# **Supporting Information**

An Unprecedented Toughening High-performance Polyhexahydrotriazines Constructed by Incorporating Point-face Cation $-\pi$  Interactions in Covalently Crosslinked Networks and the Visual Detection of Tensile Strength

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## **Materials and Methods**

4-Aminoindole (4-In) was purchased from J & K Technology Co., Ltd., and purified by column chromatography on silica gel. 4,4'-(1,3-phenylenedioxy)dianiline (POD) was purchased from TCI Development Co., Ltd., and used without further purification. Other high purity reagents and solvents were used without further purification.

Fourier Transform Infrared Spectra (FTIR) were recorded on a 380 FTIR spectrometer (Thermo Electron, US) using KBr disks, and the scan times and range were 32 and 400~4000 cm<sup>-1</sup>, respectively. The solid state <sup>13</sup>C CP/MAS NMR measurement was carried out on a Bruker Avance 600. <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectra were recorded on a Bruker AMX600 MHz NMR spectrometer within CDCl<sub>3</sub>. The thermogravimetric analysis (TGA) was performed on a TGAQ500 at a heating rate of 10 °C/min under nitrogen atmosphere. Differential Scanning Calorimetry (DSC) measurements were carried out on a PerkinElmer DSC-7 calorimeter under N<sub>2</sub> atmosphere. Each sample was rapidly heated to 250 °C and then, the scan was carried out in nitrogen atmosphere over a temperature range of 50~250 °C at a scanning rate of 10 °C/min. The stress-strain experiments were carried out on a electromechanical universal testing machine (CMT4303, China Academy Of Engineering Physics, Chengdu, China) at a strain rate of 2 mm/min. Dynamic Mechanical Analysis (DMA) were measured on Q800 (TA Instruments) working in the tensile mode. The Energy Dispersive Spectroscopy (EDS) experiments were conducted using a field emission SEM (JEOL JSM-7400F). Fluorescent

emission spectra were collected on a Shimadzu RF-6000 fluorescence spectrometer. UV-Visible spectroscopy was performed on a Solidspec-3700 instrument.

#### Synthesis and characterization of the In-PHT

The In-PHT mentioned in the main text with a molar ratio, 4-In/(4-In+POD) = 5% is illustrated as an example. Formaldehyde (2.5 mmol), 4,4'-(1,3-phenylenedioxy) dianiline (0.9 mmol), and 4-aminoindole (0.1 mmol) were weighed out into a 2-Dram vial equipped with stirbar inside the glovebox and N-methylpyrrolidone was added (NMP, 3.0 mL). The reaction mixture was heated at 50 °C for 30 min, and then heated to 200 °C for 3 h. The solution was allowed to cool to room temperature and the vial containing the polymer was filled with acetone, then filtered and dried in a vacuum oven overnight and collected an brown solid. Synthesis of other In-PHT with different 4-In/(4-In+POD) were carried out in the same manner with polymerization yields all being above 96%. The FTIR and <sup>13</sup>C CP/MAS NMR spectra of with different molar fraction of 4-In/(4-In+POD) are shown in Figure S1 and S2.

The characterization of In-PHT with 4-In/(4-In+POD) = 5%: Polymerization Yield: 95%; FTIR spectrum (KBr pellet, cm<sup>-1</sup>): 3409, 3047, 2918, 2817, 2383, 1867, 1677, 1472, 1390, 1121, 768; <sup>13</sup>C CP/MAS NMR: 150-100 (C of benzene and indole ring), 70-40 (C of -N-CH<sub>2</sub>-N-) ppm.

The characterization of In-PHT with 4-In/(4-In+POD) = 10%: Polymerization Yield: 96%; FTIR spectrum (KBr pellet, cm<sup>-1</sup>): 3409, 3047, 2918, 2817, 2383, 1867, 1677, 1472, 1390, 1121, 768; <sup>13</sup>C CP/MAS NMR: 150-100 (C of benzene and indole ring), 70-40 (C of -N-CH<sub>2</sub>-N-) ppm. The characterization of In-PHT with 4-In/(4-In+POD) = 20%: Polymerization Yield: 96%; FTIR spectrum (KBr pellet, cm<sup>-1</sup>): 3409, 3047, 2918, 2817, 2383, 1867, 1677, 1472, 1390, 1121, 768; <sup>13</sup>C CP/MAS NMR: 150-100 (C of benzene and indole ring), 70-40 (C of -N-CH<sub>2</sub>-N-) ppm.



**Figure S1.** FTIR spectra of In-PHT with varying indole groups. The 4-In/(4-In+POD) ratio is annotated on bottom of each curve in the form of the percentage.



**Figure S2.** <sup>13</sup>C CP/MAS NMR spectra of In-PHT with varying indole groups. The 4-In/(4-In+POD) ratio is annotated on top of each curve in the form of the percentage.

## **Representative procedure for casting polymer films**

Representative procedure for casting In-PHT films: 4,4'-(1,3-phenylenedioxy) dianiline (0.36 mmol), 4-aminoindole (0.08mmol), formaldehyde (1.00 mmol) and N-methylpyrrolidinone (2.0 mL) were weighed into a glass bottle vial equipped with a stirbar, and the solution was allowed to stir at room temperature until complete dissolution. The clear solution was then filtered onto a clean, flat glass plate, and allowed to cure according to the following two procedure. Firstly, the aromatic diamines was polymerized with formaldehyde at low temperatures (~50 °C) to .form the hemiaminal dynamic covalent networks. Subsequently, the first-stage resin was heated to 200°C to form highly cross-linked PHT covalent networks. The light brown In-PHT film was then carefully floated from the glass plate cutting the edges with a razor blade and soaking in deionized water. Preparation of other In-PHT films were carried out in the same manner. This is the preparation procedure of thermoset films mentioned in the main text.

<u>Representative procedure for casting Fe-In-PHT films:</u> The typical preparation procedure for Fe-In-PHT mentioned in the main text with a molar ratio, Fe : (4-In) = 1:30, is illustrated as an example. The desired mole equivalent of the Fe<sup>3+</sup> was added into the In-PHT prepolymer solution, the solution was subsequently cast onto a clean, flat glass plate, and allowed to cure in the same manner as described above. The brown Fe-In-PHT film was then carefully floated from the glass plate cutting the edges with a razor blade and soaking in deionized water.

#### Molecular dynamics (MD) simulation

Simulation Method: MD simulation was performed using the amorphous cell module of Materials Studio (Accelrys Software Inc.) with a dreiding force field whose intermolecular parameters were optimized using quantum mechanics. A parent Fe-In-PHT chain (as described in Figure 2A in the main text) with 15 repeating units was built, with 10% repeating units including indole group. The  $Fe^{3+}$  is randomly distributed on the polymer chain. Although size of the parent Fe-In-PHT chain is not sufficiently long to represent conformations of a real polymer chain, a previous study has reported a good agreement between experiments and simulations when simulated polycarbonate chains are short (merely 10-15 repeat units on average).<sup>[1]</sup> Moreover, a periodic boundary condition were imposed and an initial density of 0.9 g/cm<sup>3</sup> was used to simulate the polymer conformation in bulk under an equilibrium state. The initial structure was optimized by a molecular mechanics technique using the conjugate gradient method. Because this optimized structure might, however, still be in a local energy minimum state, the polymer in simulation box was relaxed through NVT for 1 ns at 800 K with time steps of 0.2 fs. The simulation of high-temperature relaxation was closely followed a protocol suggested previously.<sup>[2]</sup> After 1 ns of simulated relaxation at 800 K, the system temperature is decreased to 273 K. In order to obtain a suitable structure for further analysis, ten different initial structures for each system were built and relaxed according to the procedure mentioned previously. The one with the lowest system energy was selected as the MD result for further analysis.

<u>Simulation Results:</u> The MD simulation was performed to analyze the conformation and crosslinking of bulk Fe-In-PHT under an equilibrium state. First, Figure 2A shows a snapshot of two highlighted polymer chains in bulk Fe-In-PHT while other polymer chains on the background were removed for clarity. It is clear that the Fe<sup>3+</sup> is close to an indole group. The correlation distance is 3.35 Å and 4.89 Å. To see this in a quantitative way, the radial distribution function,  $g_{AB}(r)$ , was introduced to describe how density of designated particles varies as a function of distance from a reference particle. Usually,  $g_{AB}(r)$  is determined by measuring the ensemble averaged distance between all particle pairs, as follows,

$$g_{AB}(r) = \frac{\langle n_{AB}(r) \rangle}{4\pi r^2 \Delta \rho_{AB}}$$
(1)

where,  $n_{AB}(r)$  is the distance of each pair between A (Fe<sup>3+</sup>) and B (indole) in the simulation box. <...> represents an ensemble average.  $\Delta \rho_{AB}$  is the rate of change in the average number density of Fe<sup>3+</sup> over distance from an indole ring. The plot of  $g_{AB}(r)$  gives the local density of B around A at a distance r.  $g_{AB}(r) = 1$  indicate the particles are completely uncorrelated. A positive peak of  $g_{AB}(r)$  reflects a definite correlation between atoms at r. As shown in Figure. 2A, two noticeable peak are observed at r = 3.35 Å and 4.89 Å, consistent with the characteristic length of the cation– $\pi$  interaction.<sup>[3,4]</sup> Meanwhile, the fluctuation of  $g_{AB}(r)$  at distances over 5 ~ 6 Å indicated the absence of a long-range interaction in the system. To conclude, the analysis of the radial distribution function indicated the presence of a large number of Fe<sup>3+</sup>-indole complexes in bulk Fe-In-PHT with a correlation distance of 3.35 Å and 4.89 Å.

## **IR** measurement

We performed FTIR measurements on both In-PHT and Fe-In-PHT(1/30) films (Figure S3). The C=C stretching peak at 1620 cm<sup>-1</sup> and 1503 cm<sup>-1</sup>, the C-N stretching peak at 1214 cm<sup>-1</sup> and the N-H stretching peak at 1671 cm<sup>-1</sup> were observed a distinct broadening after adding the Fe<sup>3+</sup>, which was attributed to the cation- $\pi$  interaction between Fe<sup>3+</sup> and part indole. This phenomenon is similar to published references (*ref.* 45 and 46).



Figure S3. FTIR spectra of In-PHT and Fe-In-PHT films.

# **SEM measurement**

The SEM was dedicated to indicate the toughness transition of the films driven by cation- $\pi$  interactions. The SEM image indicates that fracture mechanism changed from the original ductile fracture to the brittle fracture (Figure S4).



Figure S4. SEM spectra of (a) In-PHT, and (b) Fe-In-PHT films.

# **Mechanical behaviors**



**Figure S5**. The stress-strain curves of the Fe-In-PHT polymers on the content of Fe<sup>3+</sup>indole interactions within the polymer films.

## **Thermal behaviors**



Figure S6. Typical TG traces of In-PHT and Fe-In-PHT.



Figure S7. Typical DSC traces of In-PHT and Fe-In-PHT.

## **Fracture energy**

The fracture energy is the work required to generate a crack per unit area. The specific expression is as follows:<sup>[5-7]</sup>

$$\Gamma = d_0 \int_0^\varepsilon \sigma(\varepsilon) d\varepsilon$$

Here,  $\sigma(\epsilon)$  represents the corresponding tensile stress when the strain is  $\epsilon$ , and  $d_0$  represents the original length of the sample before stretching. The original length of the sample is 2 cm.

## Swelling capacity of In-PHT and Fe-In-PHT

In this part, the swelling capacity of the In-PHT and the Fe-In-PHT to organic reagents are evaluated by immersing an approximately 0.12 g films in 10 mL of N,N-dimethylformamide (DMF) at room temperature, respectively. Due to its dense cross-linked network, the indole-containing polymer network is difficult to swell in organic solvents at room temperature, so we heated it at 50 °C to study its swelling. Firstly, weigh the initial mass ( $W_1$ ) of the film, then put it into a swelling tube, add the DMF

and swell in a 50 °C thermostatic water bath. The mass of the sample was measured every two hours, and gently remove the swollen body each time, quickly wipe the solvent attached to the surface of the sample with filter paper, weigh it and put it back into the swelling tube to continue swelling. Until the difference between the two weighed masses does not exceed 0.005 g, it is considered that the swelling process has reached equilibrium. The mass of the swelling body at the swelling equilibrium is  $W_2$ . The specific expression of swelling capacity is as follows:

Swelling Capacity = 
$$\frac{W_2 - W_1}{W_1} \times 100\%$$

The swelling data were collected and illustrated at Table S1. According to the data in Table S1, we can conclude that the swelling capacity decreases with the increasing of the Fe<sup>3+</sup>- indole content, which indicates the existence of cation- $\pi$  from the side.

	In-PHT	Fe-In-	Fe-In-	Fe-In-	Fe-In-	Fe-In-
		PHT(1/60)	PHT(1/40)	PHT(1/30)	PHT(1/20)	PHT(1/10)
$M_1/g$	0.120	0.120	0.120	0.120	0.120	0.120
$M_2/g$	0.141	0.137	0.133	0.130	0.129	0.127
Swelling capacity	17.5%	14.1%	10.8%	8.3%	7.5%	5.8%

Table S1. The swelling data of In-PHT, Fe-In-PHT.

## Workflow of the Tensile Strength Detection analysis program

Figure 4D showed the *Tensile Strength Detection* analysis program workflow: Firstly, the optical image of the Fe-In-PHT films were recorded with the camera of a smartphone in the auto-focus state under the lighting conditions of a 15-watt energy-saving lamp. Then, running the home-built analysis program. Upon clicking on the

"Select image path" and "Read target image" button, open the image of the film. Once the picture was taken, by clicking the "Calculation" button, the program would automatically select five points from the selected area to calculate the average RGB intensity values. We directly extract the mean RGB values to calculate the adjust intensity I (Table S1). The adjusted intensity (I) was calculated by the following equation.

$$I = 1 - (I_R + I_G + I_B) / I_{R0} + I_{G0} + I_{B0})$$

where  $I_R$ ,  $I_G$ , and  $I_B$  and  $I_{R0}$ ,  $I_{G0}$ , and  $I_{B0}$  are the RGB intensities in the presence and absence of Fe<sup>3+</sup>, respectively. Finally, the adjusted intensity (I) was quantitatively converted into tensile strength through a calculation methods.

Fe-In-PHT	0	60:1	40:1	30:1	20:1	15:1	10:1
	0	0.16%	0.25%	0.33%	0.5%	1.0%	2.0%
R	206	183	176	147	126	89	56
G	173	116	100	59	41	14	1
В	21	0	0	0	0	0	0
R+G+B	400	299	276	206	167	103	57
Ι	0	0.25±0.01	0.31±0.01	0.48±0.01	0.58±0.01	0.74±0.01	0.85±0.01

**Table S2.** The RGB value of Fe-In-PHT with different Fe<sup>3+</sup> contents.

# References

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