## Supplementary Information

## Modification of epoxy resin through the self-assembly of a surfactant

## like multielement flame retardant

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We analyzed the reaction mechanism in detail. Based on the literature<sup>1</sup>, the pathway of the Kabachnik-Fields reaction depends on the nature of the reactants. Generally, the basicity of the amine is the crucial factor that determines the reaction pathway. In this paper, POSS-NH<sub>2</sub> as an aliphatic primary amine, which can nucleophilic interaction of the pre-reaction complex so in this condition the reaction follows the 'hydroxy phosphonate' pathway. As show in Scheme S1, the reaction starts with the addition of a phosphite to formaldehyde to form  $\alpha$ -hydroxyl phosphate **3**, followed the hydroxyl group was replaced by the amino group and release the water molecular, finally the target product was obtained.



Scheme S1. The proposed mechanism for the synthesis of POSS-bisDOPO.





Figure S2. 2D NMR spectra for POSS-bisDOPO.

## (a)





Figure S3. Mass spectra of POSS-NH<sub>2</sub> (a) and POSS-bisDOPO (b).



Figure S4. TGA and DTG curves of POSS-bisDOPO under air (a) and under nitrogen (b).



Figure S5. The TGA and DTG curves of control samples (a, b nitrogen atmosphere, c, d air atmosphere, 10 °C min<sup>-1</sup>).



Figure S6. SEM images of fracture surface of Control Samples.

1. R. A. Cherkasov and V. I. Galkin, Russ. Chem. Rev., 1998, 67, 857-882.