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Supplementary Information

A manganese porphyrin-α-cyclodextrin conjugate as an artificial enzyme for the catalytic epoxidation of polybutadiene

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1. Materials, instruments and synthesis of compounds.

1.1 Materials.

Unless stated otherwise, all reagents were purchased from Sigma-Aldrich Co. and used without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed by ^{1}H NMR, ^{13}C NMR, and high-resolution ESI or MALDI-TOF mass spectroscopy.

1.2 Instruments.

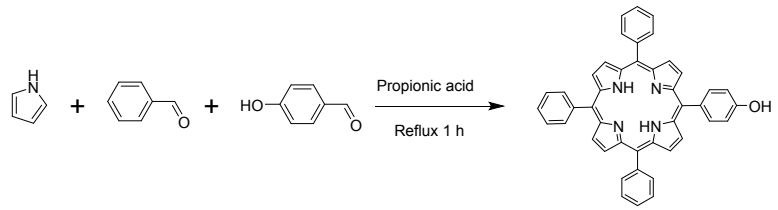
^{1}H, and ^{13}C NMR spectra were measured at 299 K on a Bruker AVIII-500 spectrometer equipped with a Prodigy BBO probe. The high resolution mass spectra were obtained on a JEOL AccuTOF CS JMS-T100CS mass spectrometer and a Bruker Microflex LRF MALDI-TOF system. Absorption spectra and ICD spectra were measured on a JASCO V-630 UV-Vis absorption spectrophotometer and Jasco-715 spectropolarimeter, respectively.

1.3 General procedure for the epoxidation of polybutadiene with porphyrin-

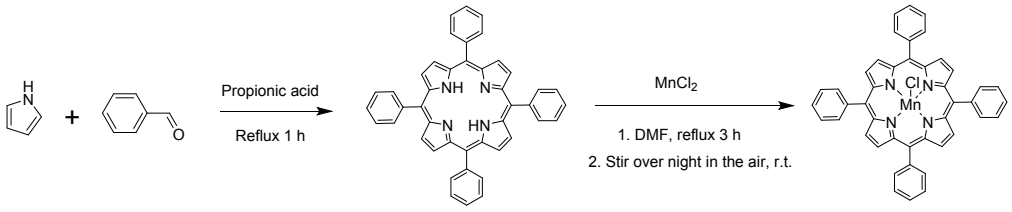
cyclodextrin conjugated catalysts.

A given catalyst (1.25×10^{-4} mmol, 1 equiv.) was dissolved in 20 μL pyridine (acting both as a ligand and as solvent) and the solution was diluted with additional dichloromethane (164 μL). Subsequently, 66 μL of polybutadiene substrate (*Aldrich*, *Mw* 200,000 ~ 300,000, 98% *cis*, [C=C] = 0.467 M, 250 equiv.) was added. The reaction mixture was stirred for 10 min., after which the oxidant PhIO (62 mmol, 500 equiv.) was added. Stirring (1100 r/min) was continued at room temperature for 7 hours, after which the unreacted oxidant was removed by filtration and the filtrate concentrated under a N_2 atmosphere. The resulting product was redissolved in 0.5 mL $CDCl_3$ and analyzed by ^1H NMR. Conversions and stereoselectivities were calculated from the peaks at 5.4 ppm (*cis*-alkene), 2.9 ppm (*cis*-epoxide), and 2.75 ppm (*trans*-epoxide). All the epoxidations were repeated three times.

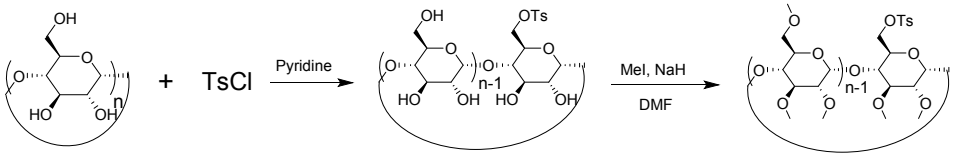
1.3 Synthesis



1a



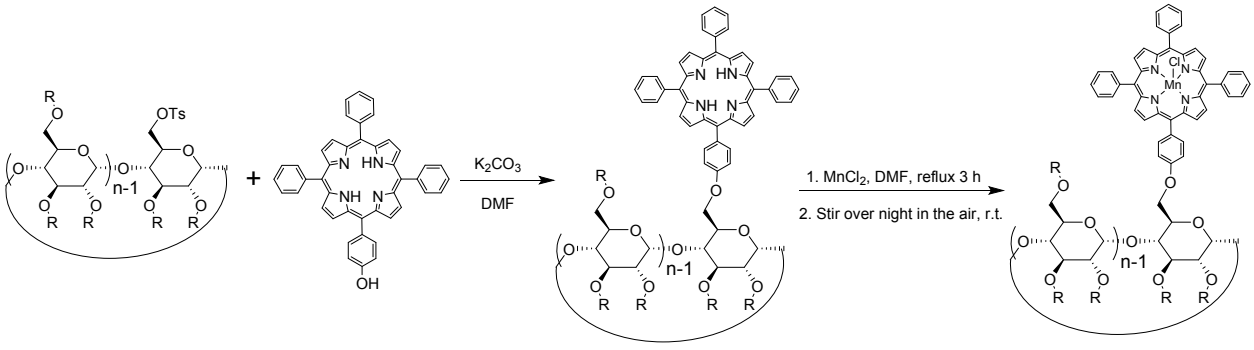
1b **MnTPP**



n=6, **αCD**
n=7, **βCD**

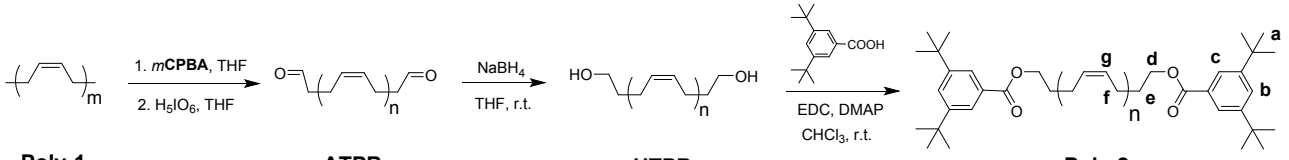
n=6, **Ts-αCD**
n=7, **Ts-βCD**

n=6, **Ts-PMαCD**
n=7, **Ts-PMβCD**



R=H, n=6, **TPP-αCD**
n=7, **TPP-βCD**
R=CH_3, n=6, **TPP-PMαCD**
n=7, **TPP-PMβCD**

R=H, n=6, **MnTPP-αCD**
n=7, **MnTPP-βCD**
R=CH_3, n=6, **MnTPP-PMαCD**
n=7, **MnTPP-PMβCD**



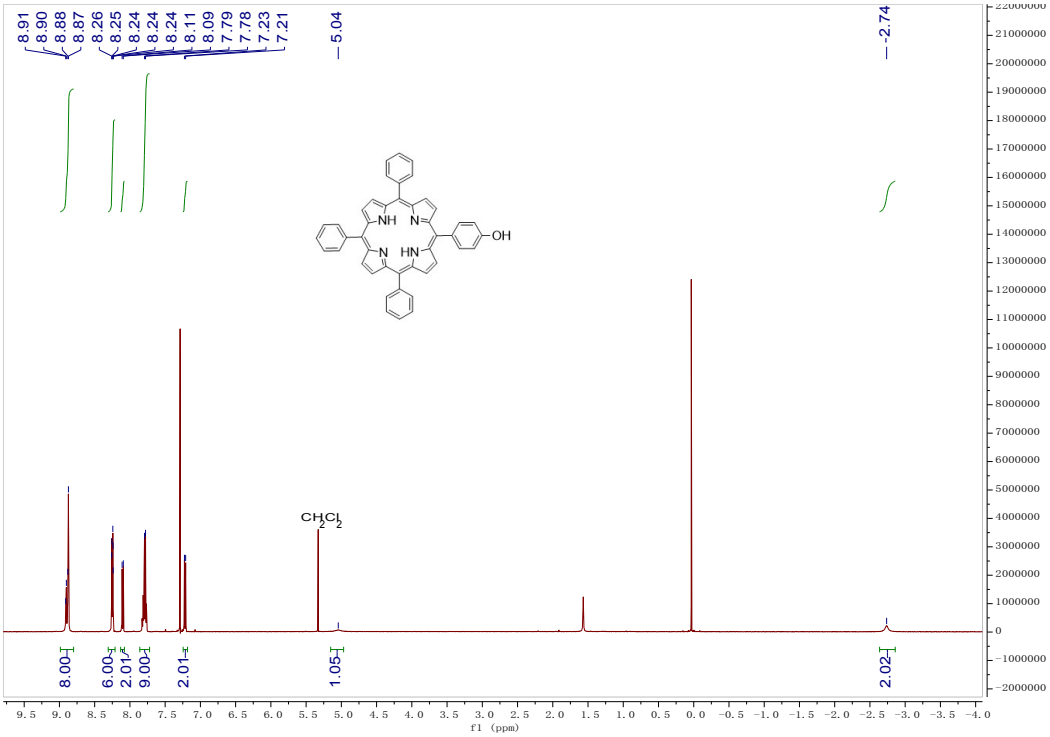
Poly-1
(*cis*-polybutadiene)

ATPB

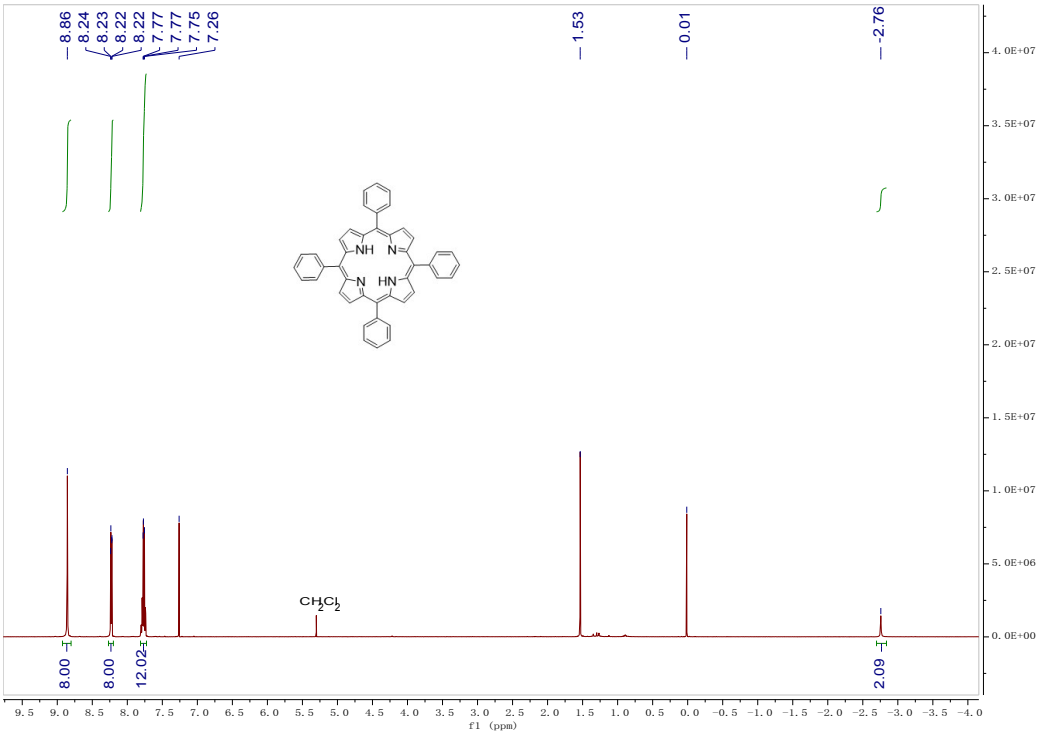
HTPB

Poly-2

Synthesis of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (1a). This compound was conveniently synthesized in one step according to the literature procedure.[1] ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.91 – 8.87 (m, 8H), 8.26 – 8.24 (m, 6H), 8.08 (d, J = 8.5 Hz, 2H), 7.85 – 7.76 (m, 9H), 7.19 (d, J = 8.5 Hz, 2H), 5.04 (br s, 1H), -2.74 (s, 2H).



Synthesis of *meso*-tetraphenylporphyrin (1b). This compound was synthesized according to the literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.86 (s, 8H), 8.23 (dd, J = 7.7, 1.7 Hz, 8H), 7.99 – 7.61 (m, 12H), -2.76 (s, 2H).

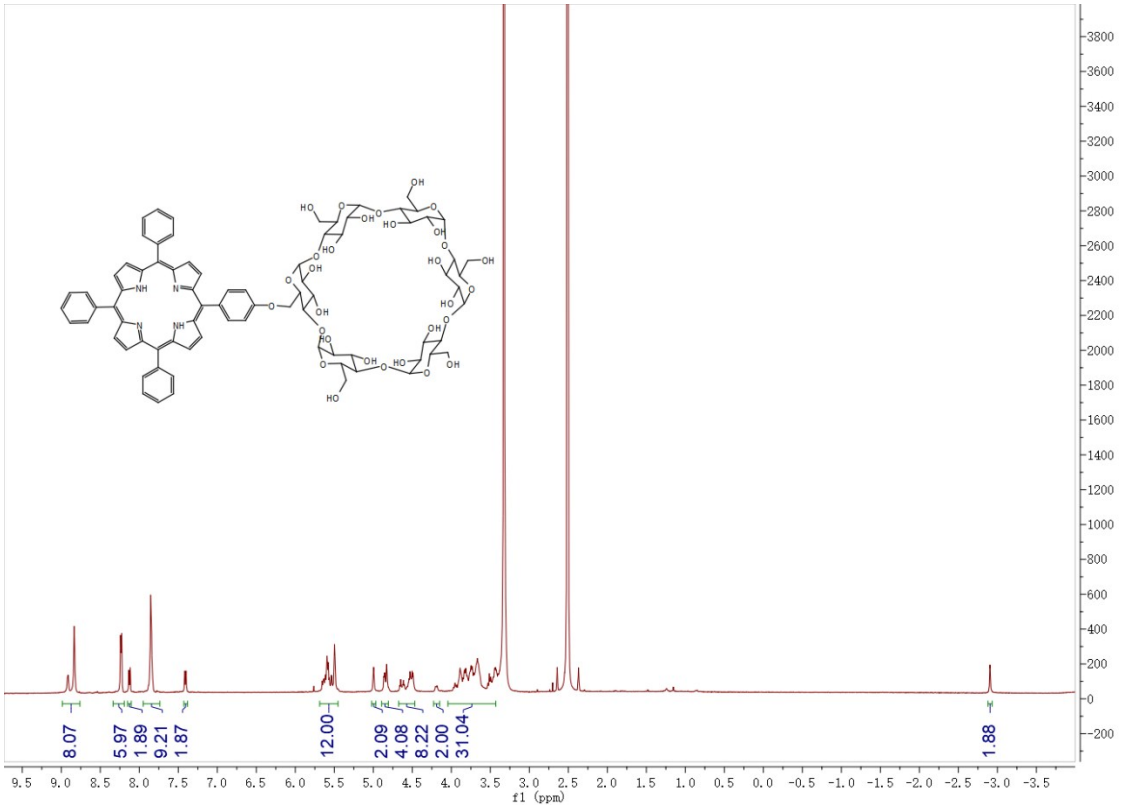


Synthesis of (5,10,15,20-tetraphenyl)porphinato manganese (III) chloride (MnTPP). This catalyst was synthesized and fully characterized as described in a published paper.[3]

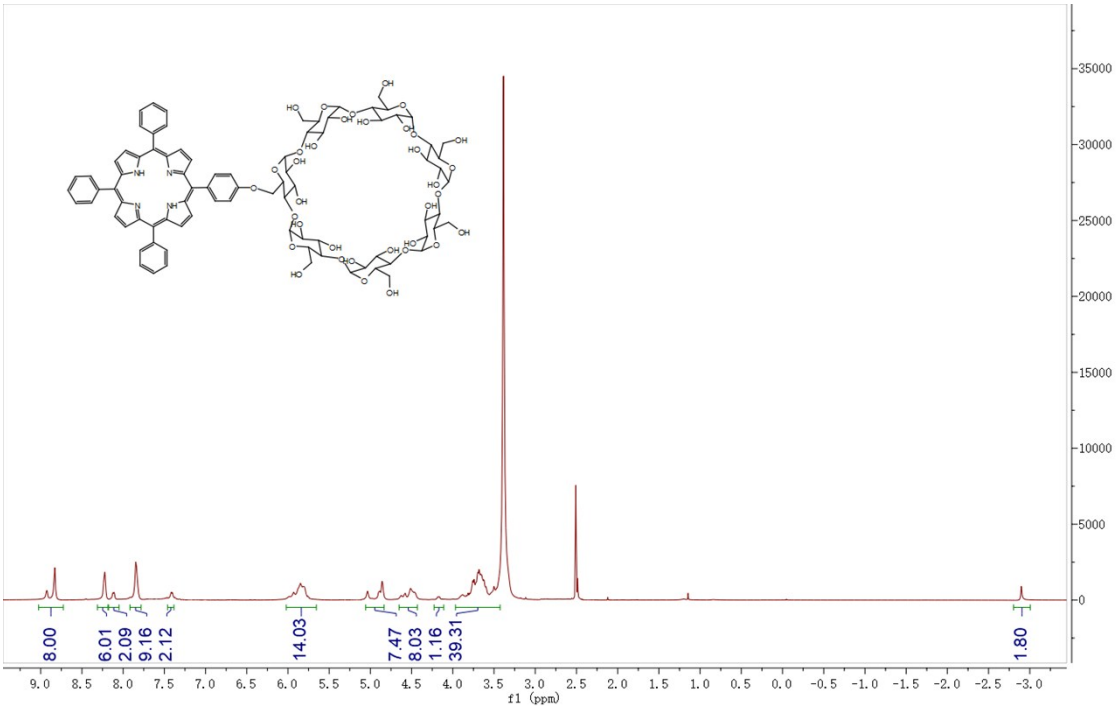
Syntheses of mono-6-(*p*-toluenesulfonyl)-6-deoxy-α(β) cyclodextrin (Ts-αCD and Ts-βCD), and mono-6-(*p*-toluenesulfonyl)-6-deoxy-permethylated α(β) cyclodextrin (Ts-PMαCD and Ts-PMβCD). These four modified cyclodextrins were obtained and characterized according to the literature: **Ts-αCD** and **Ts-βCD**,[4] **Ts-PMαCD**,[5] and **Ts-PMβCD**.[6]

Synthesis of mono-6-(5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrinyl)-6-deoxy-(permethyl) α(β) cyclodextrins (TPP-αCD, TPP-βCD, TPP-PMαCD, and TPP-PMβCD). General procedure for the coupling reactions between porphyrin **1a** and monotosyl cyclodextrins: 6-tosyl cyclodextrin (0.13 mmol, 1 equiv.) was added to a dry DMF solution (10 mL) of **1a** (88.4 mg, 0.14 mmol, 1.1 equiv.) and K_2CO_3 (179.3 mg, 1.3 mmol, 10 equiv.). The mixture was stirred under argon at 90 °C for three days. The solvent was removed under vacuum and the obtained product was purified by column chromatography (Diaion® HP-20 column with 30% methanol in water as the eluent for **TPP-αCD, TPP-βCD**, and silica gel column with 5% MeOH in CH_2Cl_2 as the eluent for **TPP-PMαCD**, **TPP-PMβCD**).

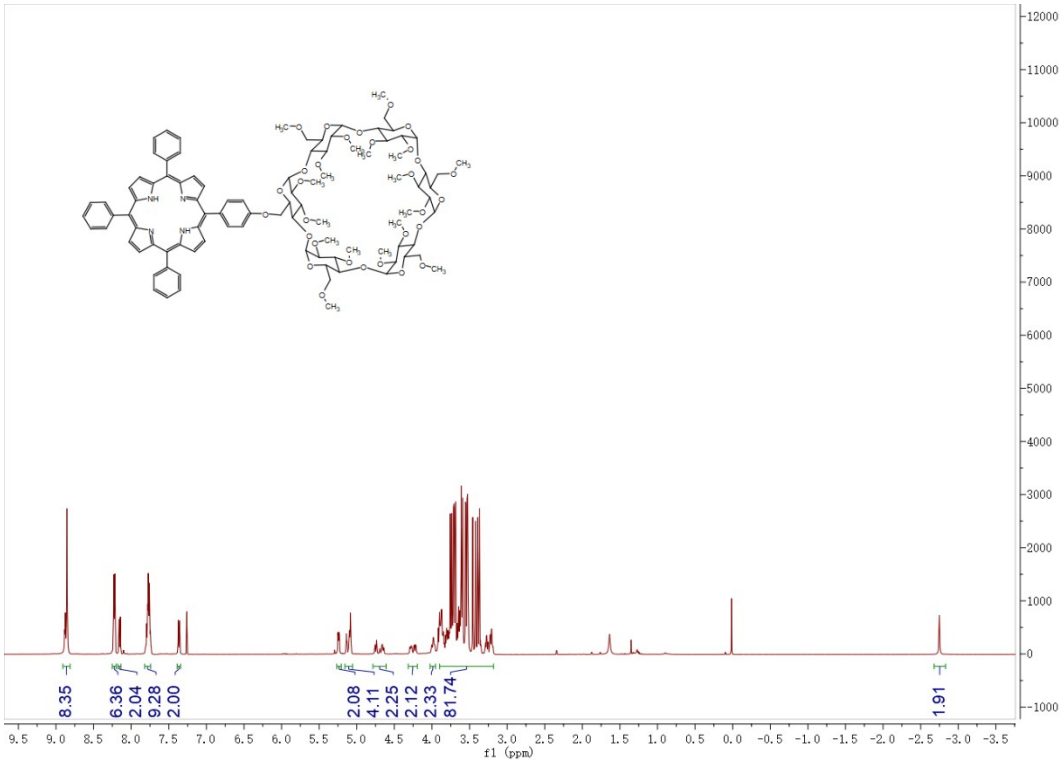
TPP-αCD (56% yield). UV/Vis (MeOH), λ/nm: 414, 512, 547, 589, 645. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.93 – 8.84 (m, 8H), 8.25 – 8.20 (m, 6H), 8.12 (d, J = 8.1 Hz, 2H), 7.94 – 7.77 (m, 9H), 7.41 (d, J = 8.2 Hz, 2H), 5.77 – 5.41 (m, 12H), 5.00 (s, 2H), 4.92 – 4.81 (m, 4H), 4.68 – 4.46 (m, 8H), 4.19 (br s, 2H), 4.07 – 3.40 (m, 31H), -2.90 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6, δ): 158.60, 141.25, 135.37, 134.22, 133.34, 131.52, 128.08, 127.01, 126.02, 120.16, 119.93, 119.78, 113.20, 102.44 – 101.91, 82.57 – 81.99, 73.57 – 71.93, 69.79, 67.27, 60.39 – 59.82, 22.12. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{80}H_{89}N_4O_{30}]^+$, 1585.5556; found, 1585.5530.



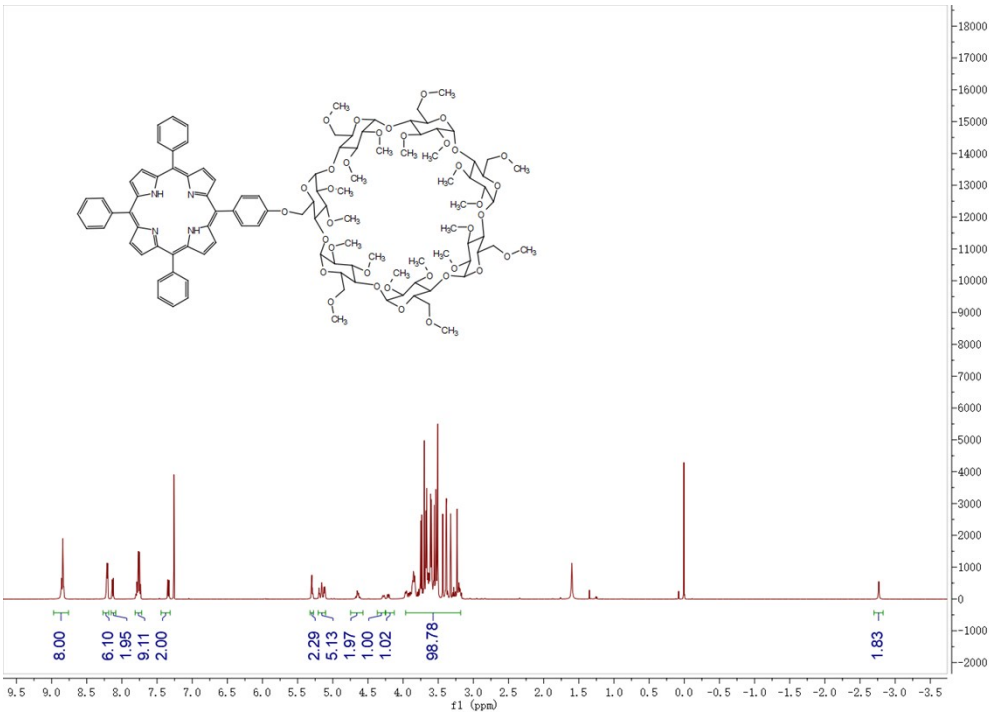
TPP-βCD (50% yield). UV/Vis (MeOH), λ/nm: 413, 512, 546, 589, 645. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.93 – 8.83 (m, 8H), 8.25 – 8.19 (m, 6H), 8.12 (d, J = 7.9 Hz, 2H), 7.90 – 7.78 (m, 9H), 7.41 (d, J = 8.0 Hz, 2H), 5.98 – 5.77 (m, 14H), 5.04– 4.82 (m, 7H), 4.66 – 4.15 (m, 6H), 3.94 – 3.20 (m, 42H), -2.90 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6, δ): 158.74, 141.29, 135.37, 134.25, 133.40, 131.53, 128.06, 127.05, 126.01, 120.23, 119.97, 119.82, 113.23, 102.63 – 101.98, 82.40 – 81.49, 73.44 – 72.01, 69.83, 67.44, 60.28 – 59.76, 29.01. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{86}H_{99}N_4O_{35}]^+$, 1747.6084; found, 1747.6130.



TPP-PMαCD (82% yield). UV/Vis (MeOH), λ/nm: 414, 512, 547, 589, 645. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.86 (m, 8H), 8.25 – 8.20 (m, 6H), 8.15 (d, *J* = 8.5 Hz, 2H), 7.77 (m, 9H), 7.36 (d, *J* = 8.6 Hz, 2H), 5.24 (dd, *J* = 7.0, 3.4 Hz, 2H), 5.16 – 5.06 (m, 4H), 4.80 – 4.61 (m, 2H), 4.25 (m, 2H), 4.03 – 3.94 (m, 2H), 3.93 – 3.19 (m, 81H), -2.75 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 158.78, 142.29, 135.71, 135.05, 134.68, 134.65, 131.19, 127.87, 126.82, 120.25, 120.20, 119.94, 113.06, 100.55 – 100.21, 83.41 – 81.45, 71.71 – 71.17, 68.36, 62.10 – 61.96, 59.43 – 59.13, 58.19 – 58.00. HRMS (ESI) m/z: $[M+Na+H]^+$ calcd for $[C_{97}H_{123}N_4NaO_{30}]^+$, 1846.8114; found, 1846.8075.



TPP-PMβCD (85% yield). UV/Vis (MeOH), λ/nm: 414, 512, 547, 589, 645. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.84 (m, 8H), 8.21 (m, 6H), 8.13 (d, *J* = 8.6 Hz, 2H), 7.85 – 7.67 (m, 9H), 7.34 (d, *J* = 8.5 Hz, 2H), 5.35 – 5.27 (m, 2H), 5.22 – 5.05 (m, 5H), 4.74 – 4.57 (m, 2H), 4.33 – 4.16 (m, 2H), 4.04 – 3.11 (m, 98H), -2.77 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 158.79, 142.28, 135.69, 134.98, 134.69, 134.65, 131.37, 127.89, 126.83, 120.26, 120.22, 119.93, 113.07, 99.69 – 98.96, 82.38 – 81.92, 81.50, 80.80 – 80.32, 71.69 – 70.77, 68.20, 61.80 – 61.56, 59.39 – 59.05, 58.83 – 58.62. MALDI-TOF m/z: $[M+K+H]^+$ calcd for $[C_{106}H_{139}KN_4O_{35}]^+$, 2066.885; found, 2066.569.



Synthesis of manganese porphyrin-cyclodextrin conjugates (MnTPP-αCD, MnTPP-βCD, MnTPP-PMαCD, and MnTPP-PMβCD). General procedure for the metallization of the porphyrin-cyclodextrin conjugates: a given porphyrin-cyclodextrin conjugate (0.03 mmol, 1 equiv.) was dissolved in 5 mL DMF and freshly crushed $MnCl_2$ (18.7 mg, 0.15 mmol, 5 equiv.) was added to the solution. The reaction mixture was refluxed for 3 h under argon, after which it was cooled to room temperature and stirred over-night open to the air. The solvent was removed under vacuum and the obtained dark green product was purified by column chromatography (Diaion® HP-20 column with 30% MeOH in water as the eluent for **MnTPP-αCD, MnTPP-βCD**, and silica gel column with 5% MeOH in CH_2Cl_2 as the eluent for **MnTPP-PMαCD**, **MnTPP-PMβCD**).

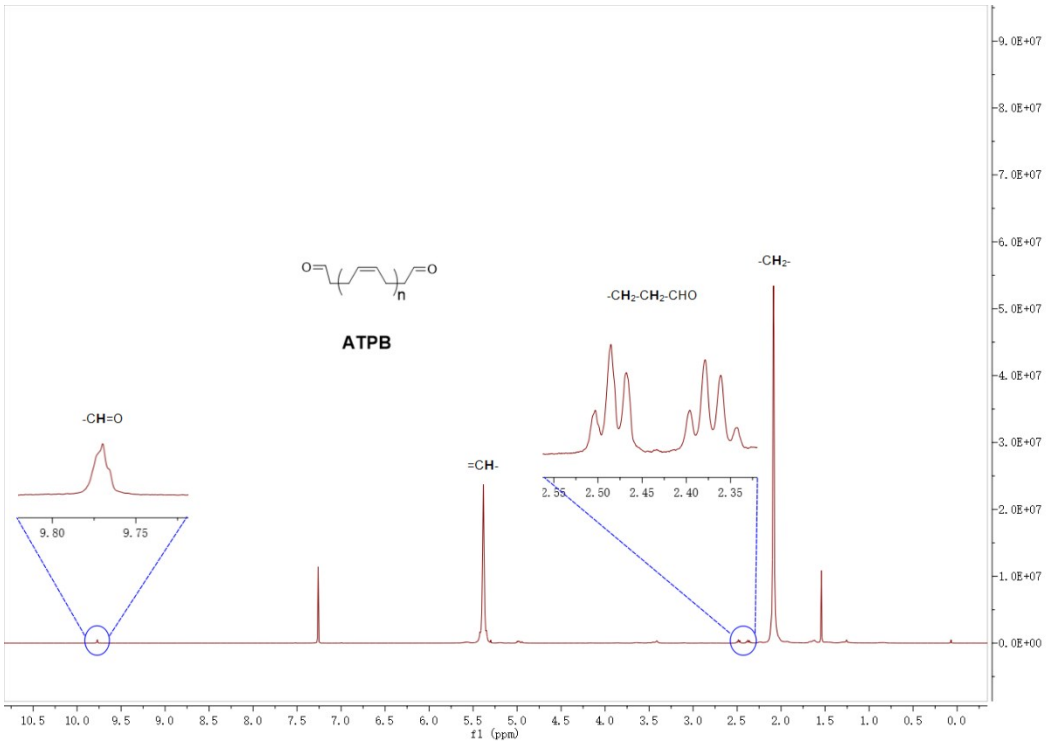
MnTPP-αCD (96% yield), UV/Vis (MeOH), λ/nm: 379, 400, 420, 468, 516, 565, 600. MALDI-TOF m/z: $[M+H-Cl]^+$ calcd for $[C_{80}H_{87}MnN_4O_{30}]^+$, 1638.478; found, 1638.844.

MnTPP-βCD (90% yield) , UV/Vis (MeOH), λ/nm: 379, 400, 420, 468, 516, 565, 600. MALDI-TOF m/z: $[M+H-Cl]^+$ calcd for $[C_{86}H_{97}MnN_4O_{35}]^+$, 1800.531; found, 1800.228.

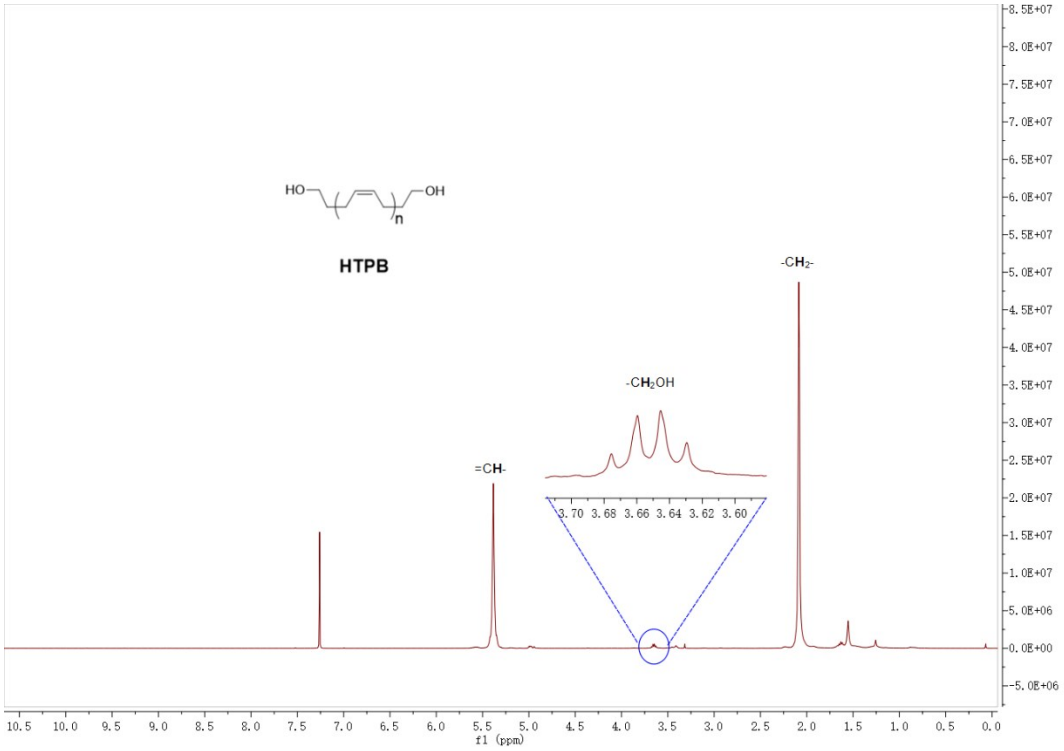
MnTPP-PMαCD (98% yield), UV/Vis (MeOH), λ/nm: 379, 400, 420, 468, 517, 566, 600. MALDI-TOF m/z: $[M+H-Cl]^+$ calcd for $[C_{97}H_{121}MnN_4O_{30}]^+$, 1876.744; found, 1876.386.

MnTPP-PMβCD (95% yield), UV/Vis (MeOH), λ/nm: 379, 400, 419, 468, 517, 566, 600. MALDI-TOF m/z: $[M+H-Cl]^+$ calcd for $[C_{106}H_{137}MnN_4O_{35}]^+$, 2080.844; found, 2080.728.

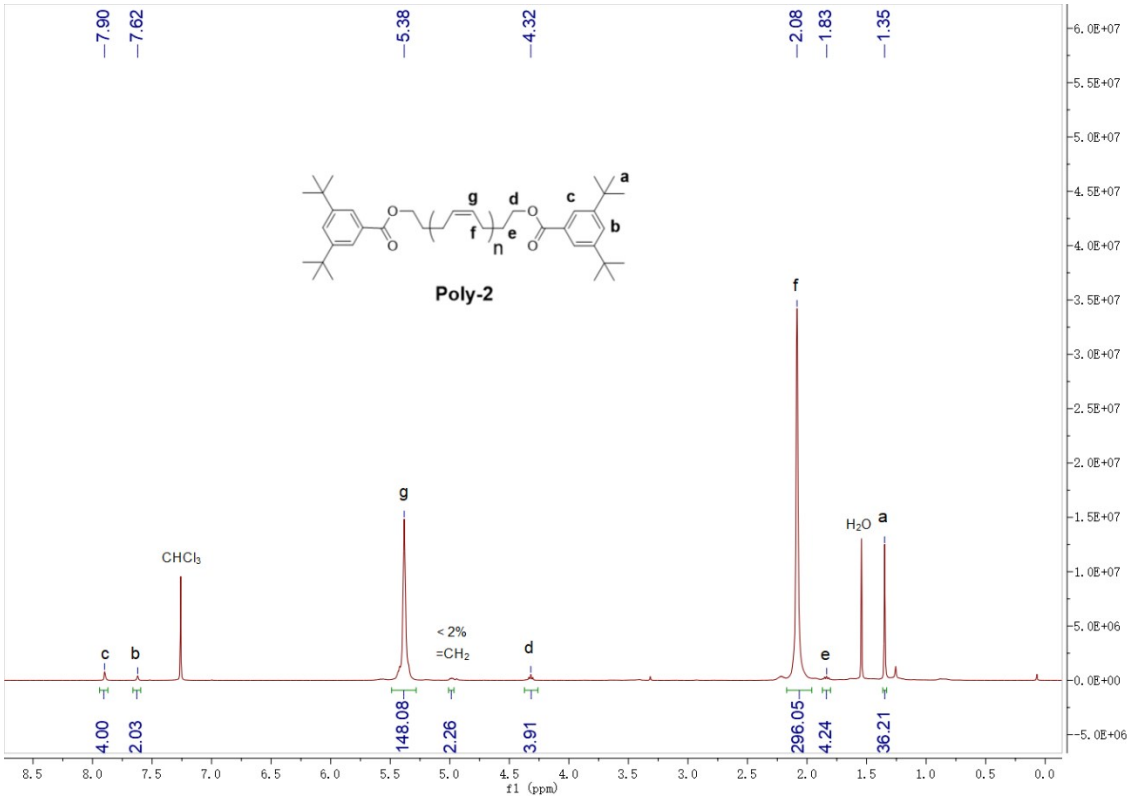
Synthesis of aldehyde-terminated *cis*-polybutadiene (ATPB). This compound was synthesized and characterized according to the literature.[7] To a solution of *cis*-Polybutadiene (**Poly-1**) (2.00 g, Aldrich, Mw 200,000~300,000, 98% *cis*) in THF (60 mL) was added dropwise a 3-chloroperbenzoic acid (Aldrich, ⩽77%) in THF (10 mL). The solution was stirred for 1 hour at 30 ^oC, after which, a H_5IO_6 solution (0.33 g, in 10 mL THF) was added. The reaction was kept stirring for 0.5 hour at 30 ^oC, and then $NaHCO_3$ and 2,6-di-*tert*-butyl-4-methylphenol were added for neutralization and antioxidation, respectively. The insoluble white iodic acid was then removed by filtration though Celite, after which the product was isolated by dropping the filtrate into methanol (200 mL). The precipitate was washed with a large amount of methanol to remove the unreacted materials and dried in vacuo to give the product (1.06 g) as colorless sticky oil.

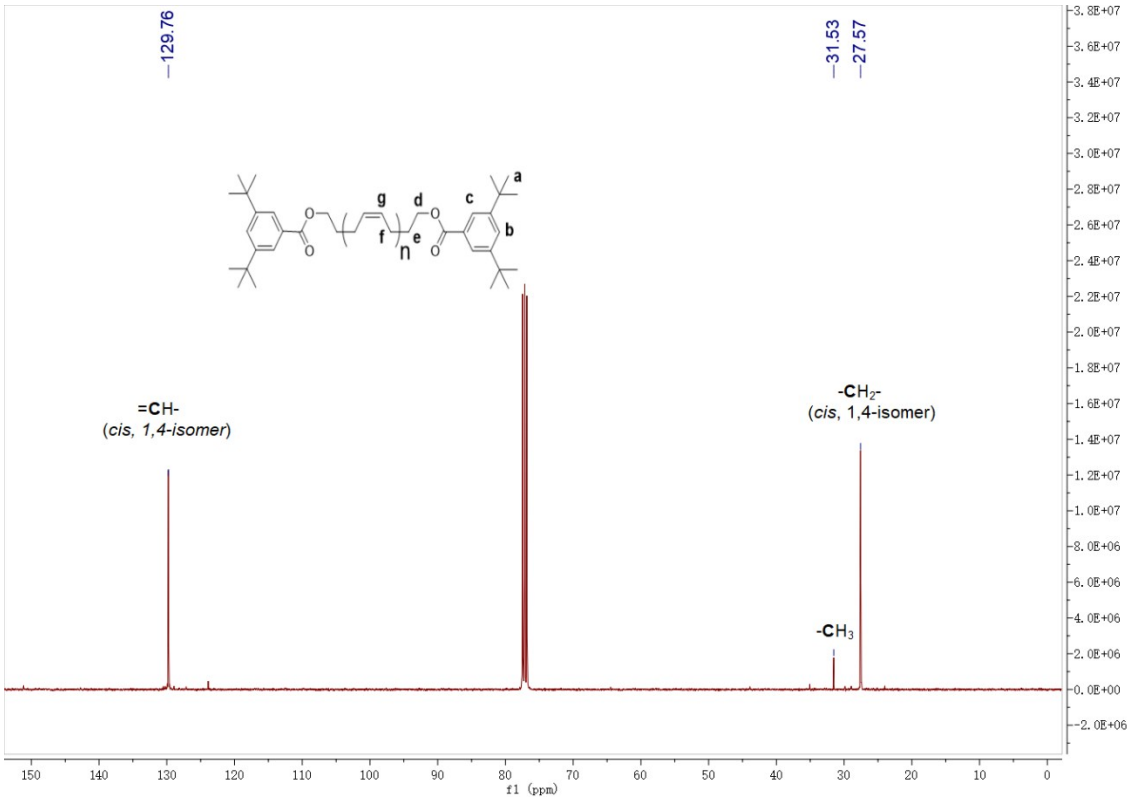


Synthesis of hydroxy-terminated *cis*-polybutadiene (HTPB). This compound was synthesized and characterized according to the literature.[7] To a solution of **HTPB** (0.90 g) in THF (60 mL) was added $NaBH_4$ (0.17 g). The reaction was carried out at 30 ^oC for 4 hours, after which a small amount of Milli-Q water was added to the solution slowly. The solvent was removed under reduced pressure with the help of a rotary evaporator and the residue was dissolved in cyclohexane and filtered though Celite to remove the salt. After evaporating the filtrate, the crude product was further washed with methanol and dried in vacuo to give the desired product as a colorless sticky oil (600 mg).



Synthesis of 3,5-di-*tert*-butylphenyl-terminated *cis*-polybutadiene (Poly-2). Polymer **HTPB** (500 mg) was dissolved in $CHCl_3$ (50 mL) at 0 °C, and a large excess of 3,5-di-tert-butylbenzoic acid (1.00 g), EDC·HCl (500 mg), and 4-dimethylaminopyridine (62.5 mg) were added to the solution. The reaction mixture was then stirred in reflux for 24 hour under argon, after which the solvent was removed and the residue was dissolved in a small amount of dichloromethane, after which this sollution was dropped into methanol (200 mL). The precipitate saparated and washed with a large amount of methanol to remove the unreacted materials. The product (220 mg) was obtained as colorless sticky oil after drying in vacuo. The structure of **Poly-2** was charactrized by ^{1}H NMR. All the protons were assigned and the 1,2-isomer was calculated as being less than 2% according to the integrals of the alkene protons in ^{1}H NMR spectrum. In the ^{13}C NMR spectra, the single peaks at 27.57 and 129.76 ppm were assigned to $–CH_2$- and =CH- carbon atoms in *cis*-1,4-isomer, while the peak for *trans*-1,4-isomer carbon (should be at 32.7 ppm according to the literature[7]) was not found. These combined NMR results proved that the desired 3,5-di-tert-butylphenyl-terminated *cis*-polybutadiene (ca. 98% *cis*) had been succesfully synthesized, while retaining the *cis*-percentage of the starting material from Aldrich (polybutadiene, 98% *cis*). GPC analysis of **Poly-2** revealed that the molecular weight (M_n) and polydispersity index (PDI) values of the polymer amounted to approximately 9.5 × 10^3 g/mol and 1.5, respectively. It should be noted that the molecular weight obtained from GPC is almost twice as large as the molecular weight calculated from ^{1}H NMR spactra, which is in accordance with the literature.[7]


7.90
7.62
5.38
4.32
2.08
1.83
1.35
Poly-2
CHCl3
H2O
< 2%
=CH2
4.00
2.03
148.08
2.26
3.91
296.05
4.24
36.21
f1 (ppm)


129.76
31.53
27.57
=CH-
(cis, 1,4-isomer)
-CH2-
(cis, 1,4-isomer)
-CH3
f1 (ppm)

2. Additional spectra.

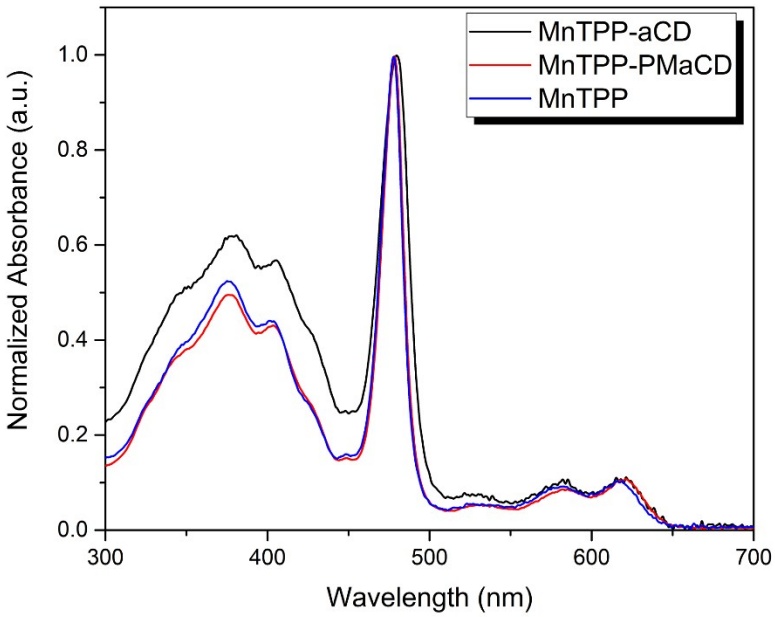


Fig. S1 Normalized absorption spectrum of **MnTPP-αCD**, **MnTPP-PMαCD**, **MnTPP**. (c = 4 × 10^{-5} M, in dichloromethane containing 4% pyridine as the co-solvent)

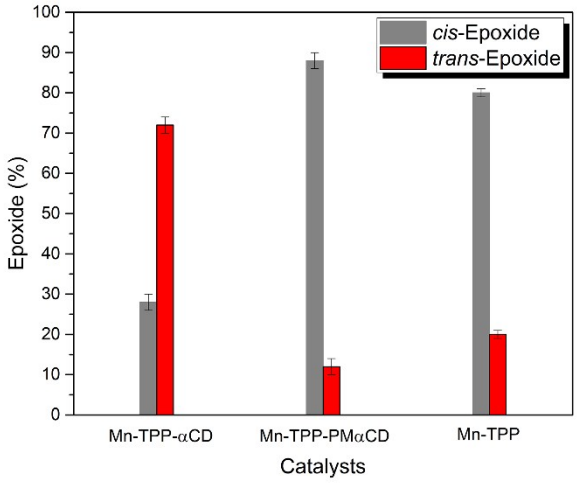


Fig. S2 Cis/trans ratios of the formed epoxide products for the epoxidation of **Poly-2** catalyzed by **MnTPP-αCD, MnTPP-PMαCD**, and **MnTPP**.

3. References

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