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**Supplementary Information** 

## Double-layer core/shell-structured nanoparticles in polyarylene

## ether nitriles based nanocomposites as flexible dielectric materials

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Corresponding author. Tel: +86-28-83207326; Fax: +86-28-83207326; E-mail address: weirb10@uestc.edu.cn Corresponding author. Tel: +86-28-83207326; Fax: +86-28-83207326; E-mail address: liuxb@uestc.edu.cn **Synthesis of PEN:** 50 mL toluene and 150 mL NMP were added into a 500 mL three-necked round-bottom flask equipped with a Dean-Stark trap and a mechanical stirrer. Then, biphenyl (BP, 0.20 mol) and 2, 6-dichlorobenzonitrile (DCBN, 0.20 mol) were sequentially added into the solvent companied with mechanical stirring. Subsequently,  $K_2CO_3$  (0.25 mol) acting as a catalyst, was added into three-necked round-bottom flask in several times. After that, the round-bottom flask was heated by a heating jacket and kept stirring. After the water-toluene azeotrope distilled off, the reaction mixture was heated to 150, 160, 170, and 180 °C for 1 h, respectively. After cooling the system to room temperature, the mixture was poured into 1000 mL of diluted HCl solution in order to remove the excess  $K_2CO_3$ , and then rinsed by acetone and alcohol till the solvent and monomers were washed out completely. After filtration, the white solid product was dried at 100 °C for 12 h.

**Synthesis of CPEN:** The synthetic process of CPEN is exactly the same as PEN except using Phenolphthalin (PPL, 0.20mol) to replace biphenyl (BP, 0.20 mol).

**Synthesis of NH<sub>2</sub>-CuPc:** The 4-nitrophthalonitrile (0.2 mol), Cu(AC)<sub>2</sub>·H2O (0.06 mmol) and 100 ml DMAC were added into a 250 mL three-necked round-bottom flask. Then, the mixture was refluxed and reacted at 160 °C for 4 h with the magnetic stirrer under the protection of nitrogen. After that, the solution was poured into 500 mL of deionized water for precipitation, and then the solid product (NO<sub>2</sub>-CuPc) by washing them three times each with acetone, ethanol and deionized water. After filtration, the deep blue solid product was dried at 80 °C for 12 h. Furthermore, the obtained NO<sub>2</sub>-CuPc was reduced to NH<sub>2</sub>-CuPc by further treating with Na<sub>2</sub>S·9H<sub>2</sub>O in DMF at 65 °C for 6 h.



Fig. S1 Synthetic route to the PEN and CPEN.



**Fig. S2** XPS survey spectrum of the CPEN-f-BT@CuPc.



**Fig. S3** FTIR spectrum of CPEN-f-BT@CuPc (a) and the enlarged FTIR spectrum of CPEN-f-BT@CuPc (b).



Fig. S4 The TGA curves of the CPEN-f-BT@CuPc/PEN composite films.



**Fig. S5** SEM micrographs of the cross-section of the samples with different content of CPEN-f-BT@CuPc. (a) 0%, (b) 2.0 wt%, (c) 10.0 wt%, (d) 20.0 wt%.



Fig. S6 The elongation at break of CPEN-f-BT@CuPc/PEN composite films.