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# Supporting Information

## Growing Nano-petals on Electrospun Micro/nano Fibers

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## 1 Experimental Section

### (a) Materials

Polyarylene ether nitriles (PEN) were provided by the High Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province. It is a copolymer derived from 2,6-difluorobenzonitrile with bisphenol A (BP-A) and resorcinol (RS) with the inherent viscosity of 1.22 dL/g (in N-methylpyrrolidone, 0.005 g mL/L). The molecular structure of PEN is shown in Figure S1. 4,4′-bis (3, 4-dicyanophenoxy) biphenyl (BPh) was synthetized following our reported procedure.[1,2] Iron pentacarbonyl (particle size 6.8 μm) was supplied with China National Nuclear Corporation No.857 New Materials Company. N-methyl-2-pyrrolidinone (NMP, 99%), and N,N'-Dimethylformanide (DMF, 99%) were purchased from TianJin BODI Chemical Company. Materials obtained commercially were used without further purification.

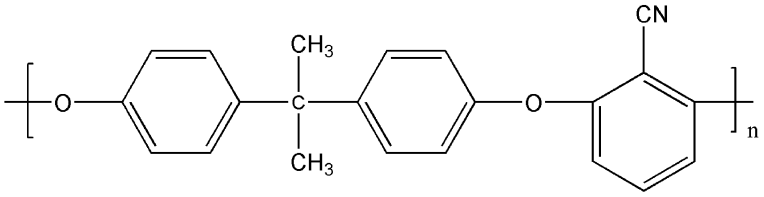


Figure S1. The molecular structure of PEN

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2 X. L. Yang, Y. J. Lei, J. C. Zhong, R. Zhao, X. B. Liu. *J. Appl. Polym. Sci.*, 2011, **119**, 882.

### (b) Preparation of Hyperbranched iron phthalocyanine

10 g BPh monomer and 12 mL NMP were added to a 250 mL three neck round bottle flask equipped with a mechanical stirrer and refluxing condenser, the mixture was heated at 180 $^{o}$C for few minutes to be dissolved sufficiently, then the solution was cooled to room temperature and 0.2 g iron pentacarbonyl was added to the bottle with vigorous stirring. The mixture was refluxed

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at 200 $^{o}$C for 2, 4 and 6 h, respectively. Finally, dark green solution was obtained. Then the solution was poured into water to precipitate the HBFePc with the vigorous mechanical stirring, moreover the excess iron pentacarbonyl was removed with millipore filter.

Scheme S1 is Synthetic route and structure of the hyperbranched FePc.

Typical FTIR characteristic data (shown in Figure S2a) were as follows: 2231 $cm^{-1}$ (stretch, –CN), 1209 $cm^{-1}$ (stretch, Ar–O–Ar), 885 $cm^{-1}$ (bend, 1,2,4-substituted benzene), and 831 $cm^{-1}$ (bend, 1,4-substituted benzene). Futhermore, a new characteristic peak at 1010 $cm^{-1}$ was observed during polymerization of the cyano groups, indicating the formation of phthalocyanine rings.[3,4]

The $^{1}$H NMR (400 MHz,DMSO) δ values are 8.13 ppm, 7.87 ppm, 7.82 ppm, 7.46 ppm, and 7.30 ppm. All resonances were assigned to H of benzene. There were four protons of the biphenyl segment in the monomer. The spectra of BPH and HBFePc oligomers were similar, indicating that the reaction occurred at the end groups.

From Figure S3, the HBFePc showed typical electronic spectra with two strong absorption bands: a Soret (B) band at around 290–340 nm and a Q band at around 620–750 nm. Increasing the reaction time caused an increase of the intensity of the Q bands and broadening of the B band. With the pre-polymerization time increased, the content of the FePc unit in HBFePc and hyperbranched degree increased, thus, the molecular weight of HBFePc increased.[4-6] GPC: Mw=1185, Mn=1183 (HBFePc treated for 2h); Mw=1765, Mn=1639 (HBFePc treated for 4h); Mw=1923, Mn=1890 (HBFePc treated for 6h).

3 A.W. Snow and J.R. Griffith, *Macromolecules*, 1984, **17**, 1616.

4 T. W. Lee, Y. Kwon, J. J. Park, L. S. Pu, T. Hayakawa and M. A. Kakimoto, *Macromol. Rapid. Commun*., 2007, **28**, 1657.

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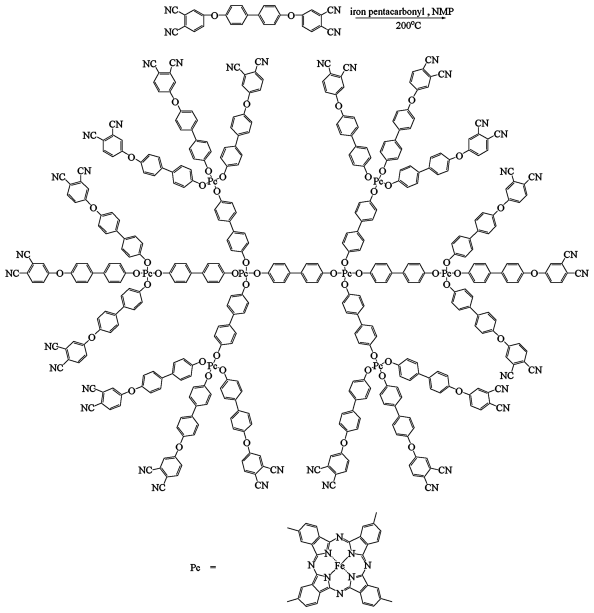


Scheme S1. Synthetic route and structure of the HBFePc

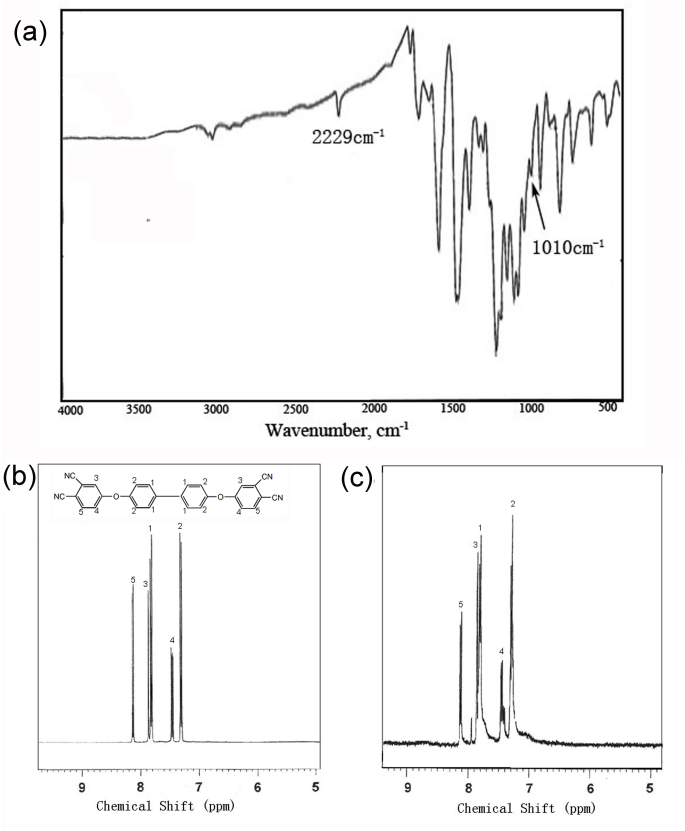


Figure S2. (a) FTIR spectra of HBFePc and 1H NMR spectra of (b) BPH and (c).

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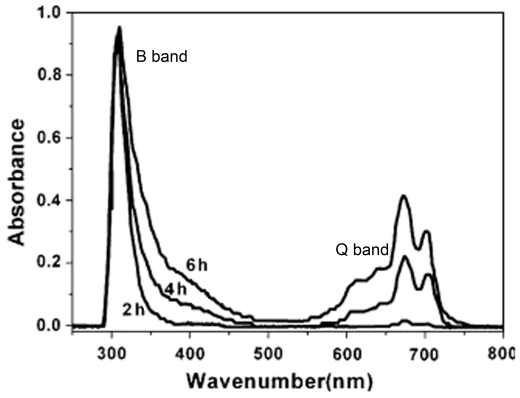


Figure S3. UV–Vis spectra of HBFePc oligomers at different treatment time in NMP

**(c) Preparation and post-treatment of PEN/HBFePc fibers**

The PEN concentration was 12% w/v (with respect to solvent DMF). Then, the HBFePc was added into the solution to form the homogeneous solution, and the HBFePc content was 100 % (w/w) (with respect to PEN). The mixture was electrospun to fabricate PEN/HBFePc micro/nano fiber membranes at a flowrate of 1 mL/h under 25 kV voltages. Collected nanofibers membranes after electrospun for 60 min were immersed in ethanol for 2 h, 4 h and 10 h, respectively. Then, the as-prepared samples were dried in a vacuum oven at 60 $^{o}$C overnight. The electrospun PEN nanofiber and composite fibers treated in deionized water were fabricated as the control samples.

**(d) Characterization**

The morphology of electrospun PEN/HBFePc nanofibers and the corresponding petals and thorns fibers after post-treatment were evaluated using scanning electron microscopy (SEM) (JSM, 6490LV). The evolution of the molecule absorption spectra upon aggregation and the formation of ordered states from the petals and thorns fibers, respectively, were characterized by the UV-3150 ultraviolet–visible spectroscopy (UV–vis spectroscopy) of Japan Shimadzu Corporation. The fibers and power were tested under diffuse reflection, and the solution were

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tested under light transmission. Gel permeation chromatography (GPC) was performed on a Shodex RI-71 refractive index detector. Nuclear magnetic resonance ($^1$H NMR) spectra were obtained using a Bruker AV400 spectrometer at a proton frequency of 400 MHz using dimethyl sulfoxide (DMSO) as the solvent. The contact angles of water on the mats were measured using a dynamic contact angle analyzer (KRUSS GmbH, model DSA-100) at room temperature. Measurements from at least six droplets of 8 mg of freshly distilled pure water were averaged. The fluorescence spectra were measured on F-4600 FL Spectrophotometer in film states.

**2**

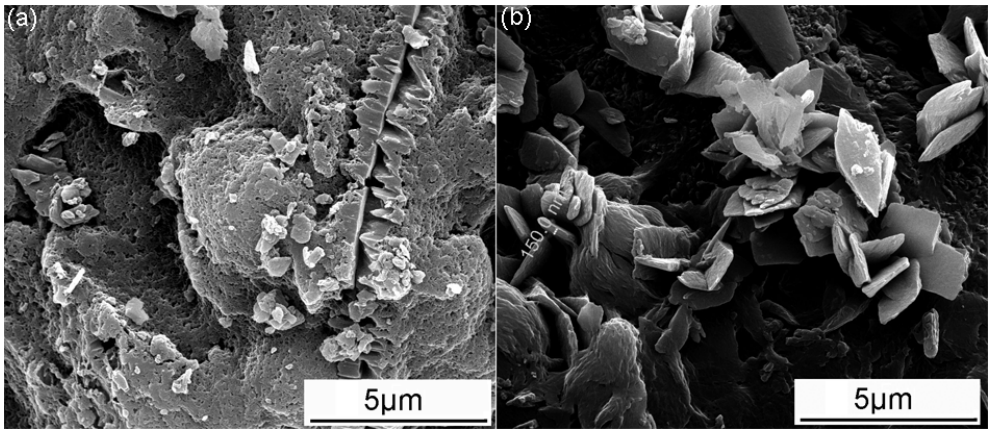


Figure S4. SEM of (a) HBFePc powder and HBFePc powder treated in ethanol for 10 h.

According to the literature[1], the addition of organic solvents (ethanol, methanol, pyridine, and dimethyl sulfoxide) and the incorporation of phthalocyanines into cationic micelles[2,3], were used to reduce the stacking. The disstacking usually reflects in a stronger emission and a longer life time of the excited state. Herein, the composite fibers can be destoryed after immersed in pyridine or dimethyl sulfoxide. Thus we choosed the ethanol with low toxic to get stronger fluorescent properties.

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**3**

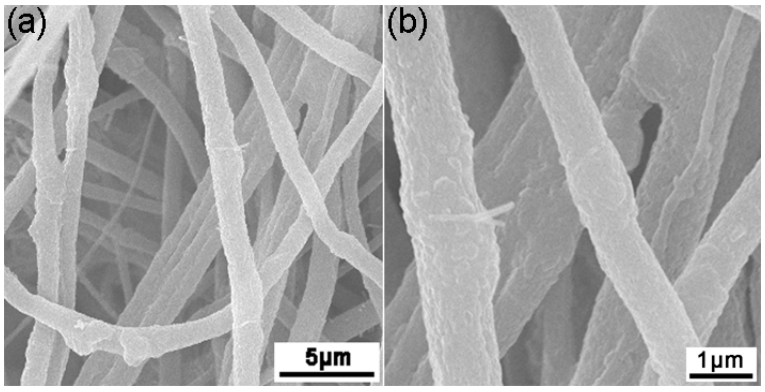


Figure S5. SEM images of electrospun PEN/HBFePc micro/nano fibers

**4**

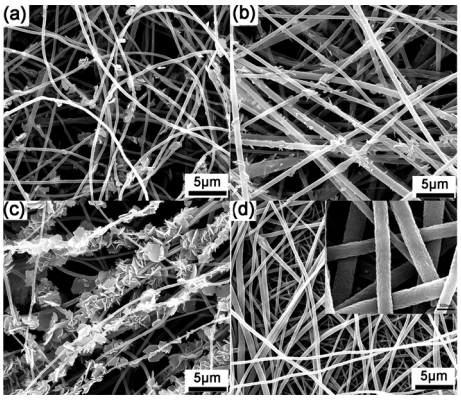


Figure S6. SEM of PEN/HBFePc micro/nano fibers treated for 12 h in ethanol containing (a) SDS (2.7×10-5 mol cm-3), (b) SDS (2.7×10-7 mol cm-3), (c) CTAB (2.7×10-5 mol cm-3), and (d) CTAB (2.7×10-7 mol cm-3).

Figure S6 shows the morphology evolution of PEN/HBFePc-4h under the SDS and CTAB, respectively. From Figure S6a, It can be seen that sparse HBFePc nanopetals were founded on the surface of PEN fibers compared with that of PEN/HBFePc treated without SDS. With increasing concentration of SDS, the surface morphology of composite fibers treated in

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ethanol/SDS gradually changed from nanopetals to nanothorns. According to the literatures[1-3] and above results, The decrease of nanopetals via self-assembly was due to the formation of micelles in which the phthalocyanines were partially disrupted.[7] Furthermore, the electrostatic forces can result into the interactions between the central metal ion and anionic SDS, and the macrocycle can link with the long alkyl chain. With the increase of treatment time in ethanol/SDS, the HBFePc gradually grow along the long alkyl chain via the self-assembly and form the thorns-like structure as shown in Figure S6b. Addition of a small amount of cationic CTAB, the electrostatic interaction between the anionic ends of the dendritic fragments and cationic CTAB, Upon further addition of CTAB, more CTAB micelles are formed, and the average number of phthalocyanine attached to each micelle decreases. Furthermore the aggregation of phthalocyanines is greatly inhibited by CTAB and eventually the anionic macrocycles, are adsorbed onto the cationic micelle surfaces. Thus only rough surface without nanopetals was observed as shown in Figure S3d. Similar results have been obtained previously for the system of CTAB.

1 S. Dhami, J. J. Cosa, S. M. Bishop and D. Phillips, *Langmuir*, 1996, **12**, 293.

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3 C. A. T. Laia and S. M. B. Costa, *J. Phys. Chem. B*., 2004, **108**, 17188.

**5**

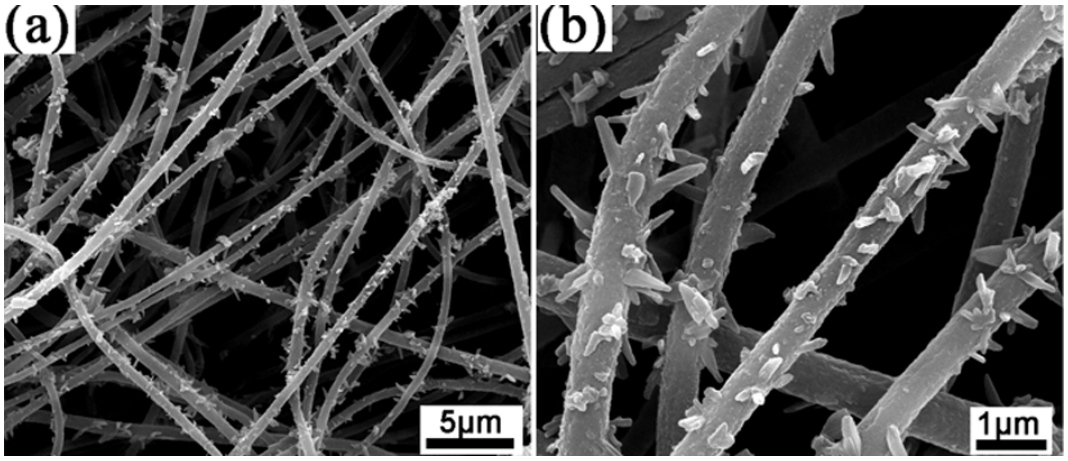


Figure S7. SEM image of PEN/HBFePc fibers treated in deionized water

The morphology of the copmpsite fiber treated in deionized water shows nanothorns-like structure rather than nanopetals. It is attributed phthalocyanines display a strong tendency to form higher-order aggregates in water as a result of the propensity of the large hydrophobic skeleton to avoid contact with the aqueous medium.[1-3] Thus nanothorns can grow on the

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nanofiber by the cooperation of π–π stacking of the Pc rings with tight packing between the benzene rings.

1 W. West, S. Pearce, *J. Phys. Chem.*, 1965, **69**, 1894.

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