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Supplementary Information

Energetic Polymeric Network Prepared via a Solvent- and Catalyst-Free Thermal Cycloaddition of Azide-Bearing Polymer with Alkynes and Hydroxyl-isocyanate Addition Reactions

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1. Synthesis of dipolarophiles with terminal alkynes

Dipolarophile **1~2** and **3, 5** were synthesized and used, as described previously.¹

1,1,1-Tris[(propioyloxy)methyl]propane **4**

To a solution of 1,1,1-tris(hydroxymethyl)propane (20.0 g, 0.149 mol) and propiolic acid (41.8 g, 0.597 mol) in benzene (800 mL) was added *p*-Toluenesulfonic acid (*p*-TsOH, 3.00 g, 0.015 mol). The mixture was heated up to 100°C for 2 days using a Dean-Stark trap to eliminate H₂O. The resulting mixture was concentrated in vacuo and the residue was subjected to column chromatography with EtOAc-hexane (1/1) as the eluent to obtain the desired product in a 35% yield: ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, *J* = 7.6 Hz, 3H), 1.54 (q, *J* = 7.4 Hz, 2H), 2.91 (s, 3H), 4.16 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 7.2, 22.7, 40.6, 65.1, 74.0, 75.6, 152.1.

1,3,5-Tripropargyloxybenzene **6**

Propargyl bromide (53.5 g, 0.450 mol) was added to a solution of phloroglucinol (14.0 g, 0.111 mol) and K₂CO₃ (62.14 g, 0.450 mol) in DMF (200 mL). The resulting solution was stirred at room temperature for 4 days and then concentrated in a vacuum. The residue was extracted with CH₂Cl₂ (200 mL × 3) and H₂O. The organic layer was separated, dried with Na₂SO₄, and concentrated in a vacuum. The residue was subjected to column chromatography with EtOAc-hexanes (1/8) as an eluent to obtain the desired product in 65% yield: ¹H NMR (400 MHz, CDCl₃) δ 2.52 (t, *J* = 2.4 Hz, 3H), 4.63 (d, *J* = 2.3 Hz, 6H), 6.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 55.9, 75.7, 78.2, 95.4, 159.3.

2,4,6-Tripropargyloxy-1,3,5-triazine **7**

Propargyl alcohol (18.7 g, 0.334 mol) was added slowly to a solution of cyanuric chloride (15.4 g, 0.085 mol) and K₂CO₃ (36.4 g, 0.263 mol) in DMF (100 mL). The resulting solution was stirred at room temperature for 2 days and then concentrated in a vacuum. The residue was dissolved in CH₂Cl₂ (200 mL × 3) and H₂O. The organic layer was separated, washed with dilute 10% citric acid, and washed with

saturated brine. Then, it was dried with Na_2SO_4 and concentrated in a vacuum. To the residue was added Et_2O (200 mL) and the solid which was not dissolved in Et_2O was filtered off. The filtrate was concentrated in a vacuum to obtain the desired product in 71% yield: ^1H NMR (400 MHz, CDCl_3) δ 2.51 (t, $J = 2.4$ Hz, 3H), 5.02 (d, $J = 2.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.9, 56.9, 75.9, 172.4.

1,1,1-Tris[(propargyloxy)methyl]propane 8

Propargyl bromide (59.5 g, 0.500 mol) was added to a solution of 1,1,1-tris(hydroxymethyl)propane (13.4 g, 0.100 mol) and KOH (57.0 g, 1.02 mol) in DMSO (300 mL). The resulting solution was stirred at room temperature for 2 days. The reaction mixture was extracted with Et_2O (300 mL \times 3) and H_2O . The organic layer was separated, dried with Na_2SO_4 , and concentrated in a vacuum. The residue was subjected to column chromatography with EtOAc-hexanes (1/30) as an eluent to obtain the desired product in 58% yield: ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, $J = 7.7$ Hz, 3H), 1.41 (q, $J = 7.6$ Hz, 2H), 2.38 (t, $J = 2.4$ Hz, 3H), 3.39 (s, 6H), 4.10 (d, $J = 2.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 7.5, 22.7, 42.8, 58.6, 70.3, 74.0, 80.1.

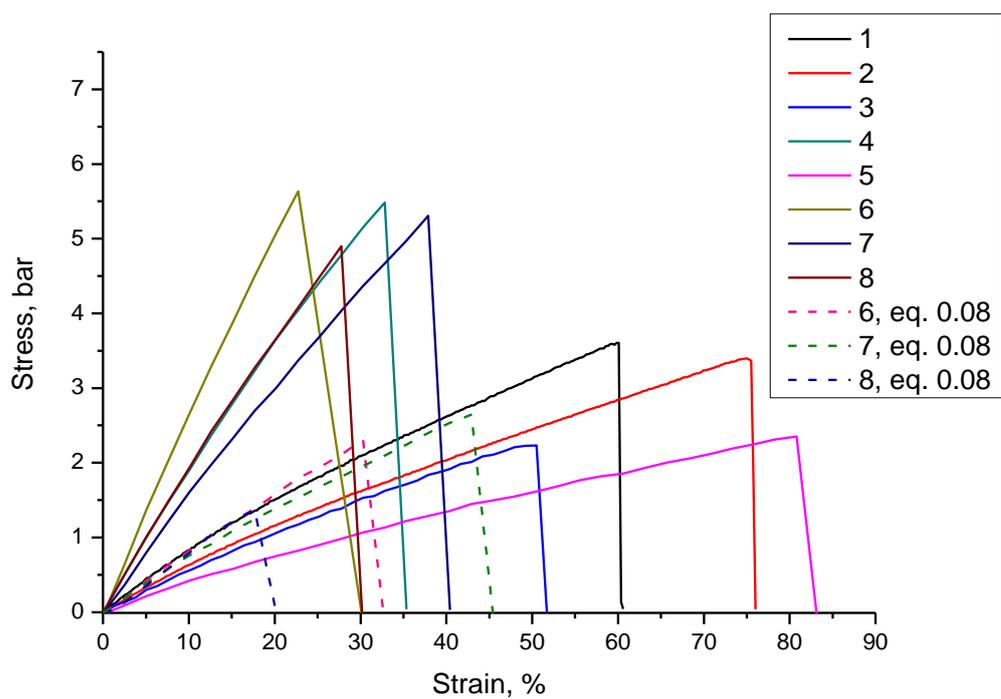
2. Stress-strain curves of the azide-bearing networks crosslinked via triazole moieties or both triazole and urethane moieties.

Fig. S1 Stress-strain curves of azide-bearing networks crosslinked via triazole moieties depending on the kind of dipolarophiles.

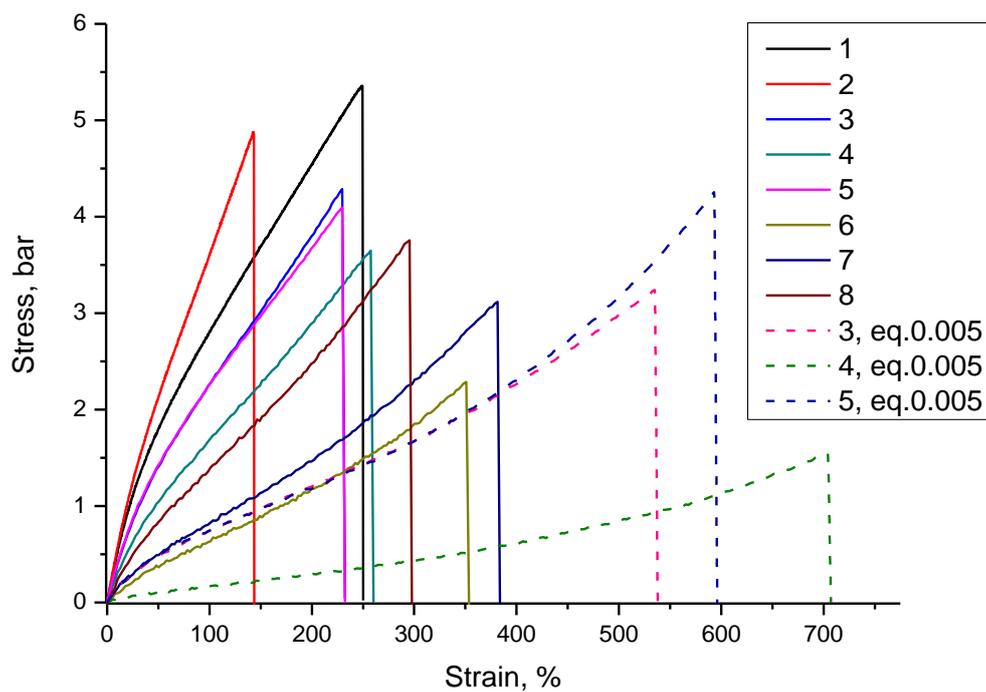


Fig. S2 Stress-strain curves of azide-bearing networks crosslinked via both triazole moieties and urethane moieties depending on the kind of dipolarophiles.

3. Gaussian calculations

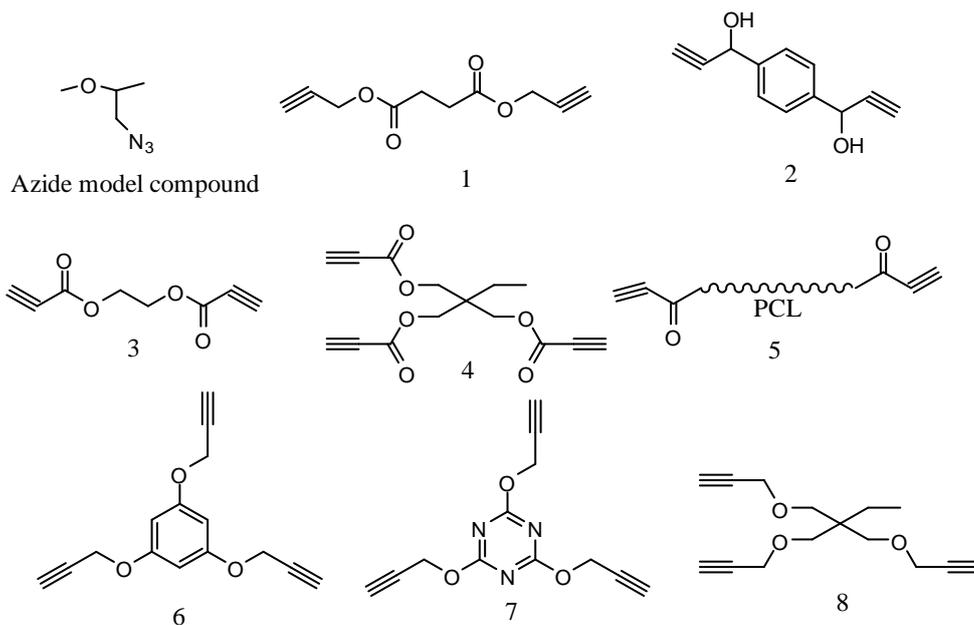
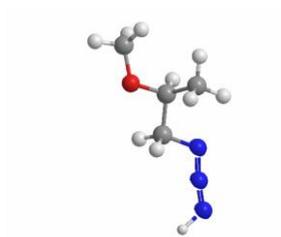


Table S1. Calculated Orbital Energies (B3LYP/6-31G*)(kcal/mol)

Dipole	HOMO	LUMO
Azide	-159.48	-17.28
Dipolarophile	HOMO	LUMO
1	-172.3	-1.36
2	-149.45	-9.19
3	-180.68	-33.23
4	-178.65	-36.53
6	-137.1	8.1
7	-171.54	-12.84
8	-157	-16.37

Azide model compound



Alpha occ. eigenvalues -- -0.25414

Alpha virt. eigenvalues -- -0.02754 0.01176 0.08526 0.09895 0.12564

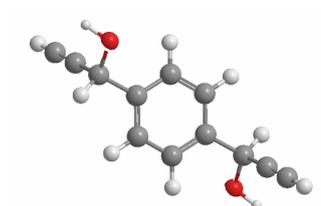
Dipolarophile 1



Alpha occ. eigenvalues -- -0.27457

Alpha virt. eigenvalues -- -0.00217 0.00828 0.01910 0.02259 0.04577

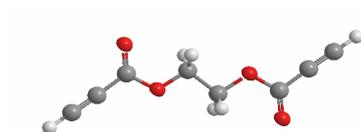
Dipolarophile 2



Alpha occ. eigenvalues -- -0.26868 -0.26791 -0.24776 -0.23816

Alpha virt. eigenvalues -- -0.01465 -0.00169 0.03006 0.04290 0.04750

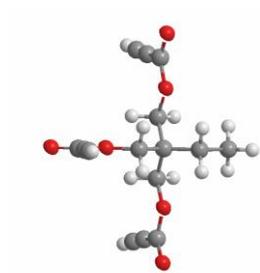
Dipolarophile 3



Alpha occ. eigenvalues -- -0.30564 -0.28846 -0.28793

Alpha virt. eigenvalues -- -0.05295 -0.05097 0.01899 0.02633 0.08864

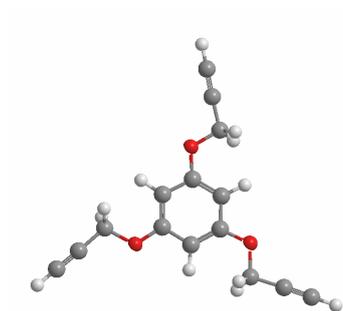
Dipolarophile 4



Alpha occ. eigenvalues -- -0.28470

Alpha virt. eigenvalues -- -0.05821 -0.05776 -0.05428 0.01362 0.01499

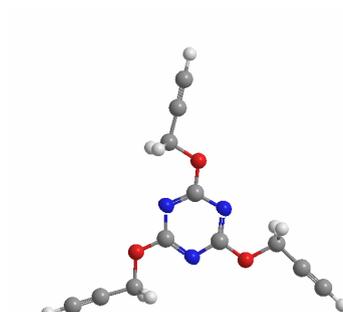
Dipolarophile 6



Alpha occ. eigenvalues -- -0.26917 -0.21851 -0.21849

Alpha virt. eigenvalues -- 0.01291 0.01293 0.02409 0.02650 0.02651

Dipolarophile 7



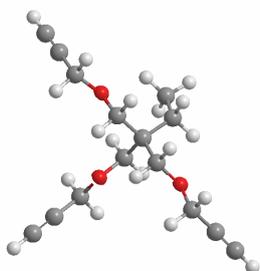
Alpha occ. eigenvalues -- -0.27566 -0.27339 -0.27337

Alpha virt. eigenvalues -- -0.02046 -0.02045 0.01972 0.02129 0.02132

Journal Name

ARTICLE

Dipolarophile 8



Alpha occ. eigenvalues -- -0.25728 -0.25019

Alpha virt. eigenvalues -- 0.02609 0.03430 0.03508 0.05468 0.05578

1. References

- 1 B.S. Min, Y. C. Park and J.C. Yoo, *Propellants, Explos. Pyrotech.*, 2012, **37**, 59; D. H. Lee, K. T. Kim, Y. Jang, S. Lee, H. B. Jeon, H. J. Paik, B. S. Min and W. Kim, *J. App. Polym. Sci.*, 2014, **131**, 40594.