Supplementary Materials

Synthesis of DOPO-Based Phosphorus-Nitrogen Containing Hyperbranched Flame Retardant and Its Effective Application for Poly(ethylene terephthalate) via Synergistic Effect

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The magnified ^{13}C NMR spectra was illustrated in Fig. S1. The peaks ~148 ppm were ascribed to the C in C-N rings from dendritic units, and the peak at 149.26 ppm was attributed to the C in C-N rings from linear unit and the peaks at 149.71 and 149.64 were came from terminal unit. DB of the hyperbranched polymers has been defined as follows:

$$DB=(D+T)/(D+T+L) \quad (1)$$

Where D, T and L refer to the numbers of dendritic, terminal and linear unites respectively. Due to the area integration of D (2.36), T (0.17) and L (1.38), the DB is calculated to be 0.65.

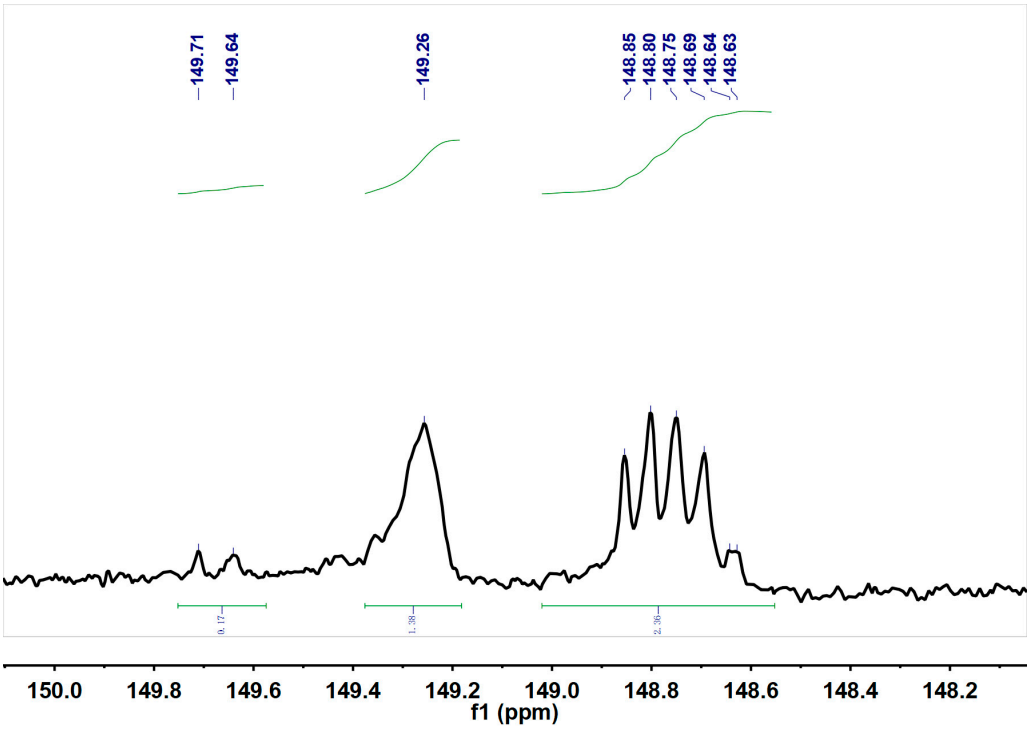

Figure S1. Magnified quantitative ^{13}C NMR spectra of C in C-N rings from THEIC part in hbDT

The Energy Dispersive Spectroscopy (EDS) spectra of hbDT/PET composite were recorded before combustion. The results showed there were P, N, C and O elements are exhibited in the composites and no impurity presented, the spectra are shown in Fig. S2.

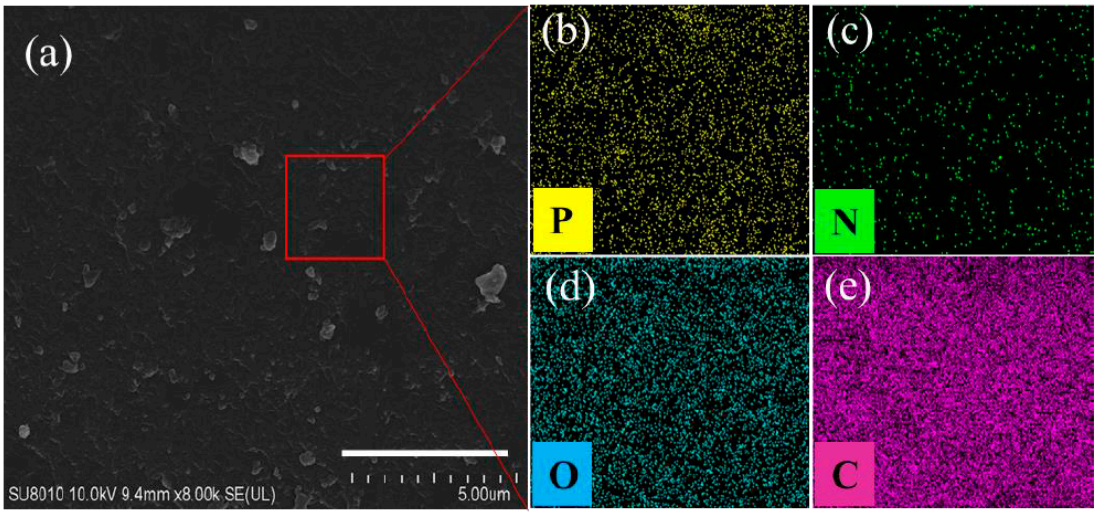

Figure S2. SEM (a) and energy dispersive spectroscopy (EDS) spectra of elements mapping distribution (b) phosphorus, (c) nitrogen, (d) oxygen and (e) carbon for 20%hbDT/PET composites.

In the Raman spectra of carbon materials, the G-peak is generally located at 1580-1600 cm^{-1} and the D-peak at 1350-1580 cm^{-1}. The smaller the ratio of the intensity of the D-peak to the G-peak, i.e. the smaller the ID/IG, the higher the graphitization of the char residue. Raman tests were carried out on the PET and hbDT/PET char residue after cone calorimeter test, the results are illustrated in Fig. S3. The ID/IG of pure PET was 2.5, while the values decreased gradually to 2.04 and 1.82 with 2 wt% and 5 wt% hbDT, respectively. Therefore, the graphitization of the residual char of the hbDT/PET composites increased with the increase of hbDT content, which indicated that the decomposition of hbDT during combustion produced a large amount of phosphoric acid compounds. These phosphoric acid compounds promoted the cross-linking between hbDT and PET matrix to produce char residues and form the char protection, making the flame retardant more efficient.

Based on the Raman and SEM results, it is concluded that in the condensed phase, the phosphoric acid derived from the decomposition of hbDT reacts with PET, followed by the formation of a dense and swollen carbon layer in the presence of refractory and volatile gases.

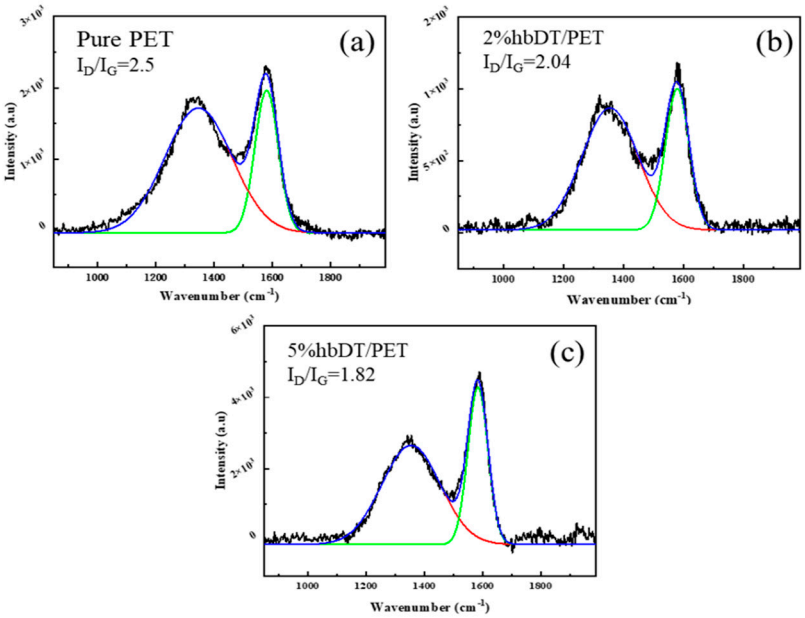

Figure S3 Raman spectra of char residue from (a) pure PET (b) 2%hbDT/PET and (c) 5%hbDT/PET after cone calorimeter test.

Table S1 Comparison of the flame retardant performances of PET composites reported in recent studies

Samples	Preparation method	Flame-retardants	LOI	△pHRR	△THR	Ref
PDPSI/PET	bulk-additive	PDPSI	27.3%	71.2%	29.1%	[1]
BA_nPETs	copolymerization	BA	31.0%	34.0%	16.0%	[2]
PET/FR2.0	bulk-additive	PRS	28.3%	31.1%	13.5%	[3]
PET/DP-DE	bulk-additive	DP-DE	30.5%	-	-	[4]
PET/PZS	bulk-additive	PZS	30.3%	45.5%	12.4%	[5]
PET/HPACP	bulk-additive	HPACP	28.3%	-	-	[6]
PDPSI/Fe_2O_3/PET	bulk-additive	PDPSI, Fe_2O_3	27.9%	66.0%	26.7%	[7]
PET/PNCP/TSCA	bulk-additive	PNCP, TSCA	30.0%	35.7%	9.6%	[8]
PET-MMT/CCS-50/d6	surface treatment	MMT CCS	-	50.2%	27.9%	[9]
hbDT/PET	bulk-additive	hbDT	30.2%	54.9%	16.3%	This work

PDPSI: Poly N-N dimethylene phosphate amidopropyl siloxane. BA: 5-(benzylidene-amino)-isophthalic acid dimethyl ester. PRS: poly (cyclotriphosphazene-resveratrol). DP-DE: 9,10-Dihydro-10-(2,3-dicarboxypropyl)-9-oxa-10-phosphaphenanthrene 10-oxide reacted with ethylene glycol. PZS: poly-(cyclotriphosphazene-co-4,40-sulfonyldiphenol). HPACP: hexa (phenylamino) cyclotriphosphazene.

TSCA: triazine oligoimides containing silicone charring agent. PNCP: hexakis (4-phenoxy) cyclotriphosphazene. MMT: modified montmorillonite. CCS: carboxymethyl chitosan.

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