

Electronic Supplementary Information

Morphology-dependent AEE performance of conjugated poly(tetraphenylethene)s

*Xiaoning Liu, Lipeng He, Chen Wang, Iram Hanif, Huanting Huang and Weifeng Bu**

Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu
Province, State Key Laboratory of Applied Organic Chemistry, and College of
Chemistry and Chemical Engineering, Lanzhou University, Lanzhou City, Gansu
Province, China

General considerations

All water- and air-sensitive reactions were performed under an anhydrous argon atmosphere. Anhydrous toluene and THF were obtained from normal pressure distillation over Na and benzophenone under argon. They were used immediately after the distillation. Other commercially available solvents and chemicals were directly used without any further purification. 1,2-Diiodobenzene, 1,3-diiodobenzene and 1,4-diiodobenzene were obtained from *J&K Chemical*. Bis(triphenylphosphine)palladium(II) chloride ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$) and copper(I) iodide (CuI) were purchased from *Kaida Chemical* and *Sinopharm Chemical*, respectively. 1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (**TPEE**) was synthesized as described previously.^{4b}

^1H and ^{13}C NMR spectra were recorded on a *JNM-ESC400* spectrometer, during which the samples were dissolved in *d*-chloroform (CDCl_3) and tetramethylsilane was used as an internal standard. GPC plots were recorded on a *Waters 1515* instrument and determined number- (M_n) and weight-average (M_w) molecular weights and polydispersity indices (*PDI*) of conjugated poly(tetraphenylethene)s. Polystyrene was used as a calibration standard and THF was the eluent. FT-IR spectra were performed on a Nicolet NEXUS 670. The spectra were recorded with a resolution 4 cm^{-1} . UV-vis absorption and fluorescence spectra were measured on a *Shimadzu 2550* spectrophotometer and a *Hitachi F-7000* spectrofluorimeter, respectively. In the latter case, a xenon lamp was used as the excitation source (150 W). TEM images were recorded on *JEM-2100* operating at 200 kV. SEM measurements were performed on a field emission *Hitachi S-4800*. Before the imaging, thin gold layer (ca. 4 nm) was coated on the specimen by using *Hitachi E-1045* ion sputter. All measurements were carried out at 20 °C.

Dispersion preparation

o-PTPE was first dissolved in good solvents such as toluene and chloroform at 20 °C. And then, methanol or hexane was added as poor solvents in one portion with vigorous stirring. The volume ratios between good and poor solvents were controlled at 33%, 43%, 50%, 67%, 75% and 90%. Finally, opaque dispersions formed with a final concentration of 0.33 mg/mL. Other dispersions were similarly prepared for *m*-PTPE and *p*-PTPE. All of these dispersions were immediately subjected to emission measurements. Meanwhile, they were cast (5 μ L) on carbon-coated copper grids and/or copper grids coated with a porous polymer membrane for TEM and SEM observations.

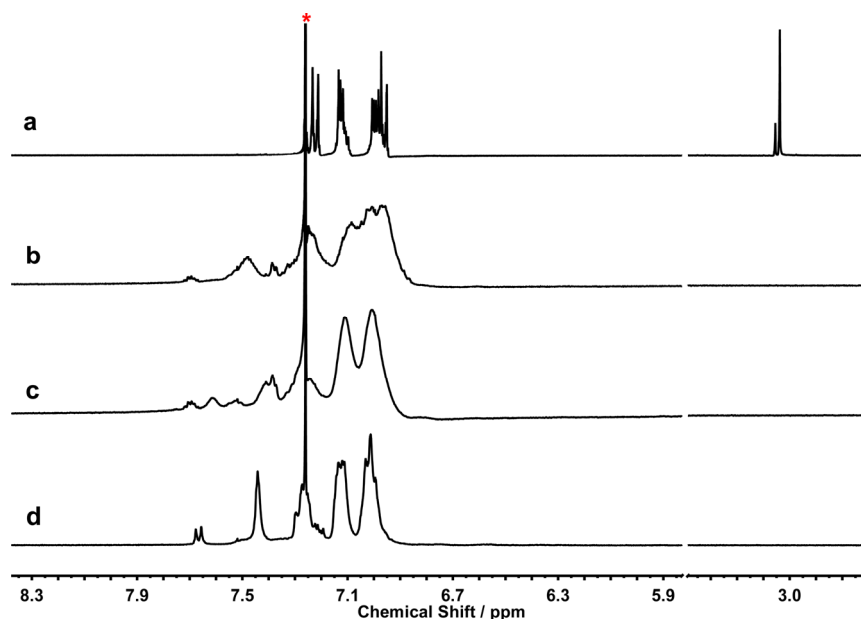


Fig. S1 ^1H NMR spectra of (a) TPEE, (b) *o*-PTPE, (c) *m*-PTPE, and (d) *p*-PTPE in CDCl_3 . The CHCl_3 peak was labeled as a red star.

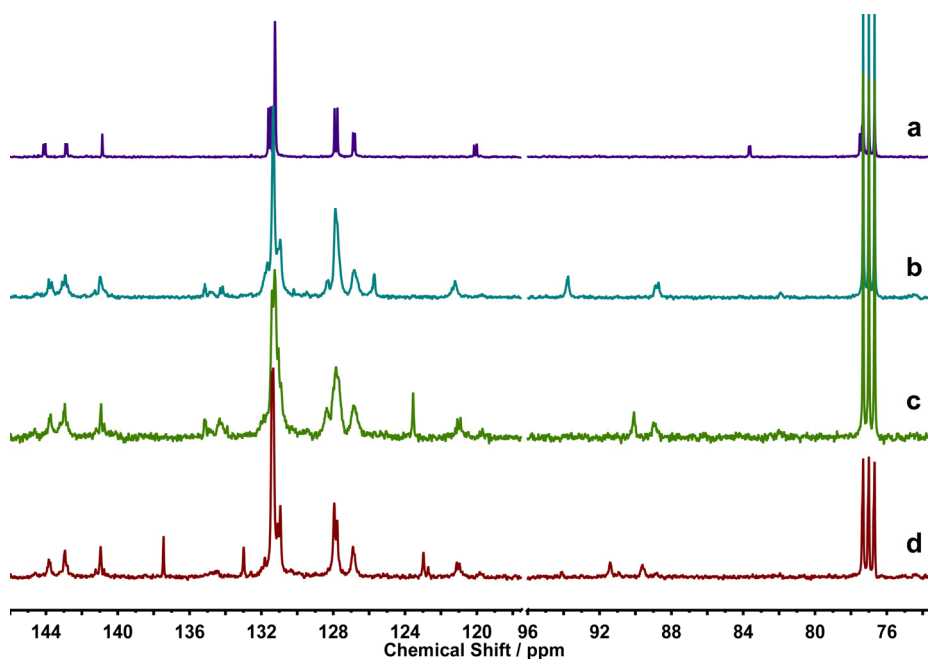


Fig. S2 ^{13}C NMR spectra of (a) TPEE, (b) *o*-PTPE, (c) *m*-PTPE, and (d) *p*-PTPE in CDCl_3 .

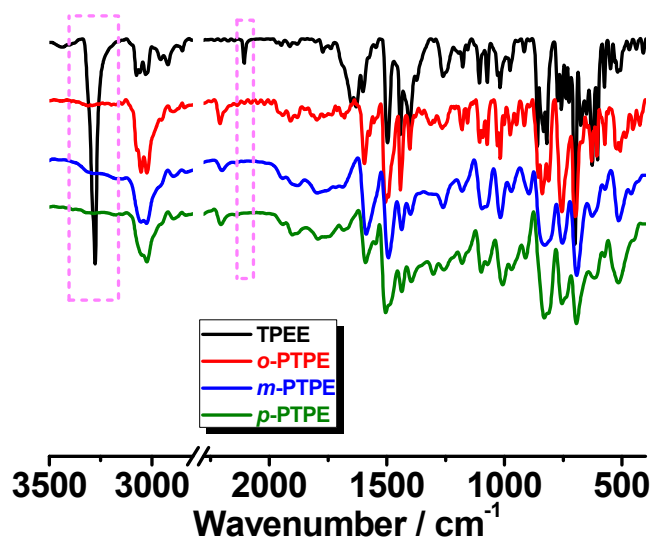


Fig. S3 FT-IR spectra of (Black) TPEE, (Red) *o*-PTPE, (Blue) *m*-PTPE, and (Olive) *p*-PTPE. The samples were compressed as KBr pellets.

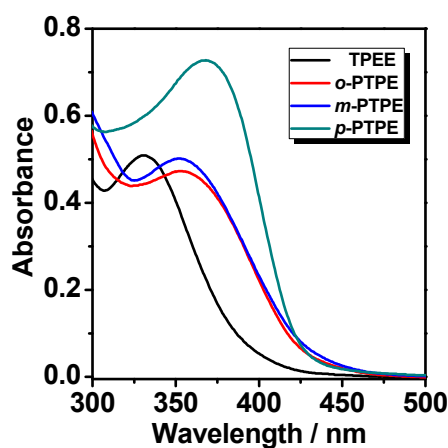


Fig. S4 UV-vis absorption spectra of TPEE, *o*-PTPE, *m*-PTPE, and *p*-PTPE in CHCl₃.

Table S1 The molecular weights and polydispersity indices (*PDI*) of *o*-PTPE, *m*-PTPE, and *p*-PTPE.

Samples	M_n	M_w	<i>PDI</i>
<i>o</i> -PTPE	7600	10500	1.38
<i>m</i> -PTPE	14900	30500	2.05
<i>p</i> -PTPE	8500	14100	1.65

The values of M_n , M_w and *PDI* were determined by GPC measurements.

GPC data are correlated the hydrodynamic volume of the randomly coiled polymer chains with polymer molecular weight. In the present case, all polymer molecular weights reported were determined by GPC analysis calibrated against polystyrene standards. Semiflexible or rigid polymers occupied more rodlike conformations in solution. Therefore, a GPC analysis of these rigid-rod polymers generally overestimates the molecular weights together with low degrees of polymerization.

Indeed, many **TPE**-containing conjugated polymers possess relative low number average molecular weight, for instance in the range of 3~10 kDa as reported in literatures.³ In the present case, as deduced by the reviewer, the DP value of ***o*-PTPE** is around 8. But in fact, these products demonstrated typical properties of macromolecules including the formation of free-standing films and possessing of evident glass transition behavior. Moreover, the fluorescent emission behavior of the products can be termed as AEE, which is different from the AIE characteristic of the TPE unit. These properties may partially be associated with the unique propeller-like configuration of TPE units.

In the ¹H and ¹³C NMR spectra of the **PTPEs**, the alkyne proton ($\delta = 3.04$ and 3.06 ppm, Fig. S1) and carbon resonances ($\delta = 77.66$, 83.77 and 83.84 ppm, Fig. S2) of **TPEE** disappeared completely. This means that the end group disappeared completely. As addressed, ¹H NMR spectroscopy has a typical detection limit of 5%. Accordingly, the degrees of polymerization would be greater than 20. The GPC values were much lower than the molecular weights estimated from the corresponding ¹H NMR spectra, which might result from the absence of poly(tetraphenylethene) standard samples. Furthermore, the steric effect of **PTPEs** including connection modes and cis-trans isomerism of **TPE** probably leads to decreasing hydrodynamic volumes and thus lower GPC values.

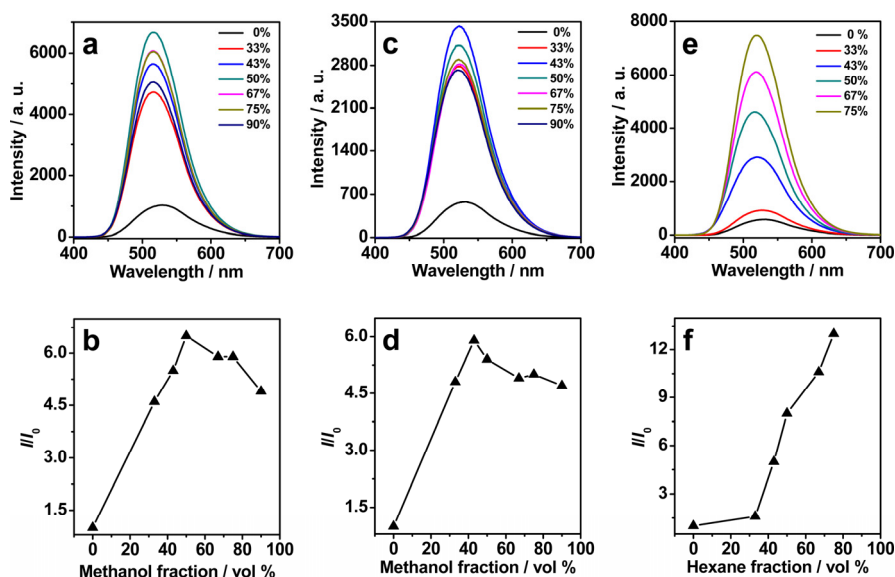


Fig. S5 Photoluminescence spectra of ***m*-PTPE** and the plots of emission intensities with poor solvent contents in the toluene/methanol mixture solvents (a and b), the chloroform/methanol mixture solvents (c and d) and the chloroform/hexane mixture solvents (e and f). Chloroform and toluene are good solvents of ***m*-PTPE**, while methanol and hexane are its poor solvents. The concentration was 0.33 mg/mL for the **TPEE** unit.

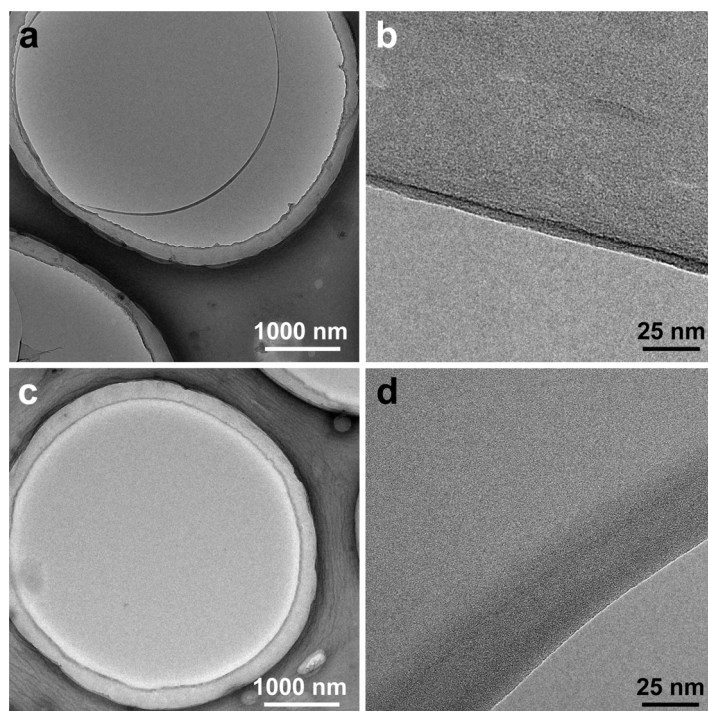


Fig. S6 Free-standing sheets of *o*-PTPE formed in the toluene/methanol mixture solvents with methanol volume ratios of 33% (a and b) and 43% (c and d).

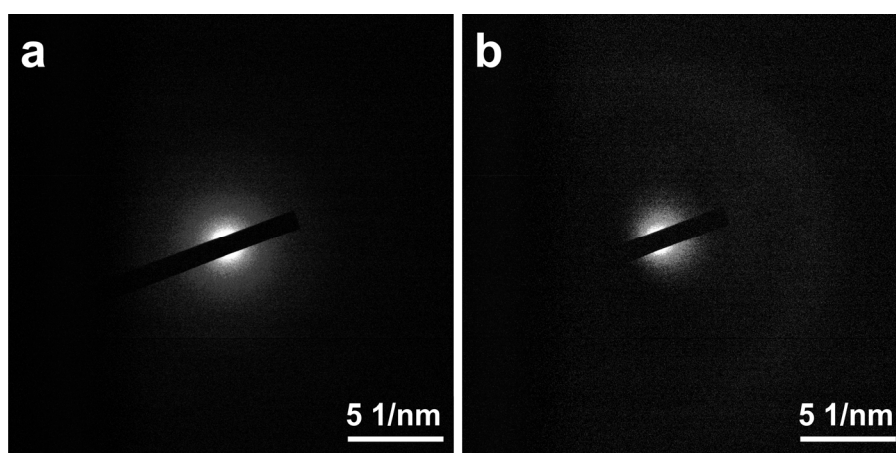


Fig. S7 Electron diffraction patterns of free-standing sheets of *o*-PTPE formed in the toluene/methanol mixture solvents with methanol volume ratios of 50% (a) and 67% (b).

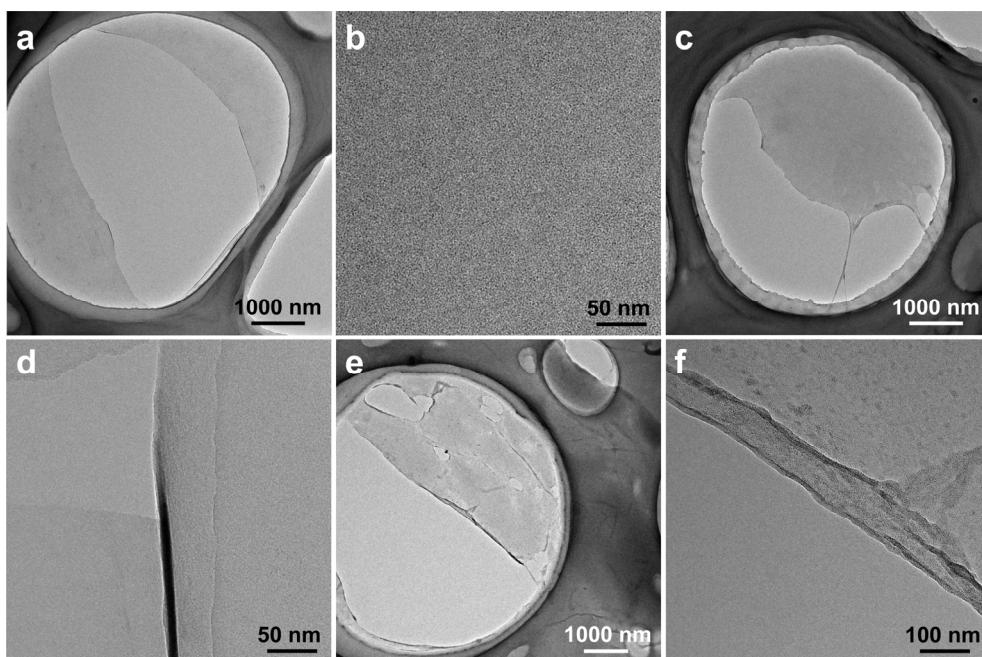


Fig. S8 Free-standing sheets of *m*-PTPE formed in the toluene/methanol mixture solvents with methanol volume ratios of 33% (a), 43% (b), 50% (c and d) and 67% (e and f). The thickness was estimated to be ca. 10 nm (d and f).

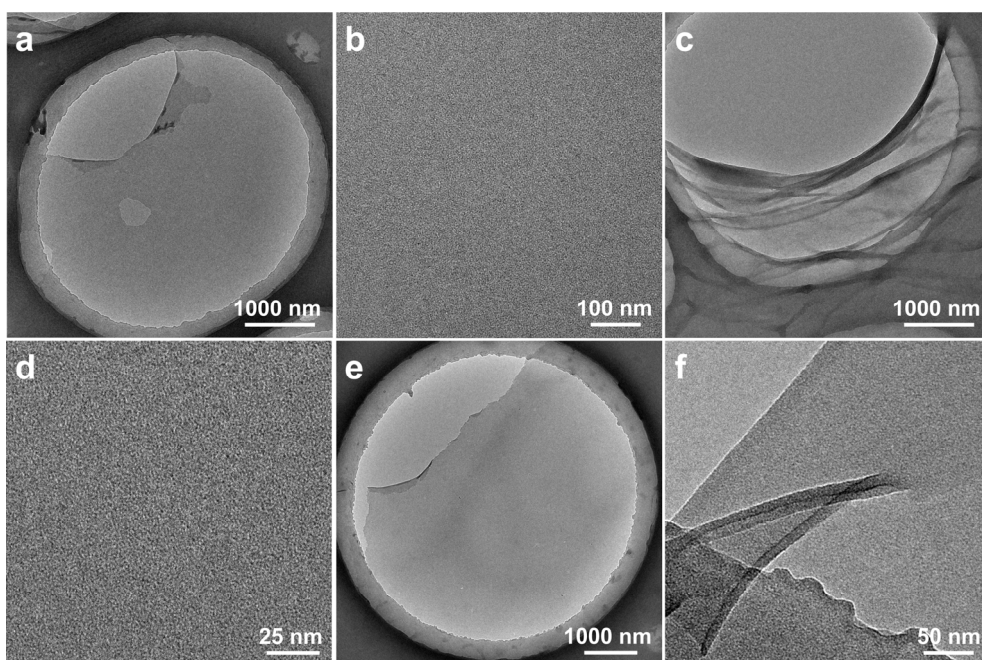


Fig. S9 Free-standing sheets of *p*-PTPE formed in the toluene/methanol mixture solvents with methanol volume ratios of 33% (a), 43% (b), 50% (c and d) and 67% (e and f).

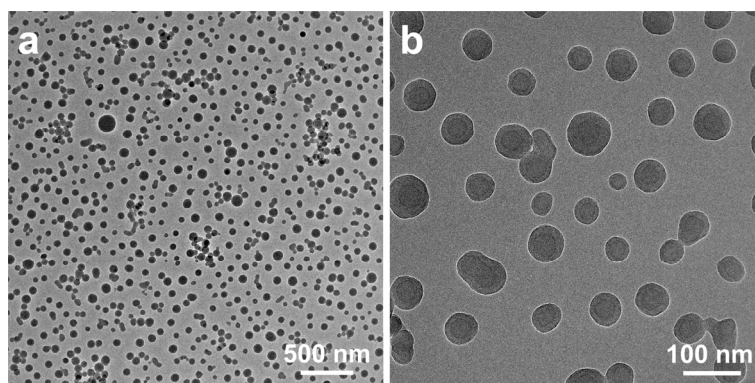


Fig. S10 *m*-PTPE self-assembled to form nanospheres in the toluene/methanol mixture solvent with a methanol volume ratio of 90%.

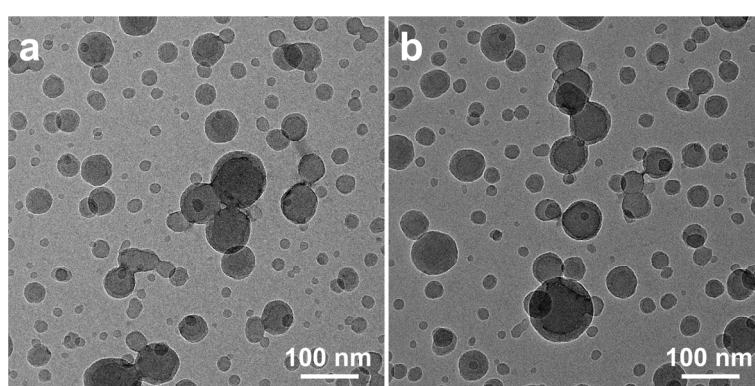


Fig. S11 *p*-PTPE self-assembled to form nanospheres in the toluene/methanol mixture solvent with a methanol volume ratio of 90%.

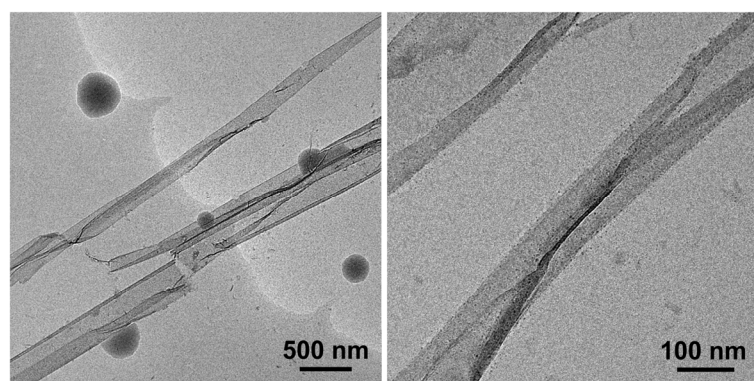


Fig. S12 The sheets of *o*-PTPE coexisted with nanospheres in the toluene/methanol mixture solvent with a methanol volume ratio of 75%.

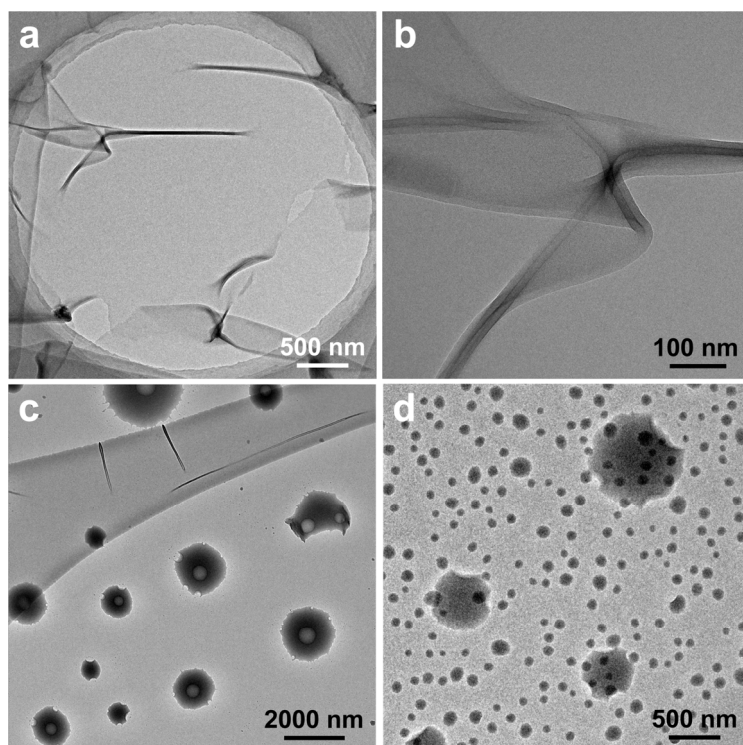


Fig. S13 The sheets of *m*-PTPE coexisted with nanospheres in the toluene/methanol mixture solvent with a methanol volume ratio of 75%.

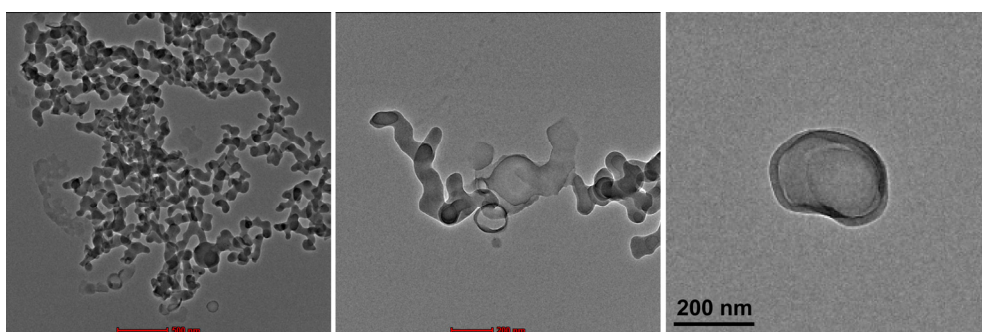


Fig. S14 *o*-PTPE self-assembled to form irregular and solid aggregates together with a few of hollow nanostructures in the chloroform/hexane mixture solvent with a hexane volume ratio of 90%.

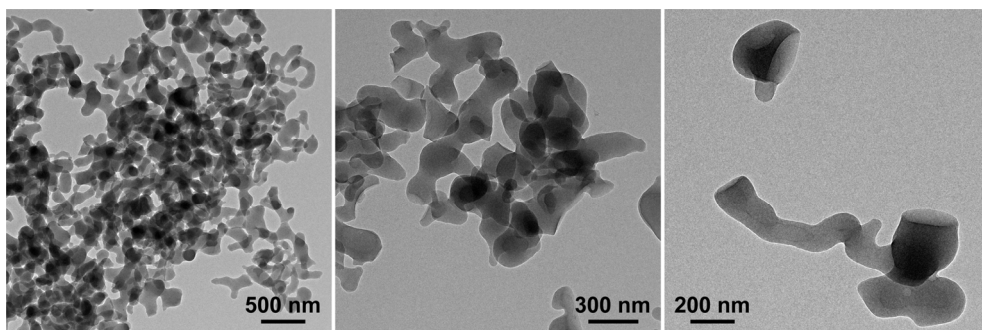


Fig. S15 *o*-PTPE self-assembled to form irregular and solid aggregates in the chloroform/hexane mixture solvent with a hexane volume ratio of 67%.

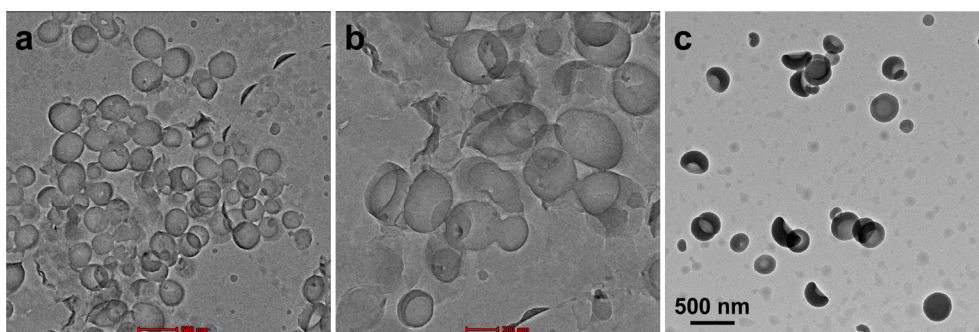


Fig. S16 *o*-PTPE self-assembled to form hollow nanostructures together with a few of solid nanospheres in the chloroform/hexane mixture solvents with hexane volume ratios of 43% (a and b) and 50% (c).

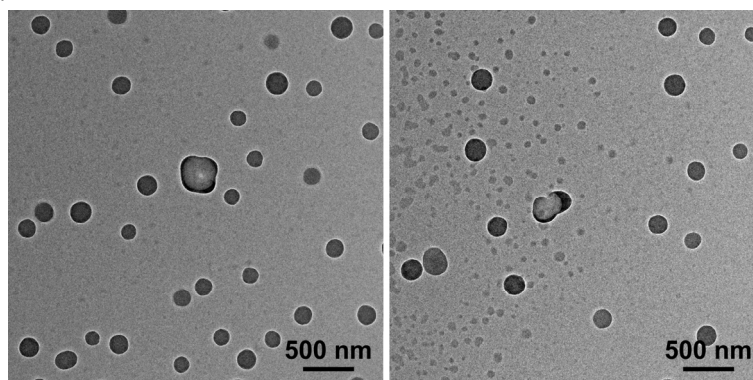


Fig. S17 *p*-PTPE self-assembled to form solid nanospheres together with a few of hollow nanostructures in the chloroform/hexane mixture solvent with a hexane volume ratio of 43%.

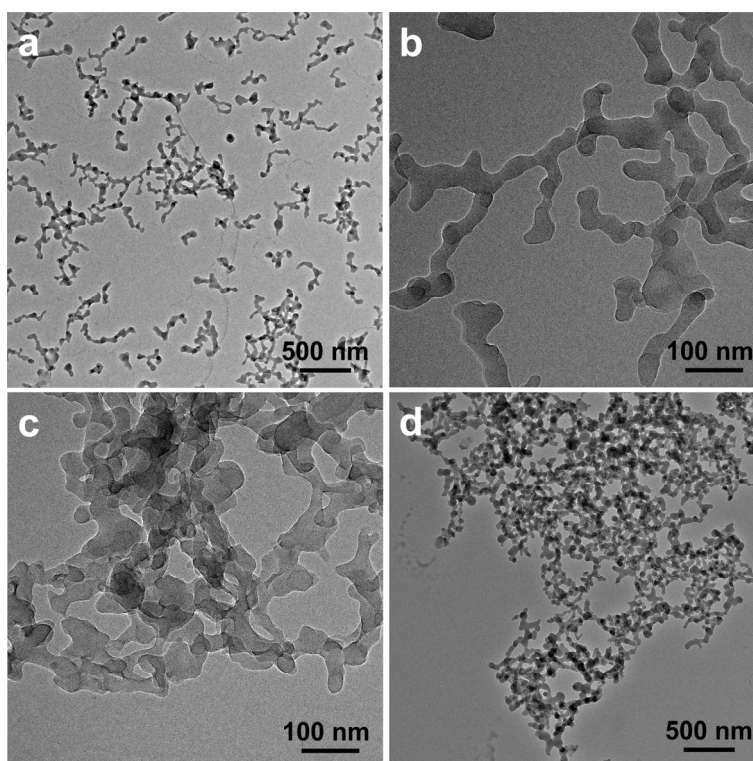


Fig. S18 *p*-PTPE self-assembled to form fused nanospheres or short worms in the chloroform/hexane mixture solvents with hexane volume ratios of 67% (a and b), 75% (c) and 90% (d).

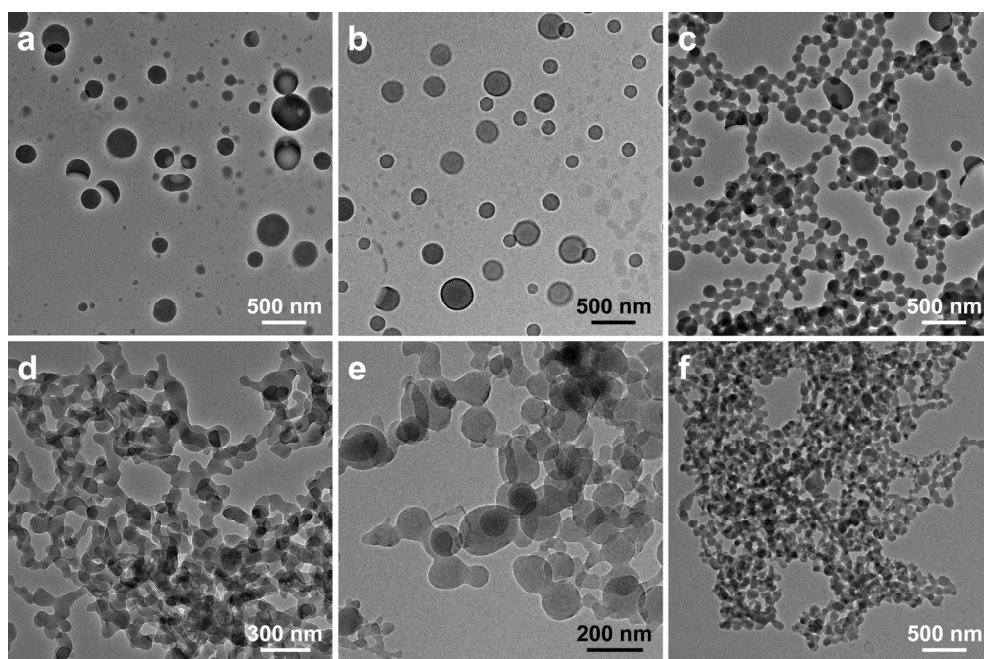


Fig. S19 TEM images of *m*-PTPE self-assembled in the chloroform/hexane mixture solvents with hexane volume ratios of 43% (a), 50% (b and c), 67% (d), 75% (e) and 90% (f).

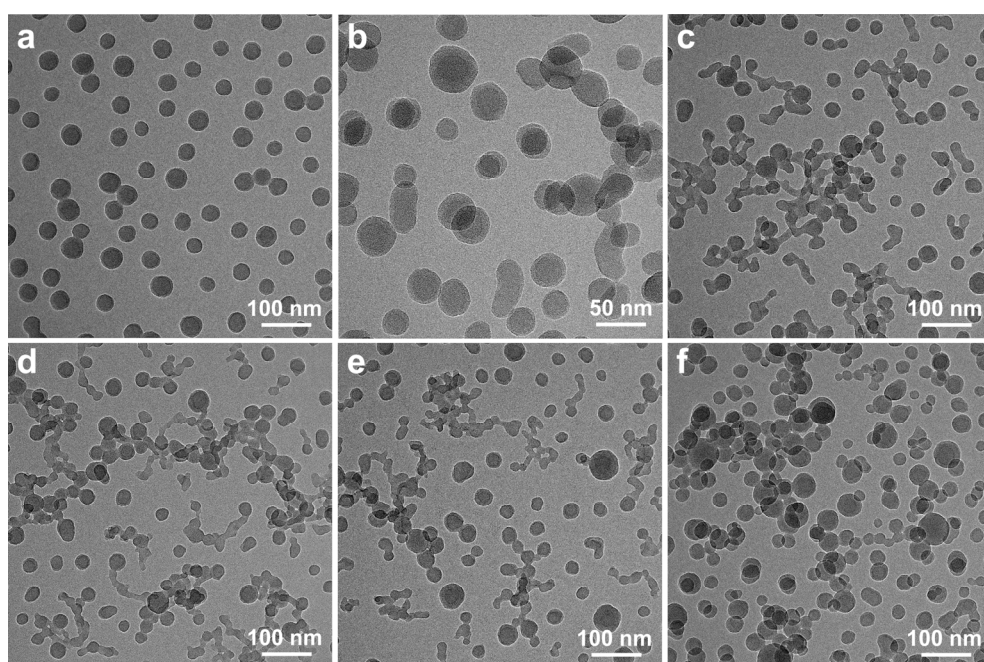


Fig. S20 *m*-PTPE self-assembled to form solid nanospheres in the chloroform/methanol mixture solvents with methanol volume ratios of 33% (a), 43% (b), 50% (c), 67% (d), 75% (e) and 90% (f).

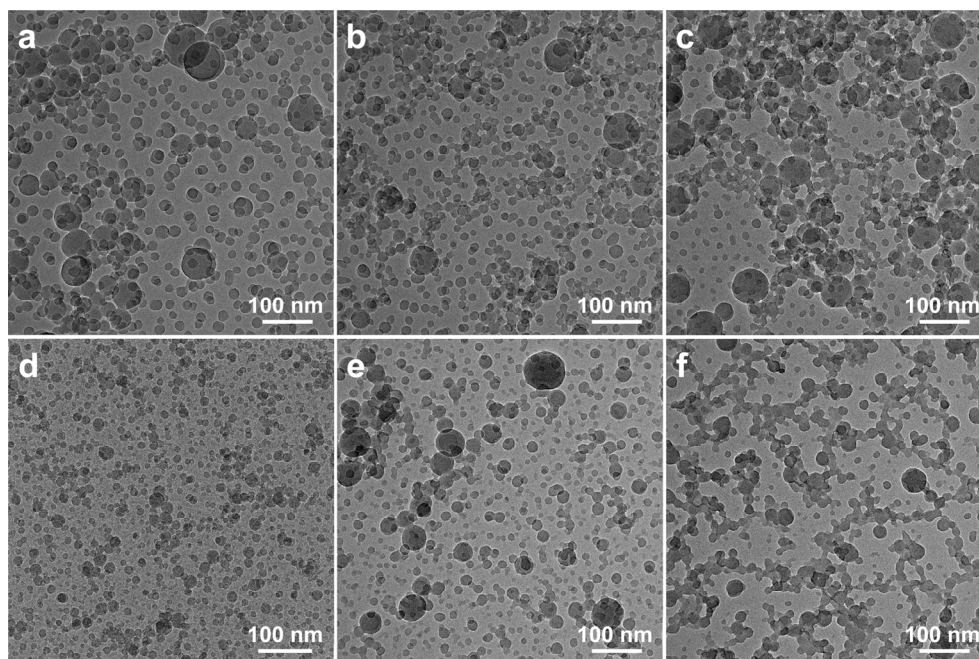


Fig. S21 *p*-PTPE self-assembled to form solid nanospheres in the chloroform/methanol mixture solvents with methanol volume ratios of 33% (a), 43% (b), 50% (c), 67% (d), 75% (e) and 90% (f).