



Electronic Supplementary Information (ESI)

Efficient synthesis of trefoil-shaped tricyclic polymers by ROMP-based blocking-cyclization technique

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1. Synthesis and characterization of monomers

Synthesis of 2,3,6,7,10,11-hexa(methyl oxohexanoate) triphenylene (HMHT)

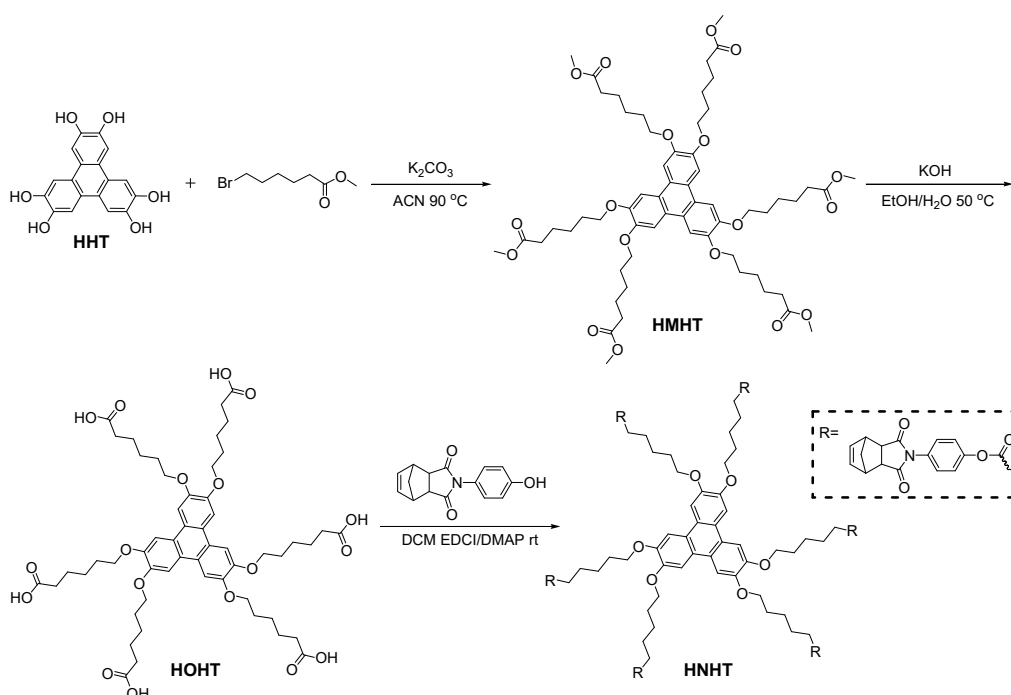
Under nitrogen atmosphere, 2,3,6,7,10,11-hexahydroxytriphenylene (HHT) (0.3 g, 0.9 mmol) and K_2CO_3 (3.7 g, 27.0 mmol) were dispersed into 40 mL of CH_3CN in a 100 mL three-necked flask, methyl-6-bromohexanoate (3.4 g, 16.2 mmol) was then added after 30 min, and the reaction mixture was stirred at 90 °C for 48 h. Upon cooling, the reaction mixture was filtered, and the solvent was removed under reduced pressure. The solid was purified by column chromatography on silica gel using PE/EA = 6:1 as eluent, to afford pale yellow powder, **HMHT** (0.7 g, 70%). 1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.81 (s, 6H, triphenylene), 4.22 (t, 12H, OCH_2CH_2), 3.68 (d, 18H, OCH_3), 2.39 (t, 12H, $O=CCH_2$), 1.96 (t, 12H, OCH_2CH_2), 1.78 (t, 12H, $CH_2CH_2CH_2$), 1.65-1.60 (m, 12H, $CH_2CH_2CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.05, 148.87, 123.63, 107.31, 69.32, 51.50, 34.01, 29.15, 25.77, 24.76.

Synthesis of 2,3,6,7,10,11-hexa(oxohexanoic acid) triphenylene (HOHT)

Under nitrogen atmosphere, **HMHT** (0.6 g, 0.55 mmol) and KOH (0.55 g, 9.9 mmol) were dissolved into mixed solvent (30 mL of MeOH and 5 mL of deionized water) in a 50 mL three-necked flask and stirred at 50 °C for 5 days. After cooling, the solvent was removed under reduced pressure, then the 4 mol/L HCl solution was added dropwise to the reaction mixture until the pH value for 2, filtered with suction and dried in a vacuum oven overnight, and a yellow solid of **HOHT** was obtained (0.47 g, 85%). 1H NMR (500 MHz, $DMSO-d_6$, ppm): δ 12.00 (s, 6H, $COOH$), 7.97 (s, 6H, triphenylene), 4.23 (t, 12H, OCH_2CH_2), 2.27 (t, 12H, $O=CCH_2$), 1.83 (m, 12H, $CH_2CH_2CH_2$), 1.64 (m, 12H, $CH_2CH_2CH_2$), 1.54 (m, 12H, $CH_2CH_2CH_2$). ^{13}C NMR (125 MHz, $DMSO-d_6$, ppm): δ 174.59, 148.65, 123.04, 107.33, 68.77, 33.86, 28.77, 25.50, 24.48.

Synthesis of 2,3,6,7,10,11-hexa(N-4-(phenyl norbornene dicarboximide) oxohexanoate) triphenylene (HNHT)

Under nitrogen atmosphere, **HOHT** (0.4 g, 0.4 mmol), **NDI** (1.2 g, 4.8 mmol) and DMAP (1.5 g, 12 mmol) were dissolved into 60 mL of dry CH_2Cl_2 in a 100 mL three-necked flask under stirring 30 min, and the EDCI·HCl (2.3 g, 12 mmol) was added to the reaction mixture and stirred at room temperature for 5 days. The solvent was removed under reduced pressure. The solid was purified by column chromatography on silica gel using PE/EA = 1:2 as eluent to afford white powder, **HNHT** (0.78 g, 80%). ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.84 (m, 6H, triphenylene), 7.14 (m, 24H, aromatic), 6.23 (t, 12H, $\text{CH}=\text{CH}$), 4.25 (t, 12H, OCH_2CH_2), 3.48 (m, 12H, OCCHCH), 3.39 (m, 12H, CHCHCH), 2.61 (t, 12H, $\text{O}=\text{CCH}_2$), 1.99 (m, 12H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.87 (m, 12H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.77 (m, 6H, CHCH_2CH), 1.70 (m, 12H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.59 (d, 6H, CHCH_2CH). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 176.76, 171.73, 150.50, 149.00, 134.75, 129.28, 127.72, 122.30, 107.39, 77.36, 69.37, 52.38, 45.90, 45.65, 34.42, 29.28, 25.88, 24.82.



Scheme S1. Synthesis of 2,3,6,7,10,11-hexa(N-4-(phenyl norbornene dicarboximide) oxohexanoate) triphenylene (**HNHT**).

HNHT was prepared according to a previously reported method.^{1,2} From ¹H NMR spectrum (Figure S1a), the ratios of the integral area of protons H_a at 6.23 ppm to those of protons H_k at 4.25 ppm and protons H_l at 7.84 ppm and were calculated to be 12:12:6, which matched well with the theoretical values. In addition, the ¹³C NMR (Figure S1b) and ATR-IR (Figure S2) spectra were also analyzed, revealing the successful synthesis of monomer **HNHT**.

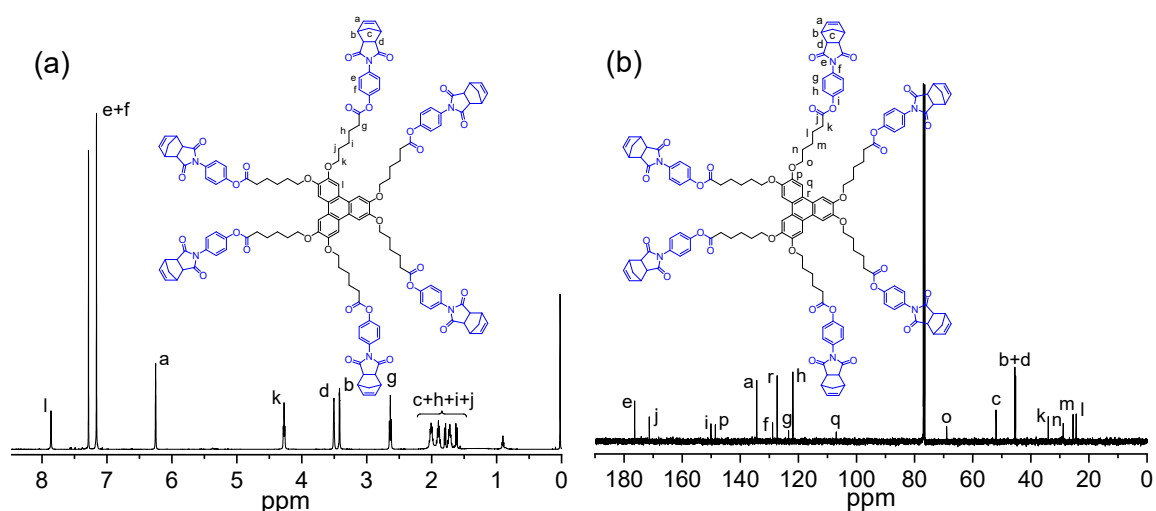


Figure S1. (a) ¹H NMR (500 MHz) and (b) ¹³C NMR (125 MHz) spectra of **HNHT** measured in CDCl₃.

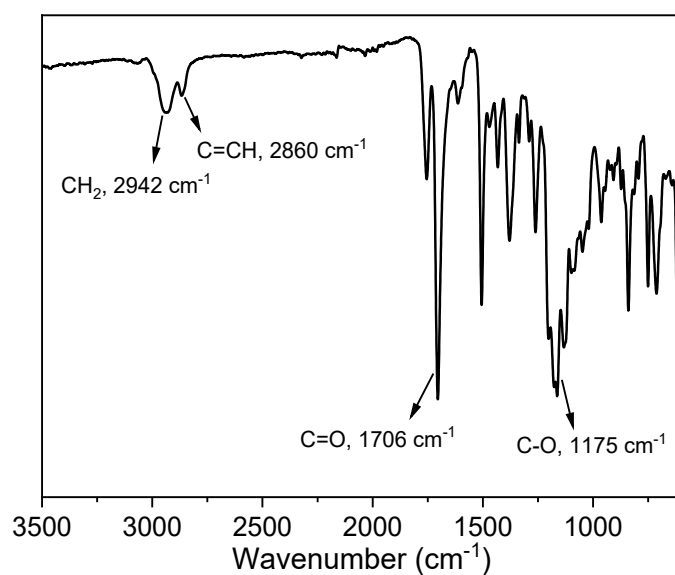


Figure S2. ATR-IR spectrum of **HNHT**.

2. Synthesis and characterization of polymers

Synthesis of complex ladderphane **PHNHT**₅

The hexafunctional monomer 2,3,6,7,10,11-hexa(N-4-(phenyl norbornene dicarboximide) oxohexanoate) triphenylene (**HNHT**) (24.3 mg, 0.01 mmol) was dissolved into 48 mL of dry CH₂Cl₂ in a 100 mL of Schlenk tube. **Ru-III** (10.6 mg, 0.012 mmol) was dissolved into 2 mL of dry CH₂Cl₂ in 10 mL of Schlenk tube. After degassed with three freeze-vacuum-thaw cycles, the solution of **Ru-III** was then injected into 100 mL Schlenk tube via a syringe under stirring at 30 °C for 1 h. The solution was precipitated into methanol and dried under vacuum to afford homopolymer **PHNHT**₅ as a colorless solid (22.8 mg, 94%). GPC: $M_n = 4.5$ kDa, $M_a = 12.8$ kDa, $D = 1.24$. ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.82 (m, triphenylene), 7.26 (d, aromatic), 6.03-5.22 (m, CH=CH on PNBE backbone), 4.45-4.05 (m, OCH₂CH₂), 3.58-2.80 (m, OCCHCH + CHCHCH), 2.76-2.47 (s, O=CCH₂), 2.18-1.52 (m, CHCH₂CH + CH₂CH₂CH₂).

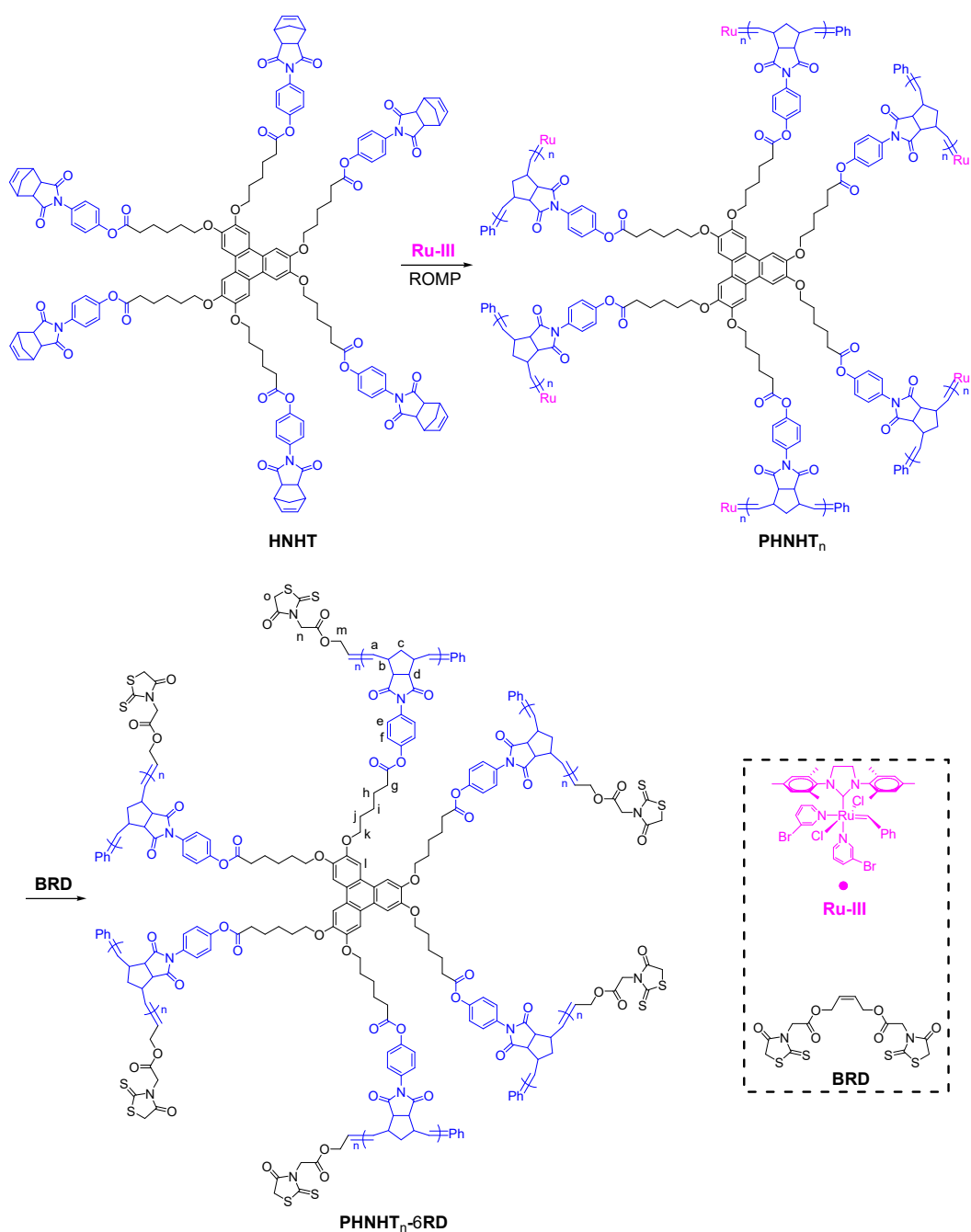
Ladderphanes **PHNHT**₃ and **PHNHT**₁₀ were also synthesized in a similar way with the above synthetic route.

Synthesis of end-capped ladderphane **PHNHT**₅-6RD

The synthesis process was similar to that of **PHNHT**₅, as shown in Scheme S2. The hexafunctional monomer **HNHT** (24.3 mg, 0.01 mmol) was dissolved into 48 mL of dry CH₂Cl₂ in a 100 mL of Schlenk tube. **Ru-III** (10.6 mg, 0.012 mmol) was dissolved into 2 mL of dry CH₂Cl₂ in 10 mL of Schlenk tube. The terminating agent **BRD** (52.2 mg, 0.12 mmol) was dissolved into 1 mL of dry CH₂Cl₂ in 10 mL of Schlenk tube. After degassed with three freeze-vacuum-thaw cycles, the solution of **Ru-III** was injected into 100 mL Schlenk tube via a syringe under stirring at 30 °C for 1 h. The solution of **BRD** was then injected into the reaction mixture and stirred for overnight. The reaction mixture was precipitated into the mixed solvent (methanol/acetone = 20:20), and dried under vacuum to

afford **RD** group-terminated homopolymer **PHNHT₅-6RD** (22.8 mg, 94%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.82 (m, triphenylene), 7.22 (d, aromatic), 5.94-5.07 (m, CH=CH on PNBE backbone), 4.77-4.58 (m, CHCH₂O), 4.46-3.99 (m, OCH₂CH₂+NCH₂CO), 3.66 (m, SCH₂CO), 3.60-2.82 (m, OCCHCH + CHCHCH), 2.75-2.47 (s, O=CCH₂), 2.20-1.53 (m, CHCH₂CH + CH₂CH₂CH₂).

End-capped ladderphane **PHNHT₃-6RD** was also synthesized in a similar way as above.



Scheme S2. Synthesis of homopolymers **PHNHT_n** and **PHNHT_n-6RD** by ROMP.

Table S1. Characteristics for homopolymers.^a

Entry	Polymer	[HNHT]/[Cat] ^b	t (h)	M_n^c (kDa)	\bar{D}^c	Yield (%)
1 ^d	PHNHT ₃	3 : 6	1.0	2.7	1.21	96
2 ^d	PHNHT ₅	5 : 6	1.0	4.5	1.24	94
3 ^d	PHNHT ₁₀	10 : 6	1.0	4.9	1.25	55
4 ^d	PHNHT ₁₀	10 : 6	4.0	/	/	68
5 ^e	PHNHT ₅	5 : 6	1.0	/	/	92
6 ^f	PHNHT ₅	5 : 6	1.0	6.1	1.34	96
7 ^g	PHNHT ₅	5 : 6	1.0	4.4	1.26	93

^aPolymerization conditions: using **Ru-III** as catalyst, CH₂Cl₂ as solvent, temperature = 30 °C. ^bThe feed ratio of monomer to catalyst for polymerization of hexafunctional monomer. ^cDetermined by GPC in THF relative to monodispersed polystyrene standards. ^d[HNHT] = 2×10⁻⁴ mol L⁻¹ refers to the concentration of monomer. ^e[HNHT] = 1×10⁻³ mol L⁻¹ refers to the concentration of monomer. ^f[HNHT] = 5×10⁻⁴ mol L⁻¹ refers to the concentration of monomer. ^g[HNHT] = 1×10⁻⁴ mol L⁻¹ refers to the concentration of monomer.

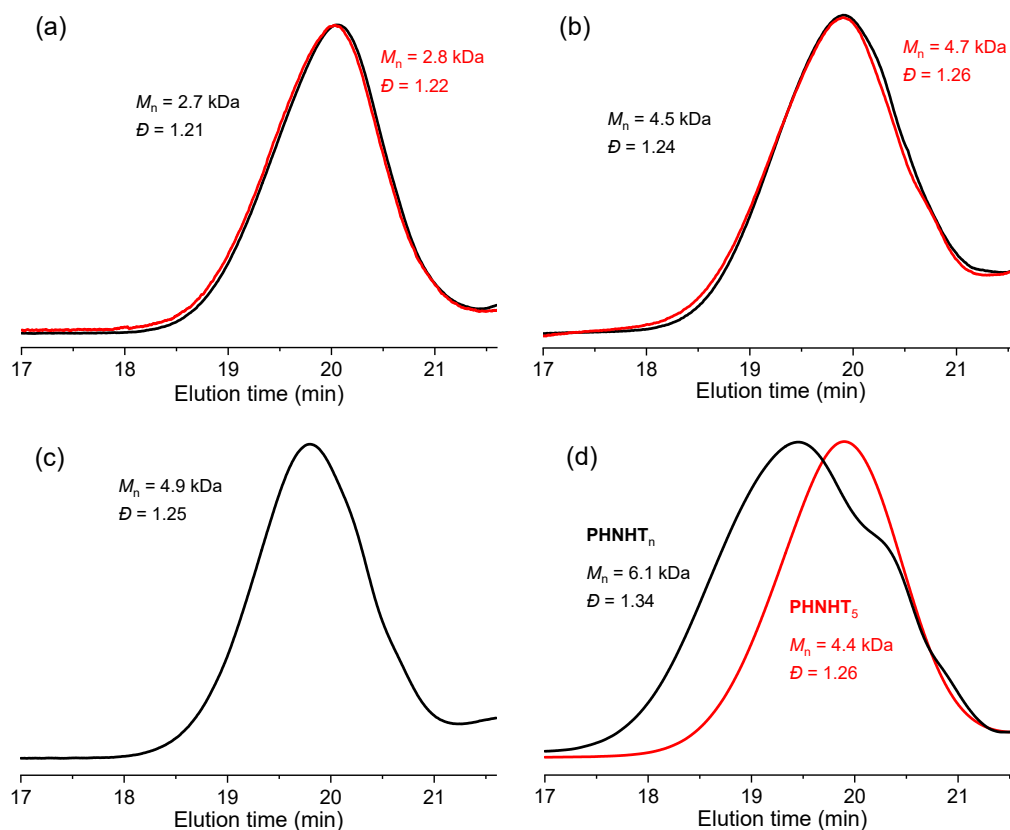


Figure S3. GPC traces in THF of homopolymers (a) **PHNHT**₃ (black) and **PHNHT**₃-6RD (red), (b) **PHNHT**₅ (black) and **PHNHT**₅-6RD (red), and (c) **PHNHT**₁₀ obtained at a monomer concentration of 2×10⁻⁴ mol L⁻¹, as well as (d) **PHNHT**_n obtained at a monomer concentration of 5×10⁻⁴ mol L⁻¹ (black) and **PHNHT**₅ obtained at a monomer concentration of 1×10⁻⁴ mol L⁻¹ (red).

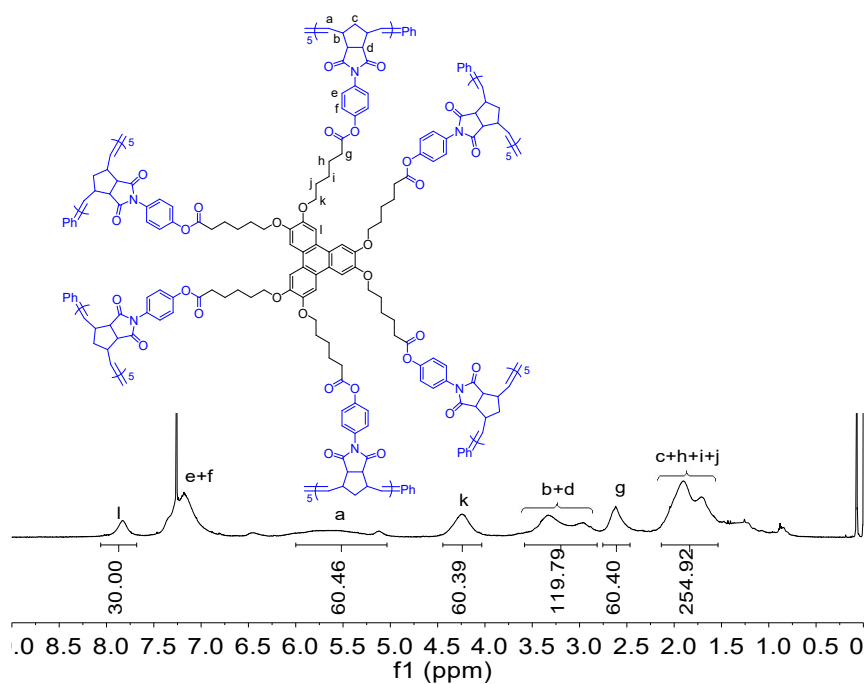


Figure S4. ^1H NMR (500 MHz) spectrum of PHNHT₅ measured in CDCl₃.

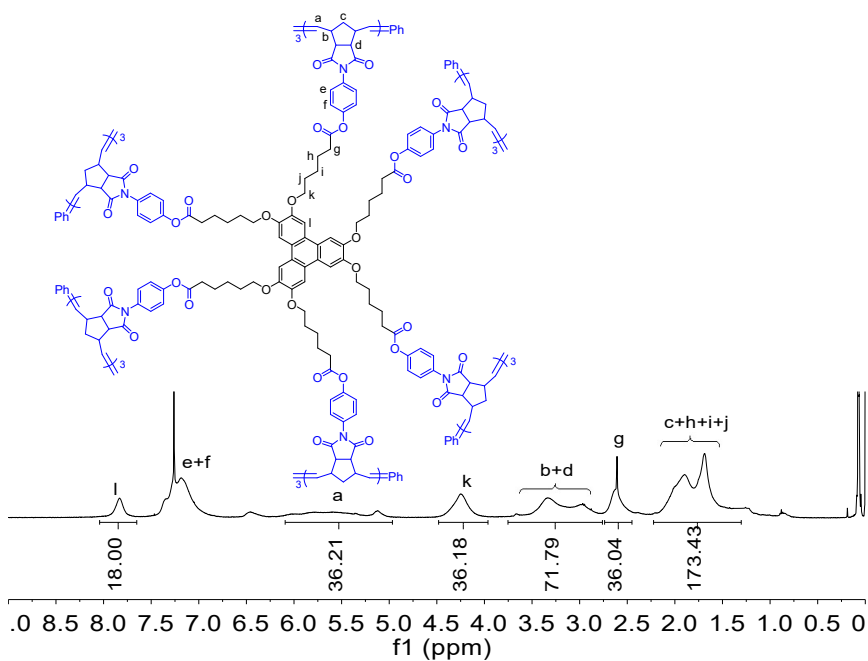


Figure S5. ^1H NMR (500 MHz) spectrum of PHNHT₃ measured in CDCl₃.

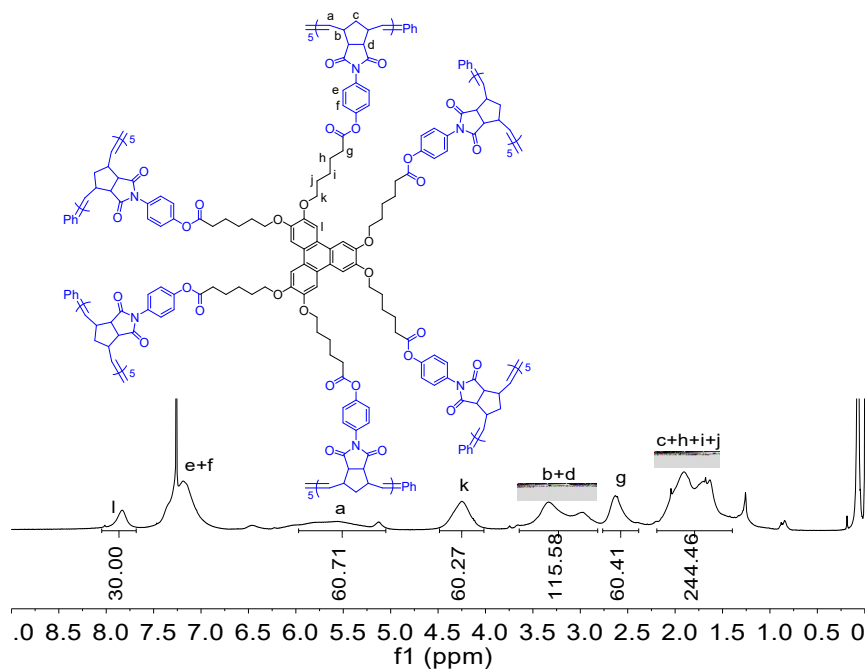


Figure S6. ¹H NMR (500 MHz) spectrum of PHNHT₅ formed under a low monomer concentration of 1×10^{-4} mol L⁻¹ measured in CDCl₃.

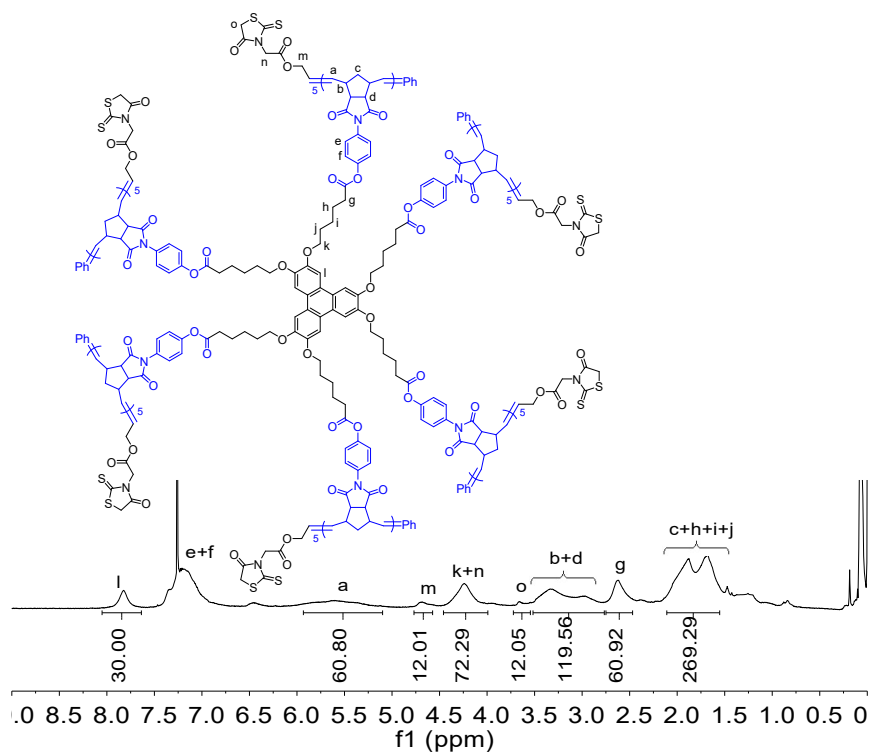


Figure S7. ¹H NMR (500 MHz) spectrum of PHNHT₅-6RD measured in CDCl₃.

The actual integral area ratio of protons H_1 to that of H_m for **PHNHT₃-6RD** (Fig. S8†) was calculated to be 18:12, which was in agreement with the theoretical area ratio of 18:12 based on three **HNHT** units and six **RD** end-groups. Furthermore, compared with the integral area ratio of 18:36.18 for the protons H_1 to the protons H_k on **PHNHT₃** (Fig. S5†), the actual integral area ratio for the protons H_1 to the protons H_{k+n} on **PHNHT₃-6RD** (Fig. S8†) increased to 18:48.07, and the increased proton numbers of about 12 ($48.07-36.18 = 11.89$) was derived from the methylene protons H_n of six **RD** groups, which also confirmed that **PHNHT₃** owned six living ends.

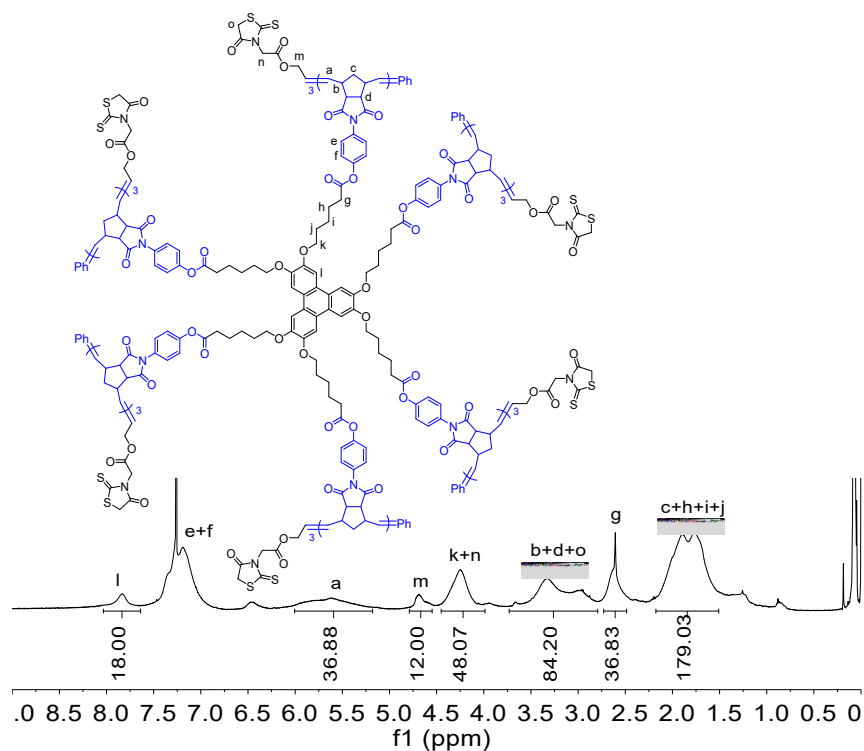


Figure S8. ¹H NMR (500 MHz) spectrum of **PHNHT₃-6RD** measured in CDCl₃.

In addition, the actual integral area ratio of protons H_1 to that of H_m for **PHNHT₅-6RD** formed under a lower monomer concentration of 1×10^{-4} mol L⁻¹ (6×10^{-4} mol L⁻¹ of norbornene group) (Fig. S9†) was calculated to be 30:12.11, which was in agreement with the theoretical area ratio of 30:12 based on three **HNHT** units and six **RD** end-groups. By comparison, the integral area ratio of 30:60.27 for the protons H_1 to the protons H_k on

PHNHT₅ (Fig. S6†), the actual integral area ratio for the protons H₁ to the protons H_{k+n} on **PHNHT**₅-6**RD** (Fig. S9†) increased to 30:72.14, and thus the increased proton number of about 12 (72.14-60.27 = 11.87) was derived from the methylene protons H_n of six **RD** groups, which also confirmed that **PHNHT**₅ owned six living ends.

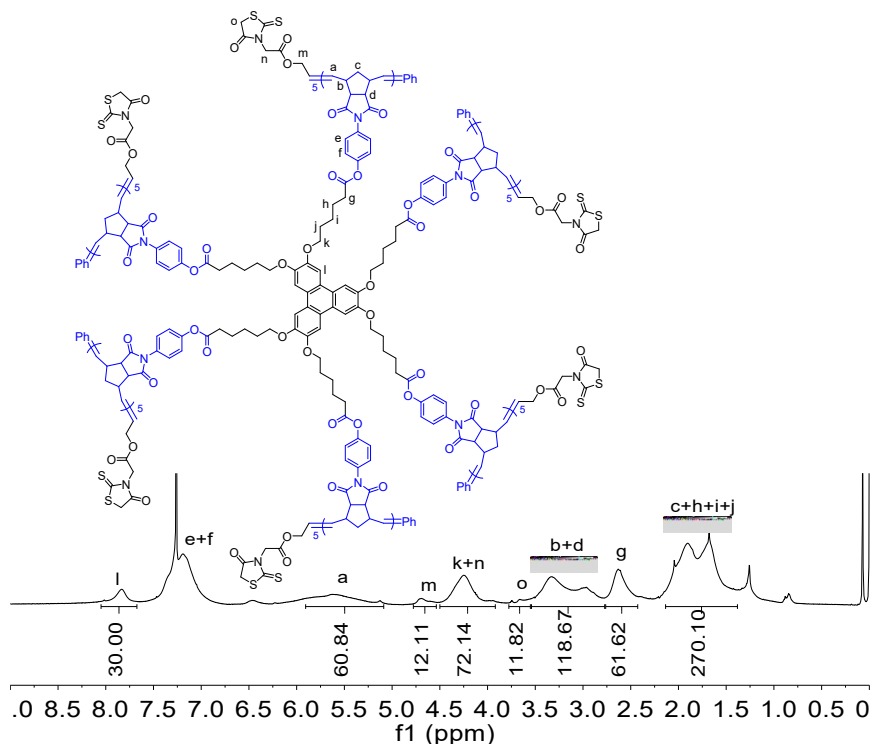


Figure S9. ¹H NMR (500 MHz) spectrum of **PHNHT**₅-6**RD** formed under a lower monomer concentration of 1×10^{-4} mol L⁻¹ measured in CDCl₃.

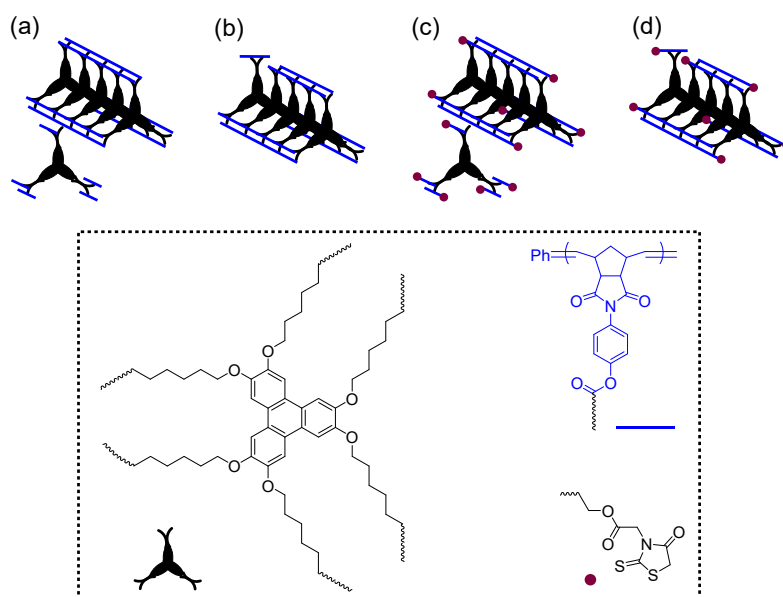


Figure S10. Possible defective ladderphane structures of **PHNHT**_n (a,b) and **PHNHT**_n-x**RD** (c,d).

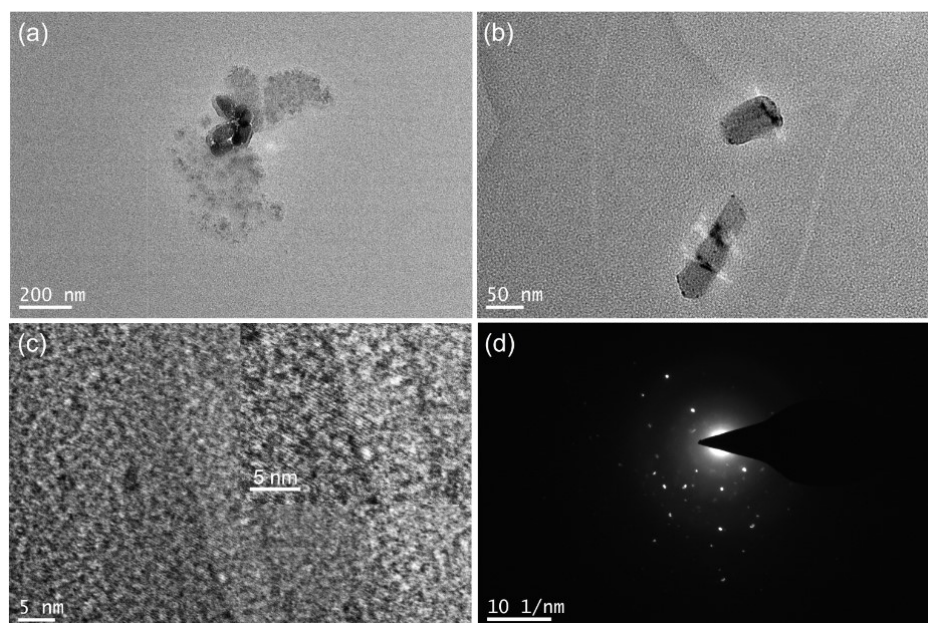


Figure S11. TEM images (a-c) and the corresponding SAED pattern (d) of polymeric ladderphane **PHNHT₅**.

Synthesis of six-arm star-shaped polymers

A 50 mL of Schlenk tube was charged with hexafunctional monomer **HNHT** (2.4 mg, 1.0 μmol) dissolved in 2 mL of dry CH_2Cl_2 . Difunctional monomer **BNP** (4 mg, 3.0 μmol) was dissolved in 1 mL of dry CH_2Cl_2 in 25 mL of Schlenk tube. **Ru-III** (1.1 mg, 1.2 μmol) and monofunctional monomer **TNP** (55.1 mg, 0.13 mmol) were dissolved in 1 mL and 4 mL of dry CH_2Cl_2 in two 50 mL of Schlenk tubes, respectively. After degassed with three freeze-vacuum-thaw cycles, the solution of **Ru-III** was injected into the **HNHT** solution via a syringe under vigorous stirring at 30 $^\circ\text{C}$ for 1 h, and then **BNP** solution was injected into the reaction mixture and stirred for further 0.5 h. At last, the solution of **TNP** was injected into the reaction mixture and stirred for 2 h, affording the six-arm star-shaped polymer βa - $\{\text{PHNHT}_5\text{-}[b\text{-PBNP}_5\text{-}(b\text{-PTNP}_{110})_2]_3\}$ (57.2 mg, 93%). GPC: $M_n = 81.8$ kDa, $D = 1.74$. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 8.64 (m, pery), 8.03-7.77 (m, triphenylene + F_3CCCH), 7.76-7.60 (m, $\text{F}_3\text{CCCHCCF}_3$), 7.58-7.32 (m, aromatic + CCCH), 7.01-6.52 (m, aromatic), 5.64-5.15 (m, $\text{CH}=\text{CH}$ on PNBE backbone), 4.32-4.11 (m, OCH_2CH_2 +

$\text{NCH}_2(\text{CH}_2)_9$), 3.52-2.50 (m, $\text{OCCHCH} + \text{CHCHCH} + \text{O=CCH}_2$), 2.10-1.11 (m, $\text{CH}_2\text{CH}_2\text{CH}_2 + \text{CHCH}_2\text{CH} + \text{OCCH}_2(\text{CH}_2)_9$). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 175.52, 173.62, 166.26, 162.545, 148.40, 143.13, 132.21, 131.94, 127.93, 127.84, 125.75, 124.58, 122.41, 119.25, 113.21, 49.91, 49.69, 47.64, 46.75, 44.90, 40.20, 39.95, 39.04, 29.69, 22.68, 14.11.

Synthesis of trefoil-shaped tricyclic polymer containing pentafluorophenyl ester units

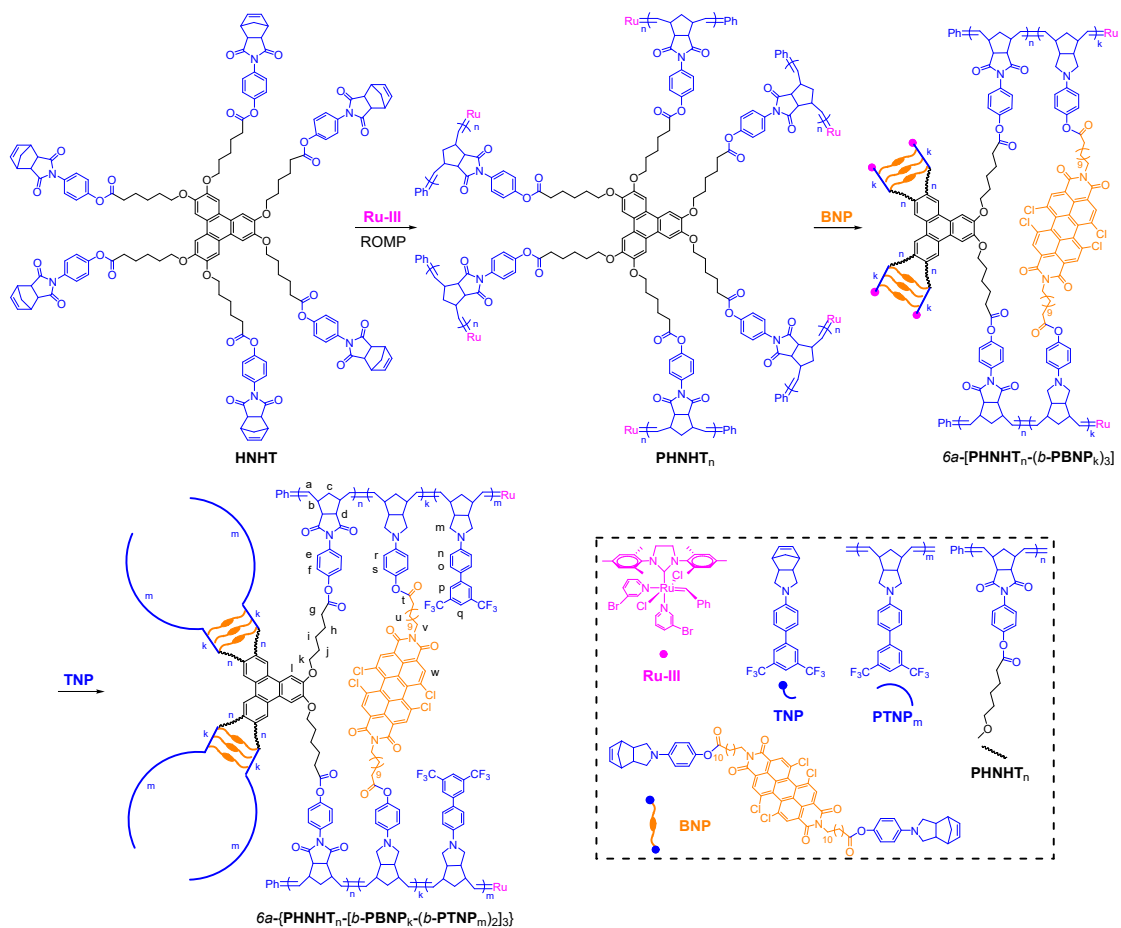
A 50 mL of Schlenk tube was charged with hexafunctional monomer **HNHT** (2.4 mg, 1.0 μmol) dissolved in 2 mL of dry CH_2Cl_2 . Difunctional monomer **BNP** (4 mg, 3.0 μmol) was dissolved in 1 mL of dry CH_2Cl_2 in 25 mL of Schlenk tube. **Ru-III** (1.1 mg, 1.2 μmol) was dissolved in 1 mL of dry CH_2Cl_2 in 25 mL of Schlenk tube, and the mixture of monofunctional **TNP** (42.6 mg, 0.10 mmol) and **PFNI** (13.3 mg, 0.03 mmol) were dissolved in 4 mL of dry CH_2Cl_2 in 24 mL of Schlenk tube. After degassed with three freeze-vacuum-thaw cycles, the solution of **Ru-III** was injected into the **HNHT** solution via a syringe under vigorous stirring at 30 °C for 1 h, and then the solution of **TNP** and **PFNI** was injected into the reaction mixture and stirred for further 0.5 h. At last, **BNP** solution was injected into the reaction mixture and stirred for 2 h, affording the trefoil-shaped tricyclic polymer $c\text{-}\{\text{PHNHT}_5\text{-}[(b\text{-P}(\text{TNP}_{85}\text{-}co\text{-PFNI}_{25}))_2\text{-}b\text{-PBNP}_5]_3\}$ (59.2 mg, 95%). GPC: $M_n = 71.6$ kDa, $D = 1.76$. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 8.67 (m, pery), 8.37-7.31 (m, triphenylene + aromatic + $\text{CCCH} + \text{F}_3\text{CCCH} + \text{F}_3\text{CCCHCCF}_3$), 6.96-6.45 (m, aromatic), 5.97-5.16 (m, $\text{CH}=\text{CH}$ on PNBE backbone), 4.34-4.13 (m, $\text{OCH}_2\text{CH}_2 + \text{NCH}_2(\text{CH}_2)_9$), 3.65-2.38 (m, $\text{OCCHCH} + \text{CHCHCH} + \text{O=CCH}_2$), 2.18-1.10 (m, $\text{CH}_2\text{CH}_2\text{CH}_2 + \text{CHCH}_2\text{CH} + \text{OCCH}_2(\text{CH}_2)_9$).

Six-arm star-shaped polymer $6a\text{-}\{\text{PHNHT}_5\text{-}[b\text{-PBNP}_5\text{-}(b\text{-P}(\text{TNP}_{85}\text{-}co\text{-PFNI}_{25}))_2]_3\}$ was synthesized in a similar way with the above synthetic route.

Post-polymerization of trefoil-shaped tricyclic polymer containing pentafluorophenyl ester units

Under nitrogen atmosphere, c -{**PHNHT**₅-[(b -**P(TNP**₈₅- co -**PFNI**₂₅))₂- b -**PBNP**₅]₃} (30 mg, 0.014 mmol of pentafluorophenyl ester group) and NH₂-POSS (61.3 mg, 0.07 mmol) were dissolved into 5 mL of dry THF in a 50 mL of Schlenk tube, and the triethylamine (14.1 mg, 0.14 mmol) was added in Schlenk tube and stirred at 50 °C for 3 days. The reaction mixture was precipitated into the mixed solvent (methanol/ether = 20:10), and dried under vacuum to afford the POSS-modified six-arm star-shaped polymer c -{**PHNHT**₅-[(b -**P(TNP**₈₅- co -**POSSNI**₂₅))₂- b -**PBNP**₅]₃}. GPC: M_n = 122.8 kDa, D = 1.68. ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.66 (m, pery), 8.09-7.30 (m, triphenylene + aromatic + CCCH + F₃CCCH + F₃CCCHCCF₃), 7.01-6.48 (m, aromatic), 6.21-5.18 (m, CH=CH on PNBE backbone), 4.36-4.09 (m, OCH₂CH₂ + NCH₂(CH₂)₉), 3.79-2.40 (m, OCCHCH + CHCHCH + O=CCH₂ + POSS-CH₂CH₂), 2.14-0.74 (m, CH₂CH₂CH₂ + CHCH₂CH + OCCH₂(CH₂)₉ + NCH₂CH₂ + CH on POSS), 0.72-0.49 (m, POSS-CH₂CH₂). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 175.28, 172.88, 166.21, 162.27, 148.41, 143.14, 132.24, 131.95, 131.70, 127.83, 126.41, 125.88, 125.75, 124.58, 122.41, 119.22, 113.21, 53.41, 49.75, 47.65, 46.73, 44.92, 40.75, 40.21, 39.98, 29.69, 29.06, 28.88, 25.66, 23.83, 22.43, 14.11, 9.46.

Six-arm star-shaped polymer $6a$ -{**PHNHT**₅-[b -**PBNP**₅-(b -**P(TNP**₈₅- co -**POSSNI**₂₅))₂]₃} was synthesized in a similar way with the above synthetic route.



Scheme S3. Synthesis of six-arm star-shaped polymers by successive ROMP.

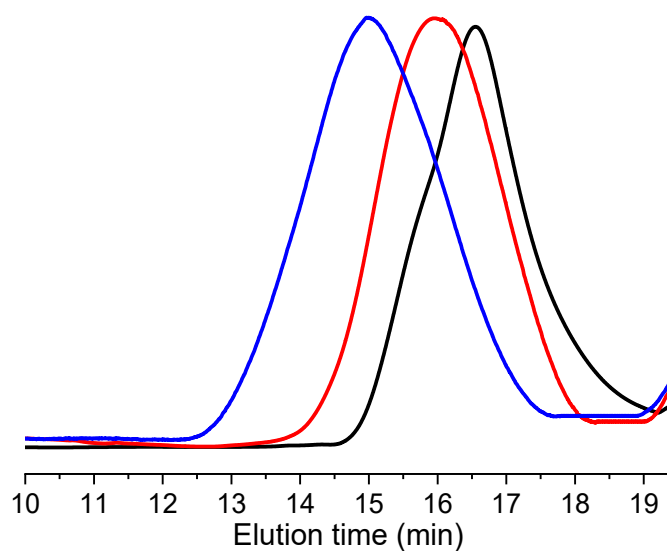


Figure S12. GPC traces of trefoil-shaped tricyclic polymers c -{PHNHT₅-[(b-PTNP_m)₂-b-PBNP₅]₃} ($m = 70, 90, \text{ and } 130$ for black, red, and blue, respectively).

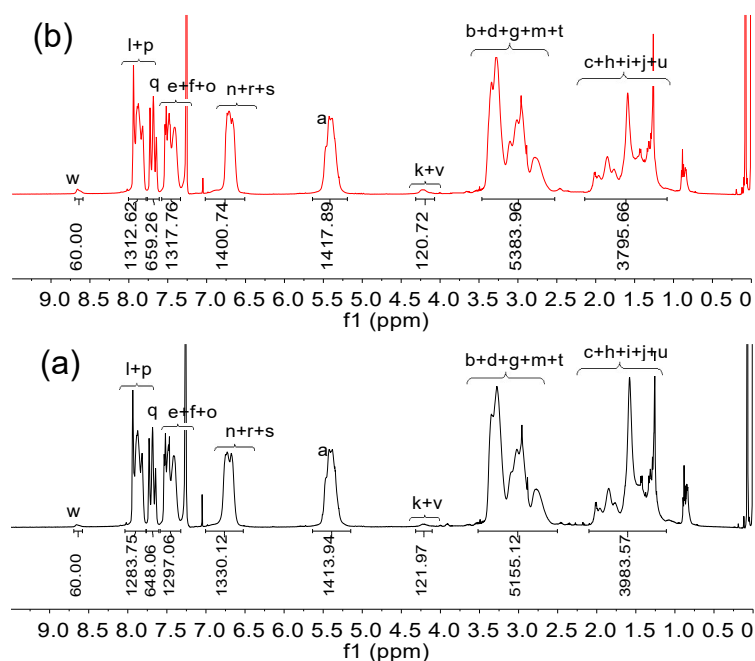


Figure S13. ¹H NMR spectra of six-arm star-shaped $6a\text{-}\{\text{PHNHT}_5\text{-}[b\text{-PBNP}_5\text{-}(b\text{-PTNP}_{110})_2\text{]}_3\}$ (a) and trefoil-shaped tricyclic $c\text{-}\{\text{PHNHT}_5\text{-}[(b\text{-PTNP}_{110})_2\text{-}b\text{-PBNP}_5\text{]}_3\}$ (b) measured in CDCl_3 .

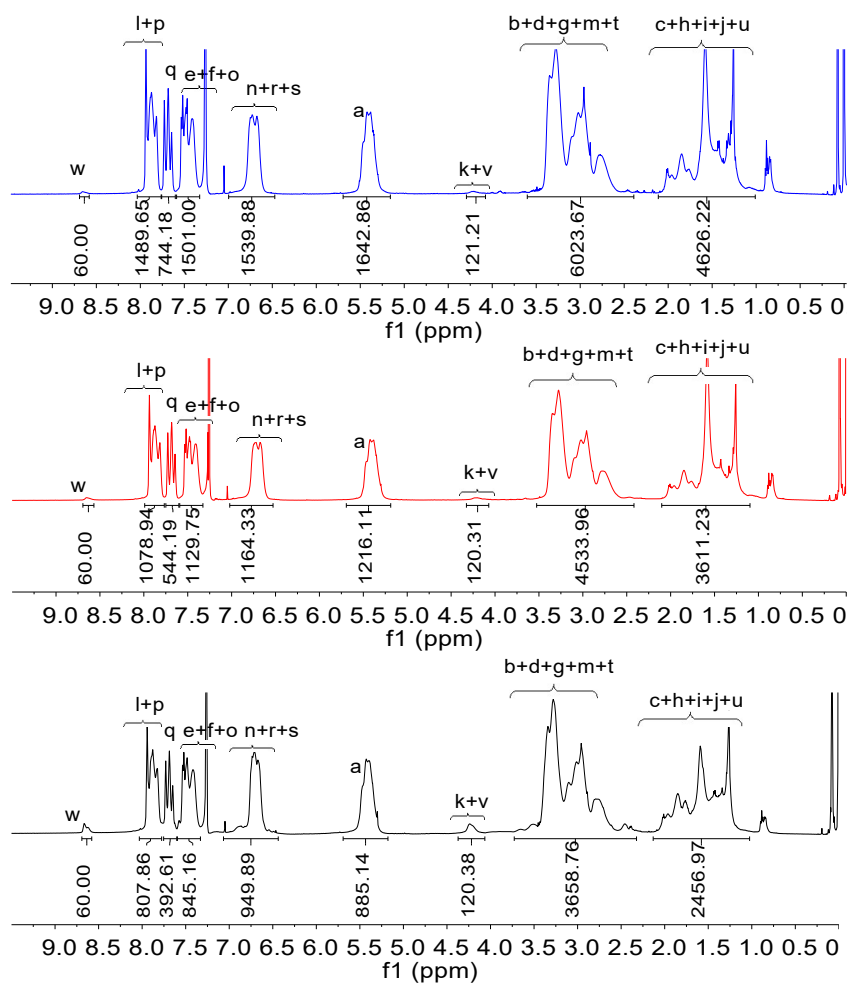


Figure S14. ¹H NMR spectra of trefoil-shaped tricyclic polymers $c\text{-}\{\text{PHNHT}_5\text{-}[(b\text{-PTNP}_m)_2\text{-}b\text{-PBNP}_5\text{]}_3\}$ ($m = 70, 90, \text{ and } 130$ as black, red, and blue, respectively) measured in CDCl_3 .

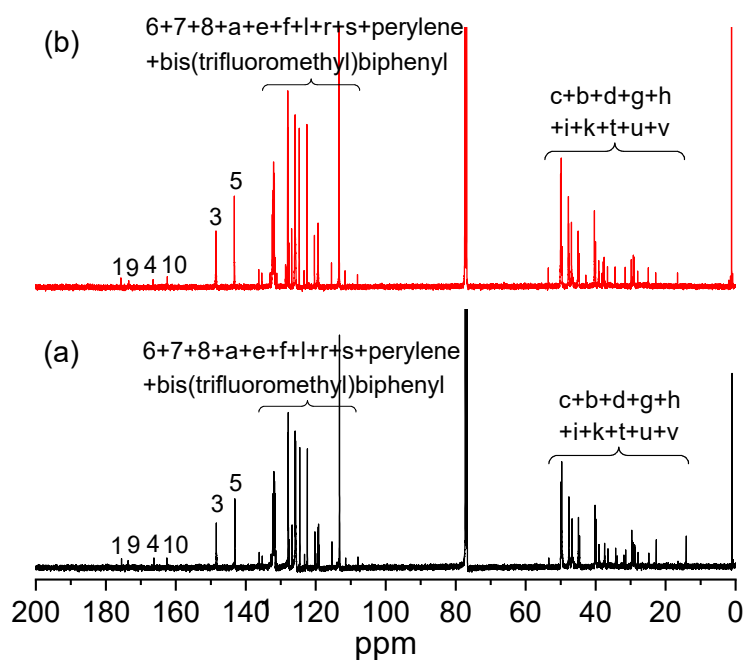


Figure S15. ^{13}C NMR spectra of six-arm star-shaped $6a$ - $\{\text{PHNHT}_5\text{-}[b\text{-PBNP}_5\text{-}(b\text{-PTNP}_{110})_2]_3\}$ (a) and trefoil-shaped tricyclic c - $\{\text{PHNHT}_5\text{-}[(b\text{-PTNP}_{110})_2\text{-}b\text{-PBNP}_5]_3\}$ (b) measured in CDCl_3 .

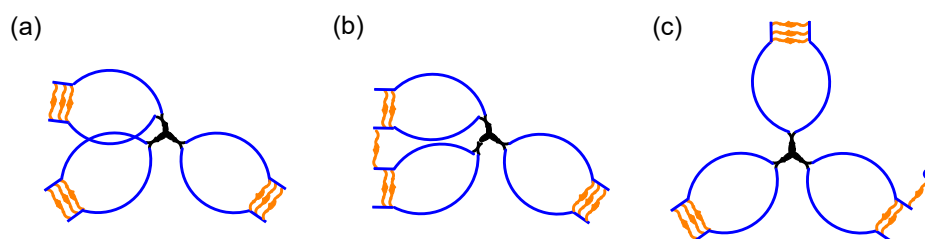


Figure S16. Some possible (defective) structures of cyclic polymers in ROMP-based blocking-cyclization process for synthesizing trefoil-shaped tricyclic polymer, including (a) one segment in one ring passes through another ring, (b) one ladderphane **PBNP** in one ring connects with another ring, and (c) a number of the residual olefinic protons on norbornenyl ring.

Table S2. Intrinsic viscosity data over a range of M_w for trefoil-shaped tricyclic and six-arm star-shaped polymers, and $[\eta]_c/[\eta]_{6a}$.

$6a$ - $\{\text{PHNHT}_5\text{-}[b\text{-PBNP}_5\text{-}(b\text{-PTNP}_{110})_2]_3\}$		c - $\{\text{PHNHT}_5\text{-}[(b\text{-PTNP}_{110})_2\text{-}b\text{-PBNP}_5]_3\}$		$[\eta]_c/[\eta]_{6a}$
$\text{Log}(M_w)$	$[\eta]_{6a}$ (mL/g)	$\text{Log}(M_w)$	$[\eta]_c$ (mL/g)	
5.14	25.1	5.14	21.4	0.85
5.2	26.7	5.2	22.3	0.84
5.3	30.1	5.3	25.2	0.84
5.4	35.6	5.4	29.4	0.83
5.5	42.1	5.5	34.0	0.81

Table S3. Hydrodynamic diameter of polymers by DLS.

Entry	Polymer	D_h (nm)
1	$c\text{-}\{\text{PHNHT}_5\text{-}[(b\text{-PTNP}_{70})_2\text{-}b\text{-PBNP}_5]_3\}$	24
2	$c\text{-}\{\text{PHNHT}_5\text{-}[(b\text{-PTNP}_{90})_2\text{-}b\text{-PBNP}_5]_3\}$	38
3	$c\text{-}\{\text{PHNHT}_5\text{-}[(b\text{-PTNP}_{110})_2\text{-}b\text{-PBNP}_5]_3\}$	51
4	$6a\text{-}\{\text{PHNHT}_5\text{-}[b\text{-PBNP}_5\text{-}(b\text{-PTNP}_{110})_2]_3\}$	59
5	$c\text{-}\{\text{PHNHT}_5\text{-}[(b\text{-PTNP}_{130})_2\text{-}b\text{-PBNP}_5]_3\}$	68

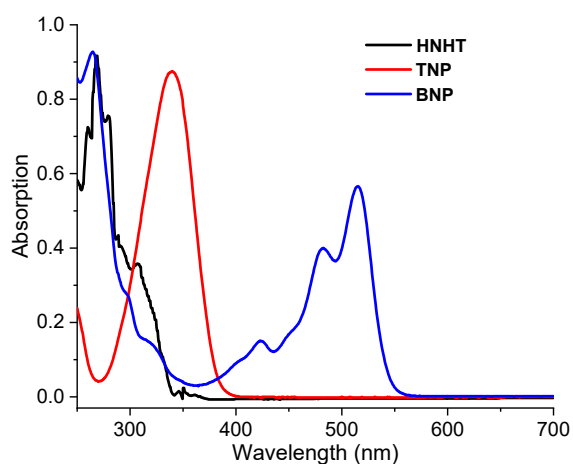


Figure 17. UV-vis spectra of hexafunctional monomer **HNHT** (black), monofunctional monomer **TNP** (red) and difunctional monomer **BNP** (blue) in THF solution at 0.02 mg mL^{-1} .

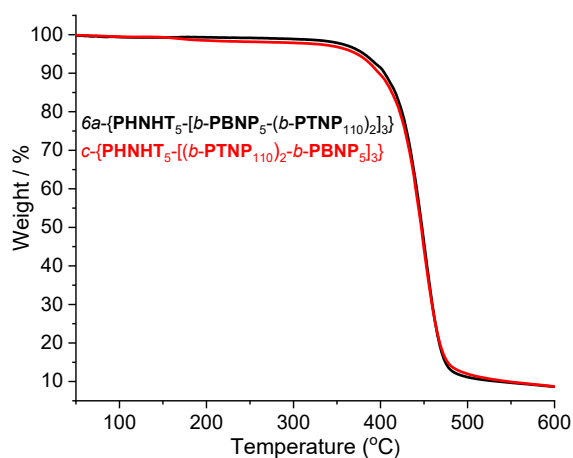
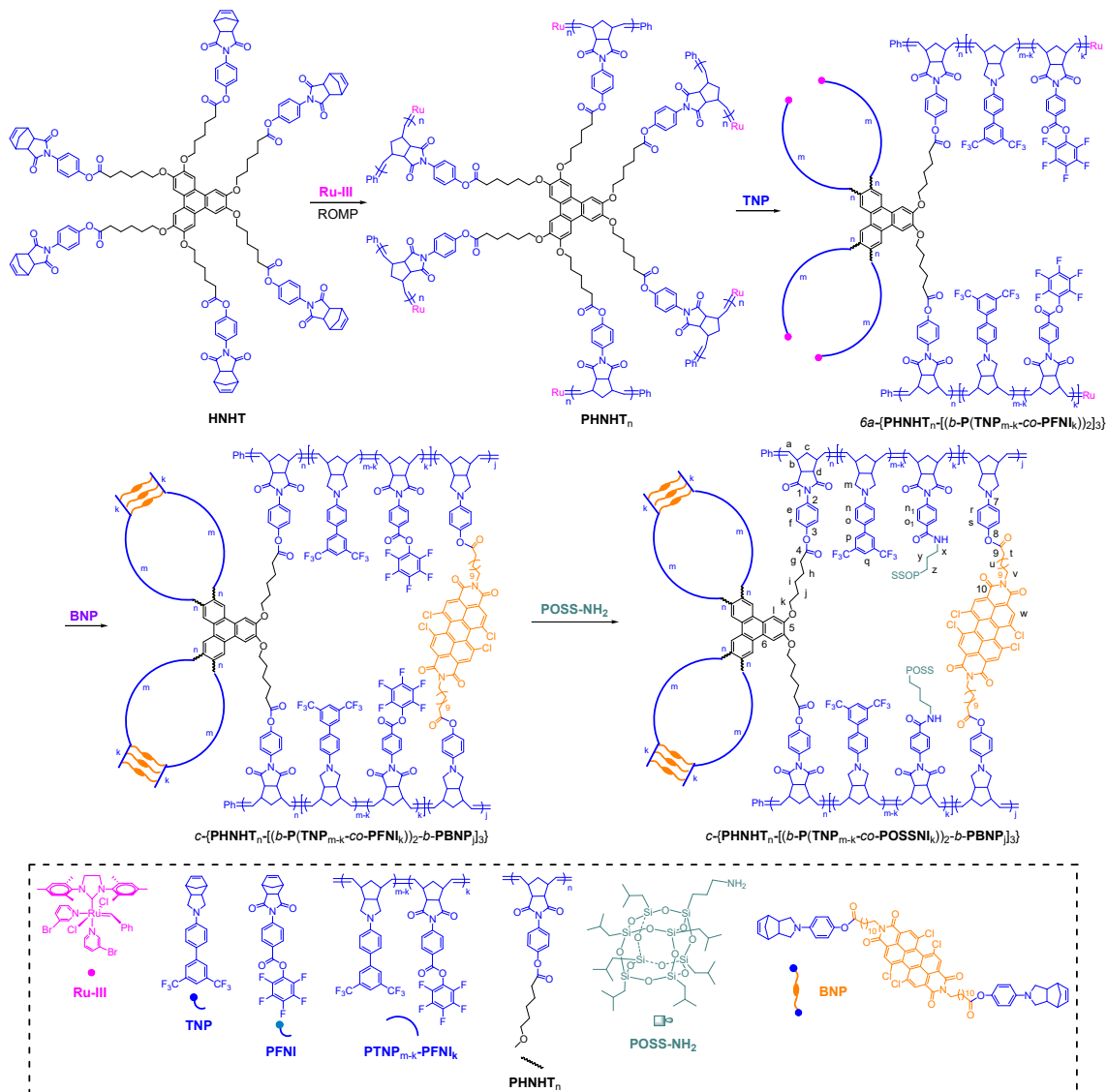


Figure S18. TGA curves of six-arm star-shaped and trefoil-shaped tricyclic polymers.

3. Modification of trefoil-shaped tricyclic polymer containing pentafluorophenyl ester units

units



Scheme S4. POSS-modification of trefoil-shaped tricyclic polymer

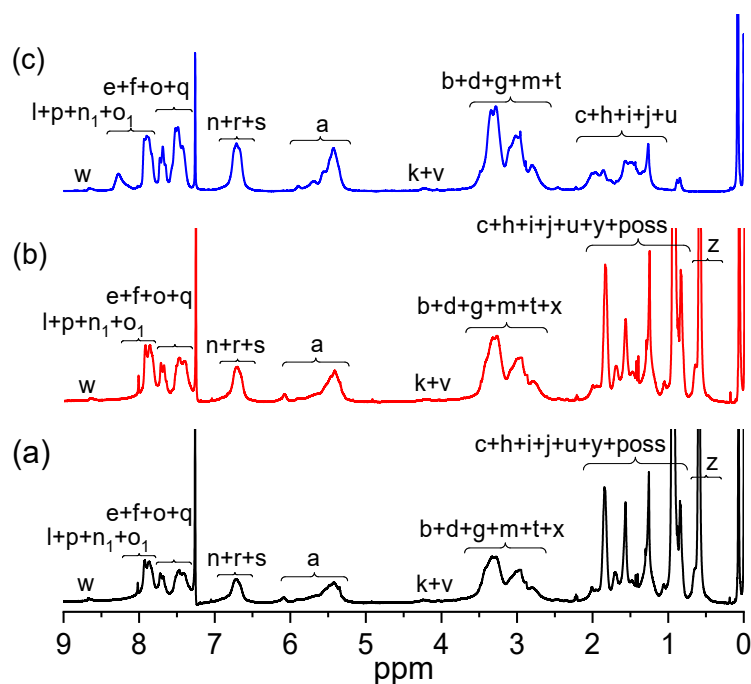


Figure S19. ^1H NMR spectra of (a) POSS-modified six-arm star-shaped $6a$ - $\{\text{PHNHT}_5$ - $[b$ - PBNP_5 - $(b$ - $\text{P}(\text{TNP}_{85}\text{-}co\text{-}\text{POSSNI}_{25}))_2$] $\}_3$, (b) POSS-modified trefoil-shaped tricyclic c - $\{\text{PHNHT}_5$ - $[b$ - $\text{P}(\text{TNP}_{85}\text{-}co\text{-}\text{POSSNI}_{25}))_2$ - b - PBNP_5] $\}_3$, and (c) trefoil-shaped tricyclic c - $\{\text{PHNHT}_5$ - $[b$ - $\text{P}(\text{TNP}_{85}\text{-}co\text{-}\text{PFNI}_{25}))_2$ - b - PBNP_5] $\}_3$ measured in CDCl_3 .

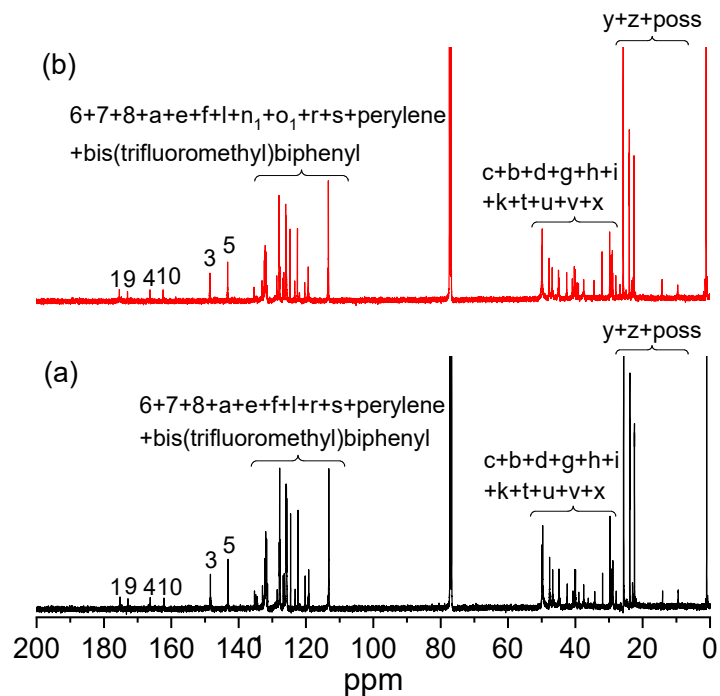


Figure S20. ^{13}C NMR spectra of (a) POSS-modified six-arm star-shaped $6a$ - $\{\text{PHNHT}_5$ - $[b$ - PBNP_5 - $(b$ - $\text{P}(\text{TNP}_{85}\text{-}co\text{-}\text{POSSNI}_{25}))_2$] $\}_3$ and (b) POSS-modified trefoil-shaped tricyclic c - $\{\text{PHNHT}_5$ - $[b$ - $\text{P}(\text{TNP}_{85}\text{-}co\text{-}\text{POSSNI}_{25}))_2$ - b - PBNP_5] $\}_3$ measured in CDCl_3 .

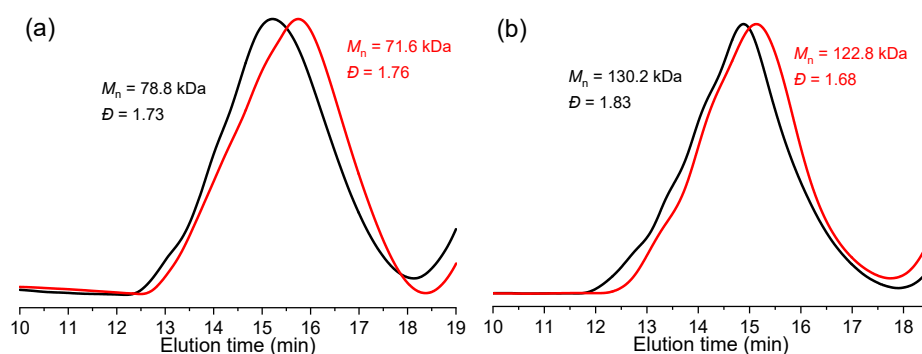


Figure S21. GPC traces of polymers (a) six-arm star-shaped $6a$ - $\{\text{PHNHT}_5$ - $[b$ - PBNP_5 - $(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{PFNI}_{25}))_2\}_3$ (black) and trefoil-shaped tricyclic c - $\{\text{PHNHT}_5$ - $[(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{PFNI}_{25}))_2$ - b - $\text{PBNP}_5]_3$ (red). (b) POSS-modified six-arm star-shaped $6a$ - $\{\text{PHNHT}_5$ - $[b$ - PBNP_5 - $(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{POSSNI}_{25}))_2\}_3$ (black) and POSS-modified trefoil-shaped tricyclic c - $\{\text{PHNHT}_5$ - $[(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{POSSNI}_{25}))_2$ - b - $\text{PBNP}_5]_3$ (red).

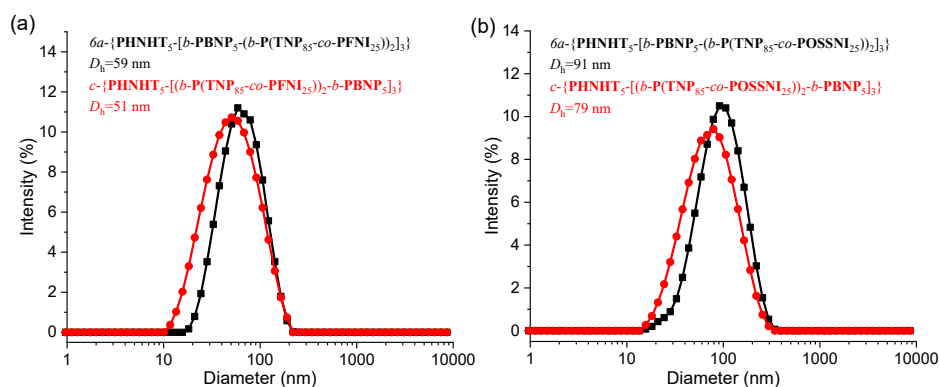


Figure S22. DLS diagrams of (a) six-arm star-shaped $6a$ - $\{\text{PHNHT}_5$ - $[b$ - PBNP_5 - $(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{PFNI}_{25}))_2\}_3$ (black) and trefoil-shaped tricyclic c - $\{\text{PHNHT}_5$ - $[(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{PFNI}_{25}))_2$ - b - $\text{PBNP}_5]_3$ (red) in THF at 1 mg mL^{-1} . (b) POSS-modified six-arm star-shaped $6a$ - $\{\text{PHNHT}_5$ - $[b$ - PBNP_5 - $(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{POSSNI}_{25}))_2\}_3$ (black) and POSS-modified trefoil-shaped tricyclic c - $\{\text{PHNHT}_5$ - $[(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{POSSNI}_{25}))_2$ - b - $\text{PBNP}_5]_3$ (red) in THF at 1 mg mL^{-1} .

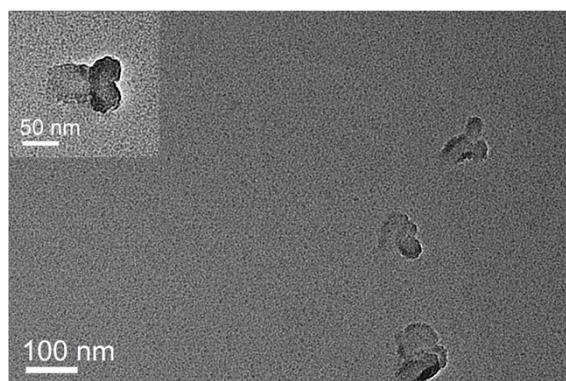


Figure S23. TEM images of modified trefoil-shaped tricyclic polymer c - $\{\text{PHNHT}_5$ - $[(b$ - $\text{P}(\text{TNP}_{85}\text{-}co$ - $\text{POSSNI}_{25}))_2$ - b - $\text{PBNP}_5]_3$ film made from THF solution at 5×10^{-4} mg mL^{-1} .

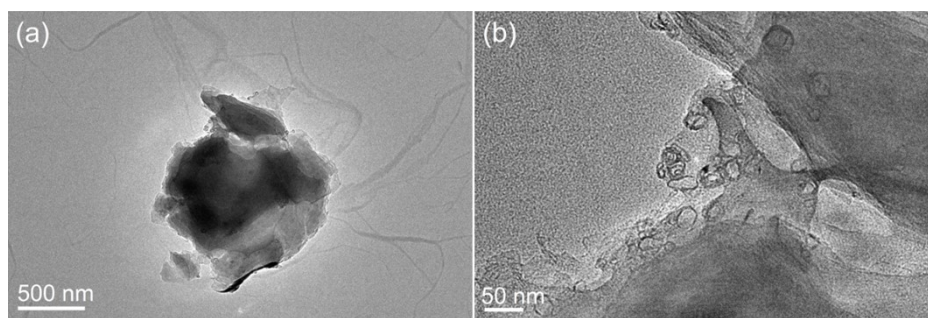


Figure S24. TEM images of modified trefoil-shaped tricyclic polymer $c\text{-}\{\text{PHNHT}_5\text{-}[(b\text{-P}(\text{TNP}_{85}\text{-}co\text{-}\text{POSSNI}_{25}))_2\text{-}b\text{-PBNP}_5]_3\}$ film made from THF solution at $1 \times 10^{-3} \text{ mg mL}^{-1}$.

References

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- 2 O. Kocyigit and E. Guler, *J. Organomet. Chem.*, 2011, **696**, 3106-3112.