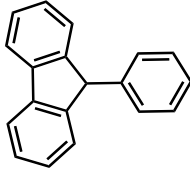
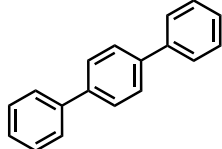
g	154	
h	170	
i	168	
j	170	
k	182	
l	242	
m	230	

Table S4 Mechanical properties of pure EP and MIL-53(Fe)-DOPI/EP blends.

Blends	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (kJ/m ²)
EP	73.22	8.21	56.7	1381	22.4
1 wt% MIL-53(Fe)-DOPI/EP	78.0	7.78	66.25	1712	23.6
2 wt% MIL-53(Fe)-DOPI/EP	83.39	7.71	81.35	2252	24.3
3 wt% MIL-53(Fe)-DOPI/EP	91.01	8.68	91.85	2557	25.5
4 wt% MIL-53(Fe)-DOPI/EP	89.67	8.57	81.45	2252	21.87
5 wt% MIL-53(Fe)-DOPI/EP	89.02	8.93	75.0	2033	24.82