Supporting Information

Recoverable Solvent-free Small Molecular Supramolecular Pseudoeutectic Adhesives with a Wide Temperature Range

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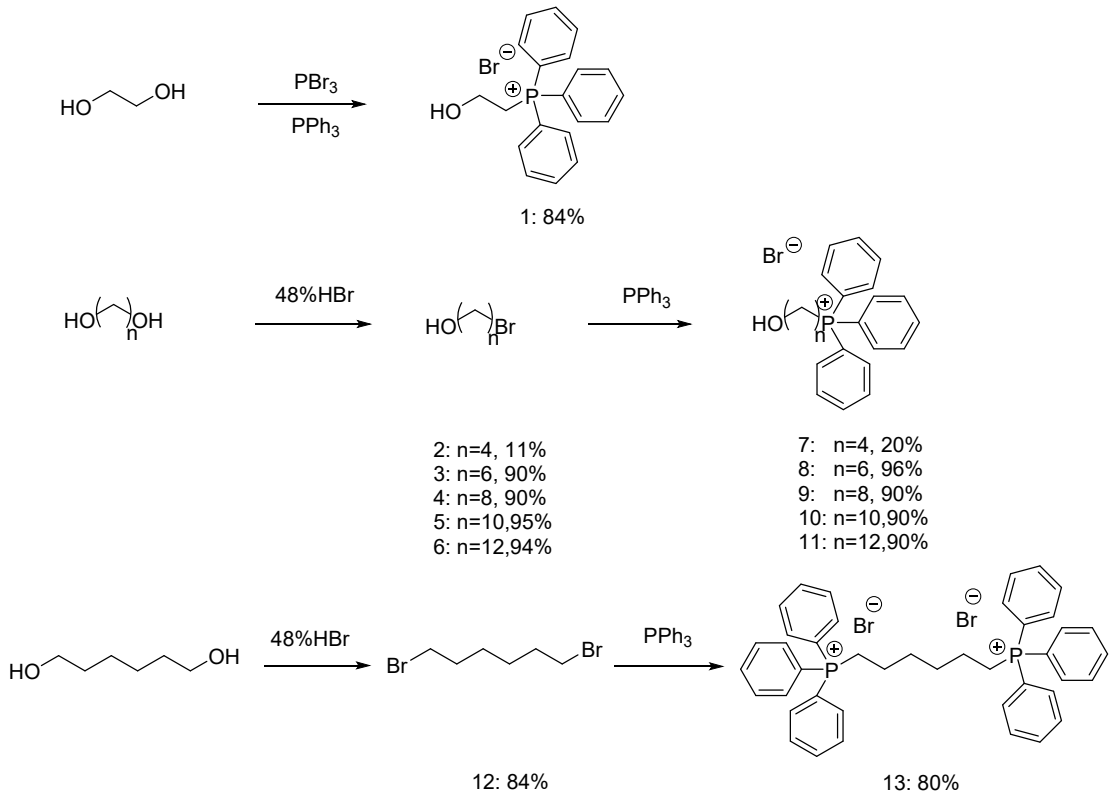

Scheme S1. The synthetic procedures of n-HTPB, 1,6-HDTPB.

Synthesis of compound 1(2-HTPB):

The concentrated hydrobromic acid (48%, 20ml, 178.38 mmol, 12.00 eq) was added 1,6-hexanediol (2g, 14.91 mmol, 1.00 eq). The heterogeneous mixture was stirred and heated at reflux for 24 h, TLC analysis indicated that substantial amounts of compound 1 still remained without diol remaining. Thus, the mixture was heated at reflux for another 6 hours, at which time TLC analysis showed little compound 1 remaining. The reaction mixture was allowed to cool to room temperature, and the phases were separated. The organic layer was diluted with ether and washed with 1M NaOH and brine. Drying over anhydrous Na_2SO_4 and concentration of the organic layer in vacuo gave a yellow oil which was purified by column chromatography (petrol) to give 3.07 g (84%) product compound 2 as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.81-7.75 (m, 9H), 7.70-7.65 (m, 6H), 5.22 (s, 1H), 4.09-4.02 (m, 2H), 3.81-3.75 (m, 2H). The data is consistent with the reported literature[S1].

General Procedure I for the Bromine-substituted hydroxyl groups

A mixture of diol (1.00 g, 1.00 equiv) and 48% HBr aqueous solution (1.20 equiv) in 20 ml toluene was refluxed for some hours. The reaction mixture was monitored by TLC. According to TLC, the reaction was stopped when no starting material remained. Allowed the reaction mixture to cool to room temperature. Separated the organic and aqueous layers, and extracted the aqueous layer with ethyl acetate. Collected the organic layer, washed sequentially with 1M NaOH, deionized water, and saturated brine. Dryed over anhydrous sodium sulfate to remove water. Distilled the crude

product under reduced pressure. Purified the crude product further by silica gel column chromatography to obtain the final products.

General Procedure II for the synthesis of quaternary phosphine salt

A mixture of compound 2 or 3 or 4 or 5 or 6 (5.00 g, 1.00 equiv) and triphenylphosphine (1.10 equiv) in 15 ml anhydrous acetonitrile was refluxed for 48 hours with nitrogen protection. Then it was cooled to room temperature, poured the solvent. Purified the reside by silica gel column chromatography (CH_3OH/DCM: 2/98), then recrystalled by CH_3OH/ ethyl ether (1:5).

Synthesis of compound 7(4-HTPB):

A mixture of 2 (0.90 g, 1.00 equiv), triphenylphosphine (1.72 g, 1.00 equiv) and 0.86 g K_2CO_3 in 5 ml anhydrous acetonitrile was refluxed for 7 hours with nitrogen protection. Then it was cooled to room temperature, filted the K_2CO_3. Added 20 mL ether to the filtrate for recrystallization to obtain the white solid, yield 20%. ^{1}H NMR(400MHz, $CDC1_3$), δ(ppm): 7.82-7.72 (m, 15H), 4.10 (t, J = 8.00 Hz,2H), 3.83-3.76 (m, 2H), 2.67 (s, 1H), 2.09-2.00 (m, 2H), 1.77-1.67 (m, 2H). The data is consistent with the reported literature[S2].

Synthesis of compound 8(6-HTPB):

Following the general procedure II, white solid, yeild 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.47 (apps, 4H), 1.65-1.66 (m, 4H), 3.57-3.67 (m, 5H), 7.70-7.75 (m, 6H), 7.79-7.84 (m, 9H). The data is consistent with the reported literature[S3].

Synthesis of compound 9(8-HTPB):

Following the general procedure II, white solid, yeild 90%. ^{1}H NMR (400 MHz, $CDC1_3$), δ (ppm): 7.84-7.79 (m, 9H), 7.75-7.70 (m, 6H), 3.56-3.54 (m, 4H), 1.63-1.60 (m, 4H), 1.53-1.46 (m, 2H), 1.32-1.18 (m, 6H). The data is consistent with the reported literature[S4].

Synthesis of compound 10(10-HTPB):

Following the general procedure II, white solid, yeild 90%. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.85-7.80 (m, 9H), 7.76-7.71(m, 6H), 3.67-3.56 (m, 4H), 1.62-1.48 (m, 6H), 1.26-1.20 (m, 10H). The data is consistent with the reported literature[S5].

Synthesis of compound 11(12-HTPB):

Following the general procedure II, white solid, yeild 90%. ^{1}H NMR (400 MHz,$CDC1_3$), δ(ppm): 7.85-7.72 (m, 15H), 3.65-3.57 (m, 4H), 1.62-1.49 (m, 6H), 1.28-1.16 (m,14 H). The data is consistent with the reported literature[S5].

Synthesis of compound 12:

A mixture of 1,6-hexanediol (2.00 g, 1.00 eq) and 24 mL 48% HBr was heated at 100 ℃ for 30 h in the dark. After it was cooled, separated organic and aqueous phases. The solvent in the organic phase was evaporated under reduced pressure to get crude product. Then it was purified by silica gel chromatography (petroleum ether) to get colorless liquid (84%).

Synthesis of compound 13[S3](1,6-HDTPB):

A mixture of compound 2 (500 mg, 2.05 mmol, 1.00 eq) and triphenylphosphine (1.18 g, 4.51 mmol, 2.20 eq) N, N-dimethyl acetamide (DMAC) as a solvent was heated at reflux for 18 h, and a white precipitate appeared. The reaction mixture was cooled to room temperature. the residue was purified by silica gel chromatography (CH_3OH/DCM 2:98) to give the product as a white powder(1.25 g, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.67 (apps, 4H), 1.83 (apps, 4H), 3.71-3.78 (m, 4H), 7.69-7.86 (m, 30H). The data is consistent with the reported literature[S6].

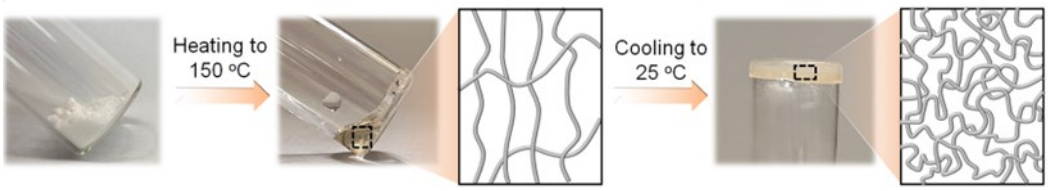

Figure S1 Preparation process of 6-HTPB.

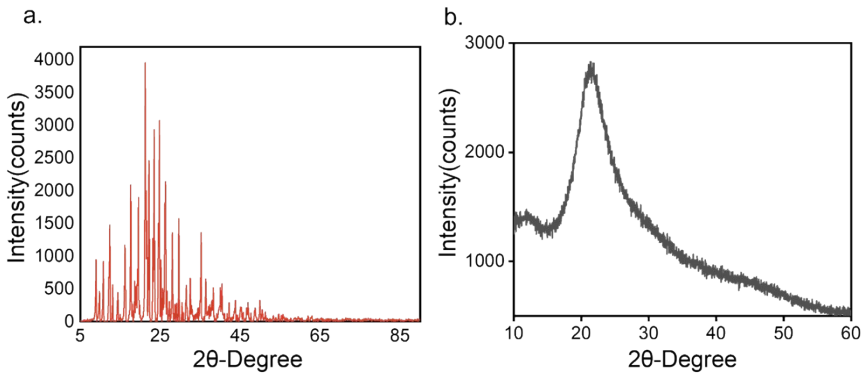

Figure S2 a. PXRD patterns of 6-HTPB powder at 25 °C; b. PXRD patterns of 6-HTPB adhesives at 25 °C.

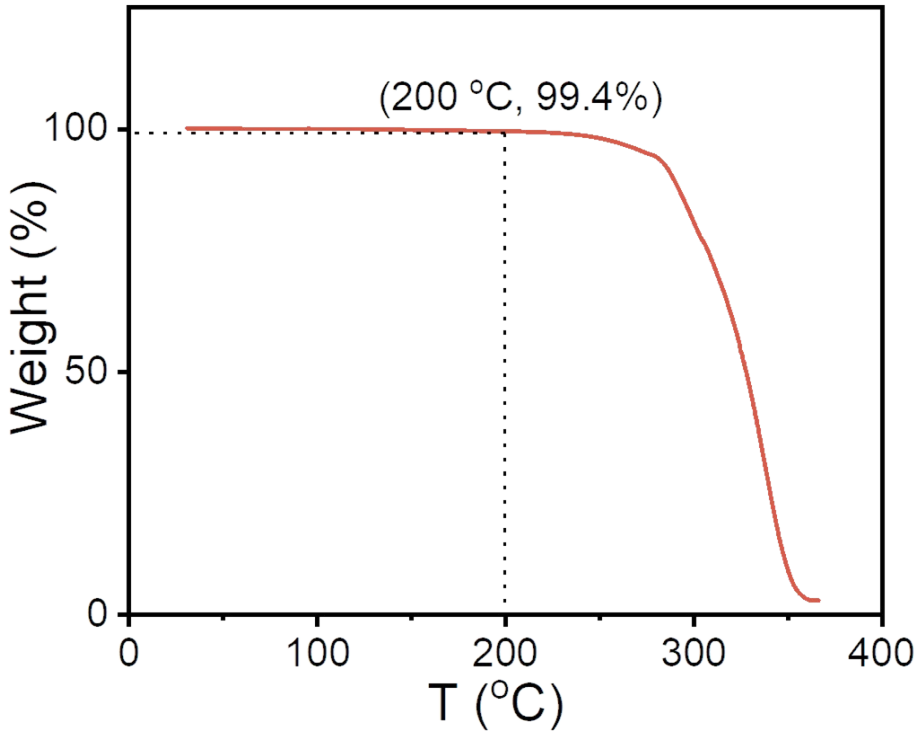

Figure S3 TGA curve of 6-HTPB

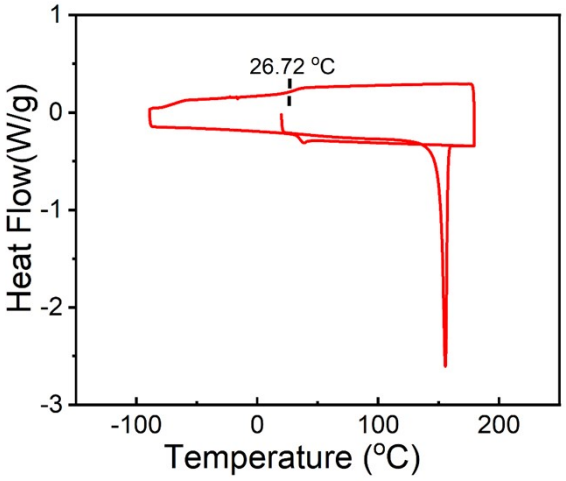

Figure S4 DSC measurements of 6-HTPB adhesive

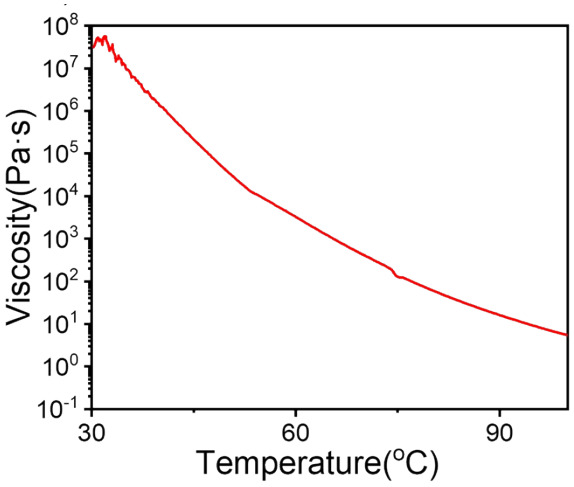

Figure S5 Temperature-dependent viscosity of 6-HTPB adhesive.

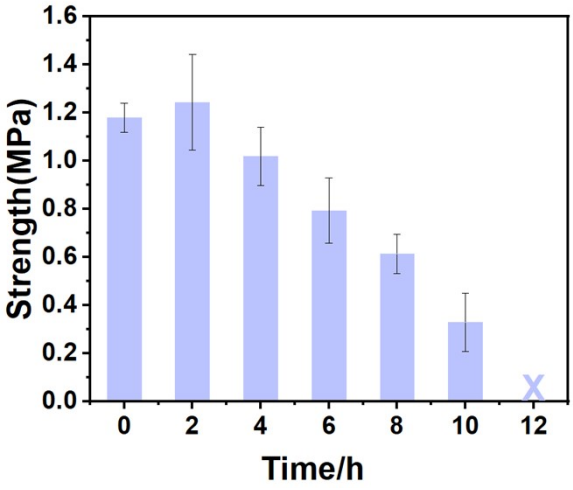

Figure S6 Time-dependent adhesive strength of 10-HTPB adhesive on PET in H_2O.

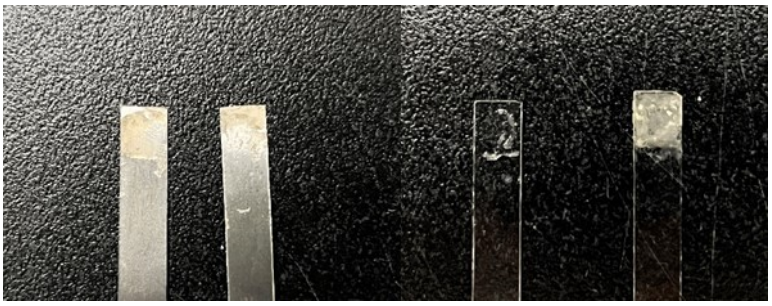

Figure S7 Photograph of cohesive failure on steel and interfacial failure on glass joined by 6-HTPB after testing at -40 ℃.

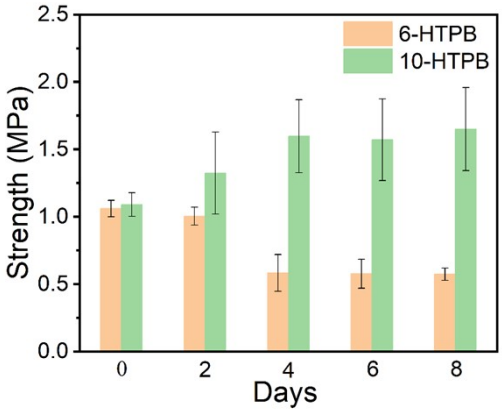

Figure S8 Time-dependent adhesive strengths of PET pairs adhered by 6-HTPB and 10-HTPB (stored at -18 ℃)

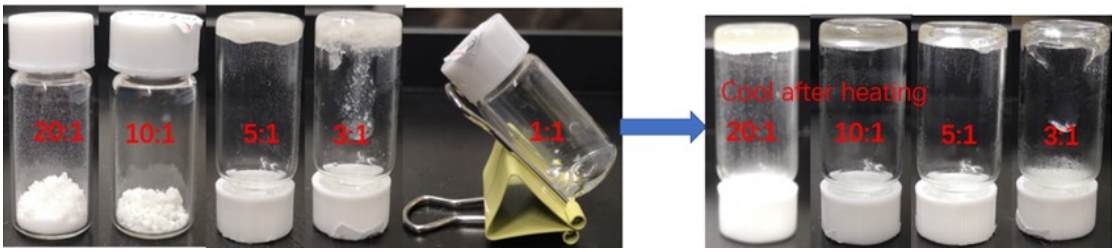

Figure S9 The process of obtained adhesion for $(6\text{-HTPB})_n\text{-EG}_m$ samples.

Figure S10 Macroscopic tests of $(6\text{-HTPB})_{20}\text{-EG}_1$ adhesive on steel at room temperature (17 cm^2; load of 50 kg). No separation or dislocation was observed.

Figure S11 Macroscopic tests of $(6\text{-HTPB})_{10}\text{-EG}_1$ on steel at room temperature (17 cm^2; load of 50 kg), a misplacement (5 mm) was observed.

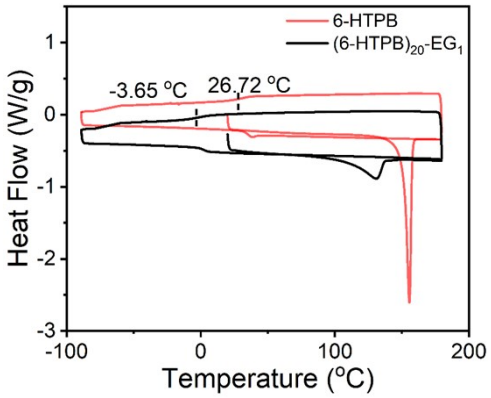

Figure S12 DSC measurements of 6-HTPB adhesive and $(6\text{-HTPB})_{20}\text{-EG}_1$ adhesive

Figure S13 The view of steel plates (adhered by 6-HTPB adhesive, load of 25 kg) which had been stored for 6th day at 18 °C.

Figure S14 The view of steel plates (adhered by $(6\text{-HTPB})_{20}\text{-EG}_1$ adhesive, load of 25 kg) which had been stored for 100th day at 18 °C.

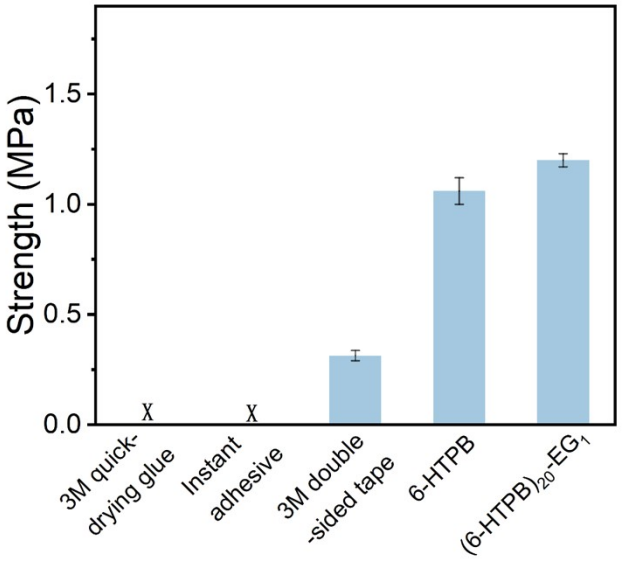

Figure S15 Comparison of adhesion strength (PET at 25 °C) of 6-HTPB and commercially available adhesives. *Instant adhesive is Aron Alpha aaPremier from Japan.

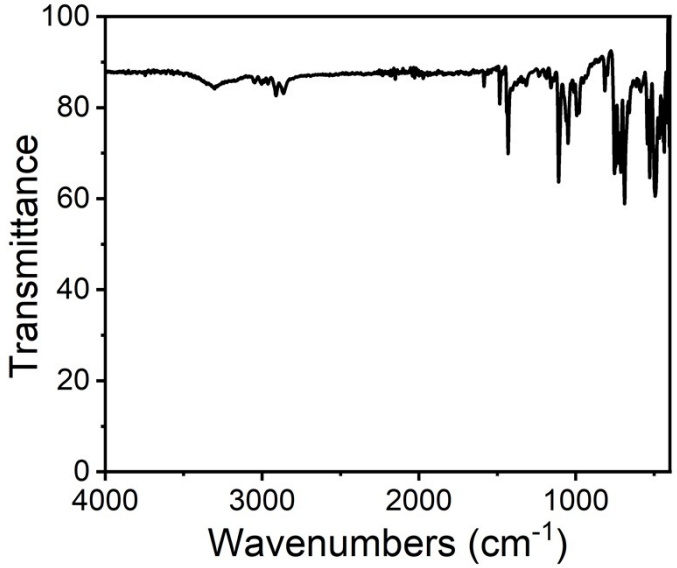

Figure S16 FT-IR of 2-HTPB.

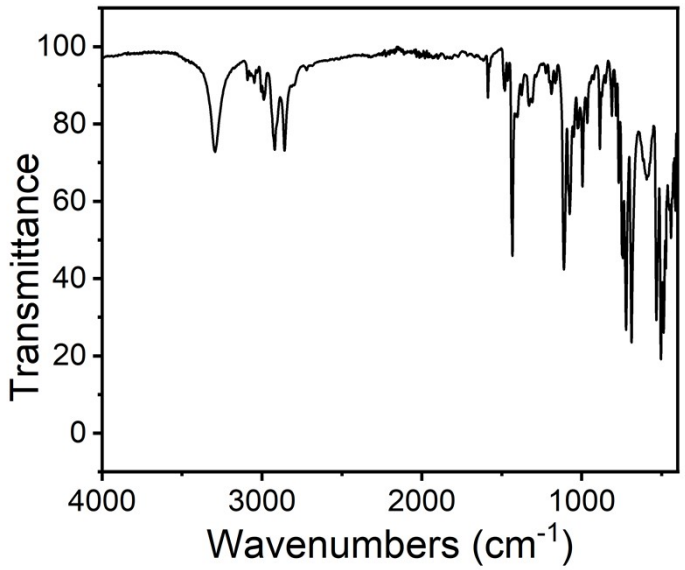

Figure S17 FT-IR of 6-HTPB.

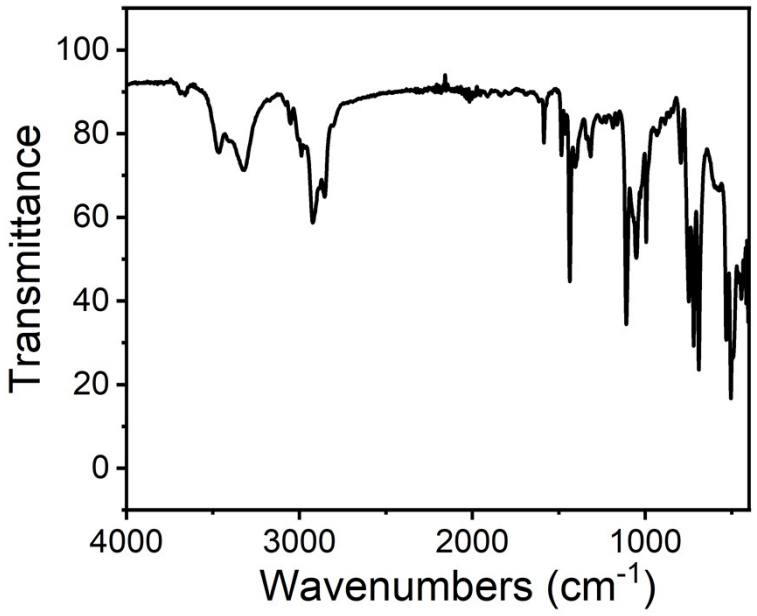

Figure S18 FT-IR of 8-HTPB.

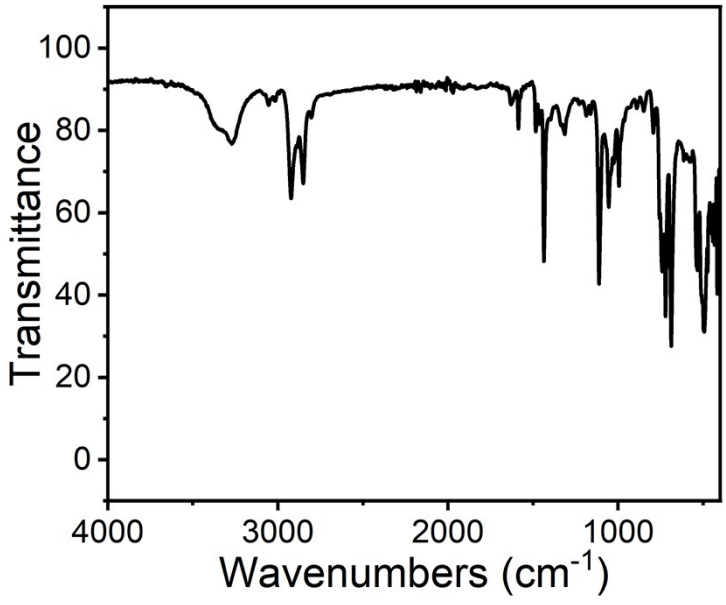

Figure S19 FT-IR of 10-HTPB.

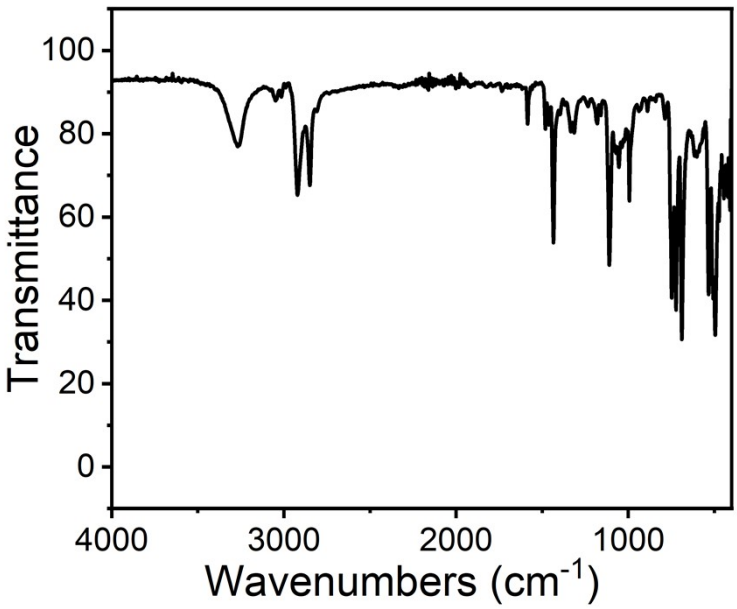

Figure S20 FT-IR of 12-HTPB.

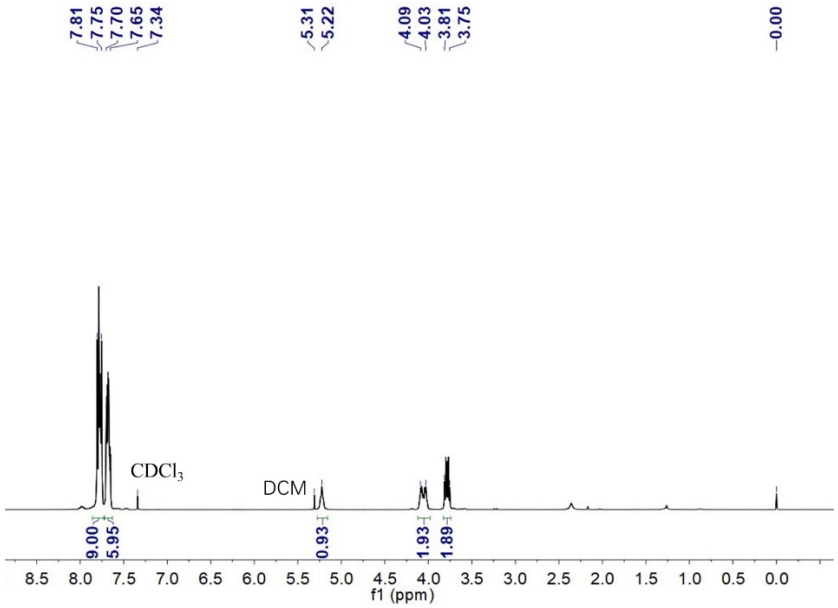

Figure S21 ^{1}H NMR of 2-HTPB.

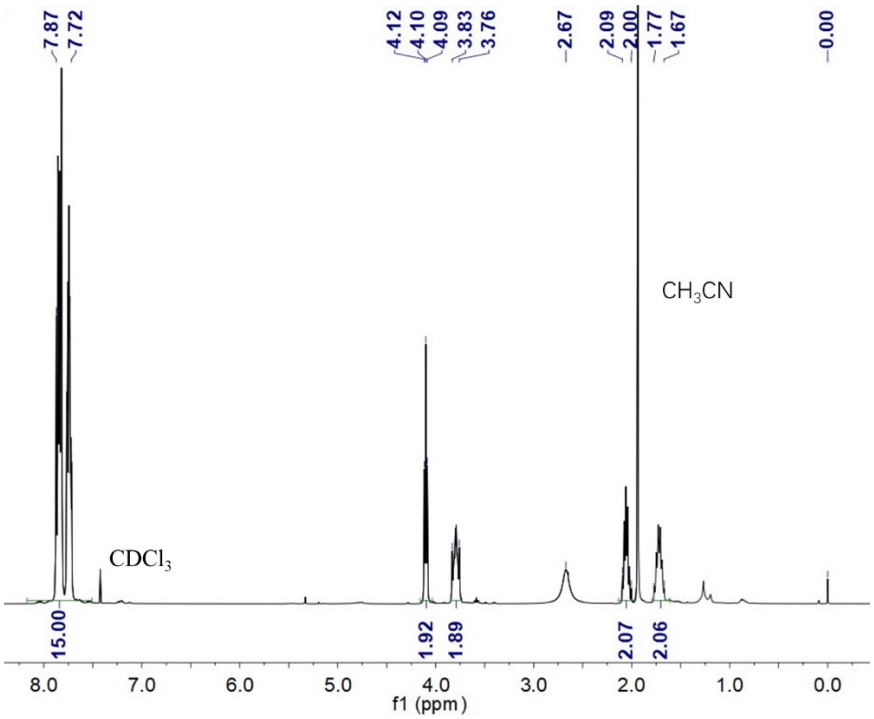

Figure S22 ^{1}H NMR of 4-HTPB.

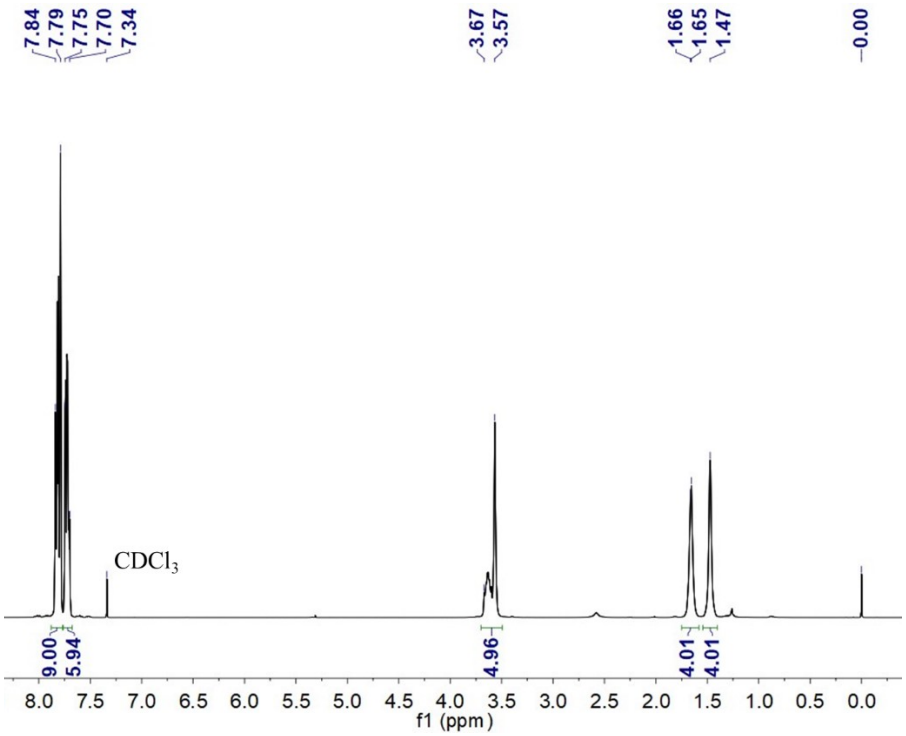

Figure S23 ^{1}H NMR of 6-HTPB

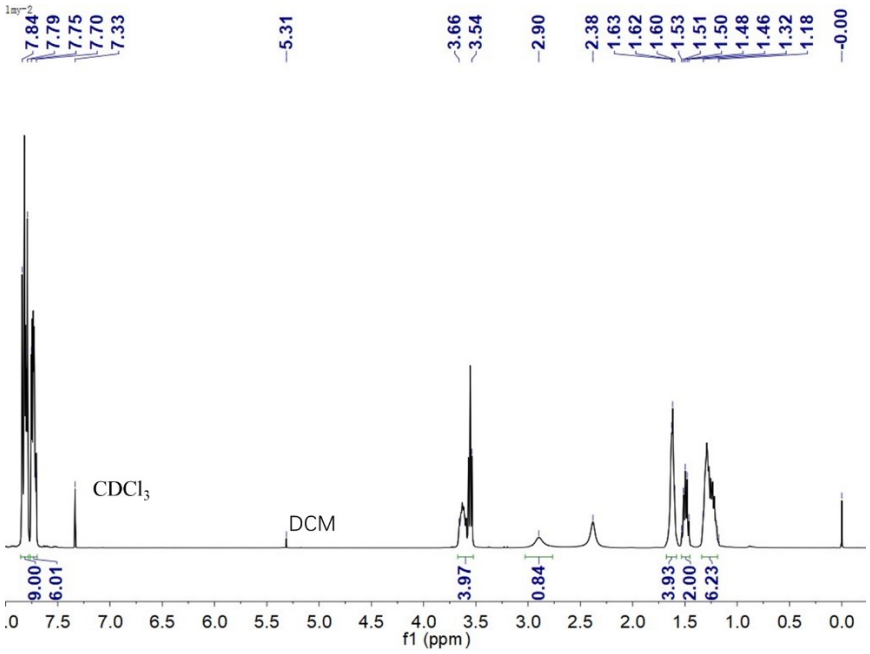

Figure S24 ^{1}H NMR of 8-HTPB

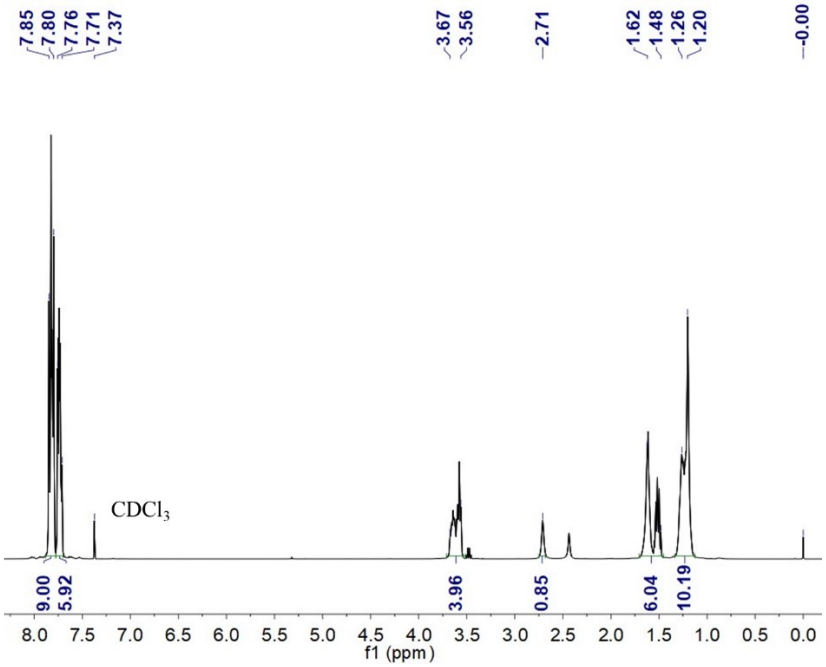

Figure S25 ^{1}H NMR of 10-HTPB

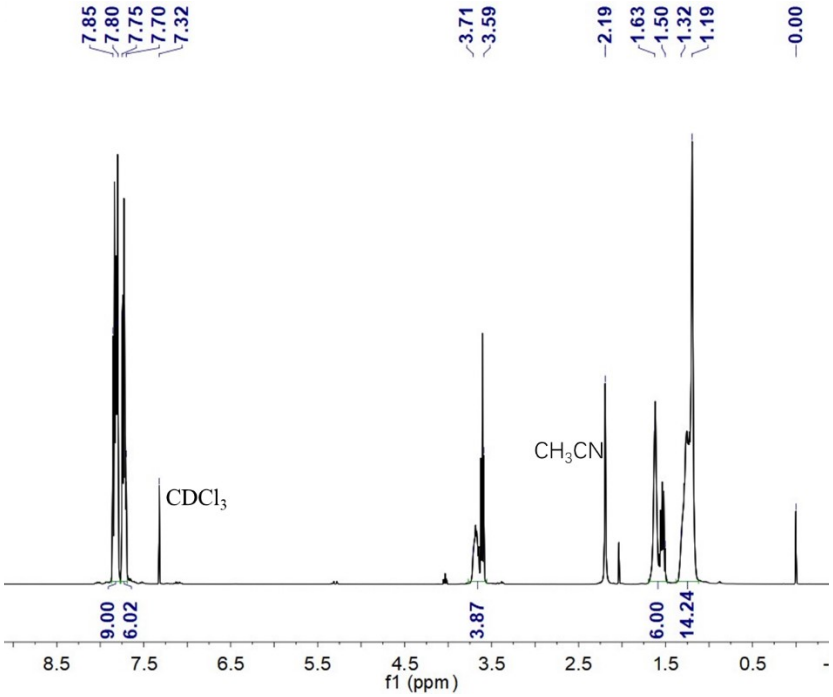

Figure S26 ^{1}H NMR of 12-HTPB

Table S1 Comparison of reported supermolecular adhesives in terms of their adhesive strength and durability.

Journals	Adhesive Strength/MPa	Durability/MPa
Angew. Chem. Int. Ed. Engl. **2022**, *61*, e202207425. (*)	22.3±2.1(Steel)	>19(steel, 30 days, -196℃)
ACS Appl. Mater. Interfaces. **2022**, *23*, 14.(*)	5.80(Glass)	N/A
Jacs. **2020**, *142*, 2579. (*)	2.00±0.5(Glass)	N/A
Sci. Adv. **2018**, *4*, eaat8192. (*)	2.50（Glass）	N/A
Angew. Chem. Int. Ed. Engl. **2021**, *60*, 5600. (*)	6.57±1.5(Steel)	N/A
ACS Appl. Mater. Interfaces. **2020**, *12*, 32054. (*)	PMMA (bearing 3.8 kg load)	N/A
ACS Appl. Mater. Interfaces.**2020**, *12*, 38700. (*)	1.52(Glass)	N/A
Chin Chem Lett. **2023**, *34*, 107830.	0.6(Glass)	0.38(PTFE, 46 days, -18 ℃)
Jacs. **2020**, *142*, 5371.	4.17±0.19(Steel)	N/A

Sci. Adv. **2017**, *3*, 15.	4.15(Glass)	N/A
J. Am. Chem. Soc. **2019**, *141*, 8058.	1.90(Glass)	N/A
Nat. Commun. **2016**, *7*, 10995.	1.20±0.2(Glass)	N/A
Jacs. **2019**, *141*, 7385.	1.34（Al）	N/A
Jacs. **2020**, *142*, 21522.	2.32(0℃, Steel)	>2.0(steel, 90 days, -18℃)
CCS Chem. **2020**, *2*, 1690.	4.409(Iron)	>1.0(Iron, a week, -80℃)
Angew. Chem. Int. Ed. **2013**, *52*, 3140.	1.10(silicone)	N/A
Mater Horiz **2022**, *9*, 1700.	0.57(Fe)	N/A
Angew. Chem. **2017**, *56*,8731.	0.038(Cu)	N/A
Adv. Funct. Mater. **2018**, *28*, 1800599.	0.014(polyether-ether-ketone)	N/A
Adv. Sci. **2022**, *9*, 2203182.	14.60(Fe)	N/A
Nat. Commun. **2022**, *13*, 5214.	10.5(Ceramic)	N/A
Chem. Commun. **2021**, *57*, 13317-13320.	4.46(Glass)	>1.5(steel, 15 days in DCM)
Our work(6-HTPB)	**2.77(Glass)**	**0.5(PET, 8 days at -18℃);**
Our work(10-HTPB)	**3.25(Glass)**	**with 500g load, >150 days**
Our work($(6\text{-HTPB})_{20}$-EG_1)	**2.68(Glass)**	**with 25kg load, >100 days**
		(stored at -18℃ for 24 h,
		and at 20℃ for 24 h,
		alternating cycles like this)

***polymeric systems**

Table S2 Interaction energy between adhesive and Fe (kcal/mol).

T/°C	E_{total}	E_{Fe}	$E_{adhesive}$	$E_{interfacial}$
-80	-159426	-156394	-1896	-1137
-40	-159133	-156233	-1730	-1170
-20	-158949	-156153	-1652	-1144
0	-158809	-156072	-1580	-1156
25	-158615	-155971	-1474	-1170
50	-158420	-155870	-1362	-1187

Table S3 Interaction energy between adhesive and glass (kcal/mol).

T/°C	E_{total}	E_{Glass}	$E_{adhesive}$	$E_{interfacial}$
-80	-36110	-34022	-1928	-160
-40	-35637	-33717	-1732	-188
-20	-35432	-33573	-1653	-204
0	-35206	-33426	-1584	-196
25	-34940	-33248	-1468	-223
50	-34620	-33071	-1370	-179

Table S4 Cohesive energy (kcal/mol) between two layers adhesives.

T/°C	E_{total}	$E_{adhesive*}$	$E_{adhesive}$	$E_{interfacial}$
-80	-3445	-1403	-1894	-148
0	-2903	-1148	-1556	-199

(The model configuration of adhesive* was the same as Fe/glass above.)

Table S5 Interaction energy of adhesive adhered between two steels (kcal/mol).

T/°C	E_{total}	E_{Fe}	$E_{adhesive}$	$E_{interfacial}$
-80	-316847	-312872	-1924	-2051
0	-315965	-311828	-1068	-2529

Table S6 Interaction energy of adhesive adhered between two glasses (kcal/mol).

T/°C	E_{total}	E_{glass}	$E_{adhesive}$	$E_{interfacial}$
-80	-70300	-67830	-1932	-538
0	-68817	-66630	-1637	-550

Information of supporting videos.

Video S1. Steel plates adhered by 6-HTPB at 25 ℃.

Video S2. Steel plates adhered by 6-HTPB in liquid nitrogen.

Video S3. Shear model of 6-HTPB and glass at 0 ℃ by molecular dynamics simulation.

Video S4. Shear model of 6-HTPB and glass at -80 ℃ by molecular dynamics simulation.

Video S5. Shear model of 6-HTPB and Fe at 0 ℃ by molecular dynamics simulation

Video S6. Shear model of 6-HTPB and Fe at -80 ℃ by molecular dynamics simulation.

Supplementary Reference

1. N. G. Yoon, H. Lee, S. Y. Kim, S. Hu, D. Kim, S. Yang, K. B. Hong, J. H. Lee, S. Kang, B. J. Kim, K. Myung, C. Lee and B. H. Kang, *J. Am. Chem. Soc.*, 2021, **143**, 19684-19696.
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