Electronic Supplementary Material (ESI) for Soft Matter

Tuning Heterogeneous Poly(dopamine) Structures and Mechanics: *In silico* Covalent Cross-linking and Thin Film Nanoindentation

Shangchao Lin[1], Chun-Teh Chen[1], Igor Bdikin[2,3], Vincent Ball[4,5], José Grácio[2,3], Markus J. Buehler[1,*]

[1] Laboratory for Atomistic and Molecular Mechanics, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

[2] Center for Mechanical Technology and Automation, Department of Mechanical Engineering, University of Aveiro, Campus Universitário Santiago, 3810-193 Aveiro, Portugal

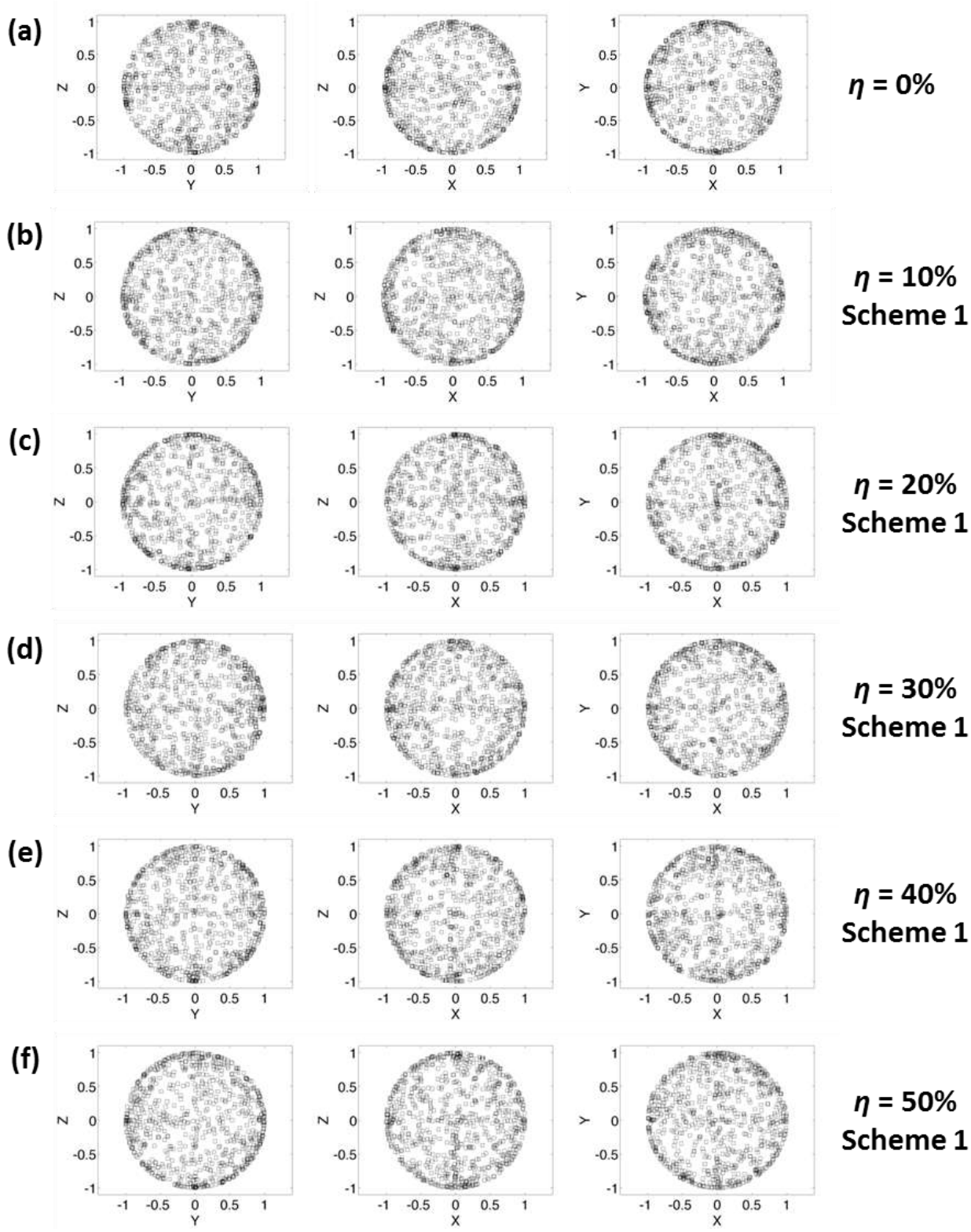
[3] Aveiro Institute of Nanotechnology, University of Aveiro, 3810-193 Aveiro, Portugal

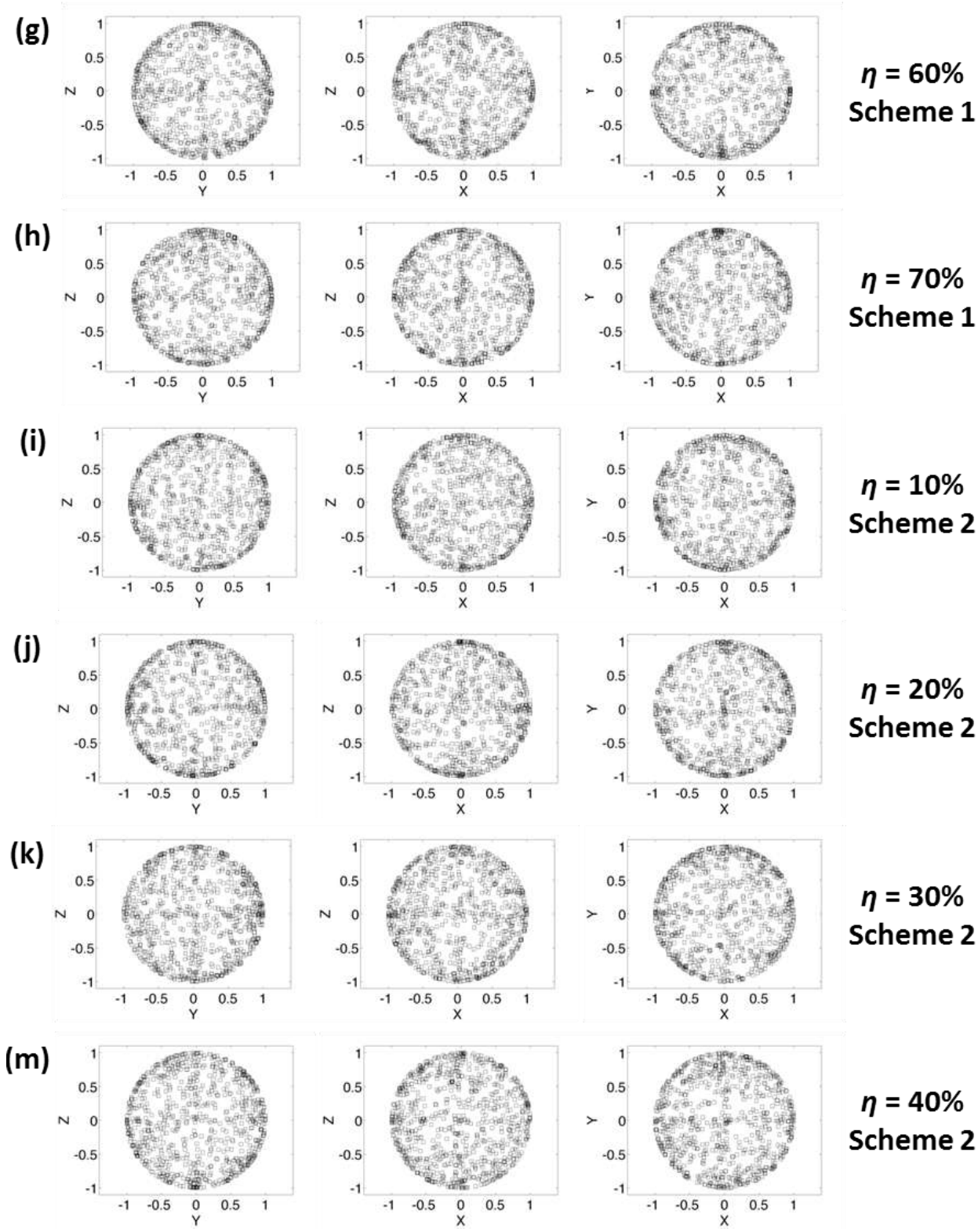
[4] Department for Advanced Materials and Structures, Centre de Recherche Public Henri Tudor, 5 rue Bommel, L-4940 Hautcharage, Luxembourg

[5] Faculté de Chirurgie dentaire, Université de Strasbourg, 1 Place de l'Hôpital, 67000 Strasbourg, France and Unité INSERM 977, 11 rue Humann, 67085 Strasbourg Cédex, France

*Corresponding Author: E-mail: mbuehler@mit.edu

Supporting Information





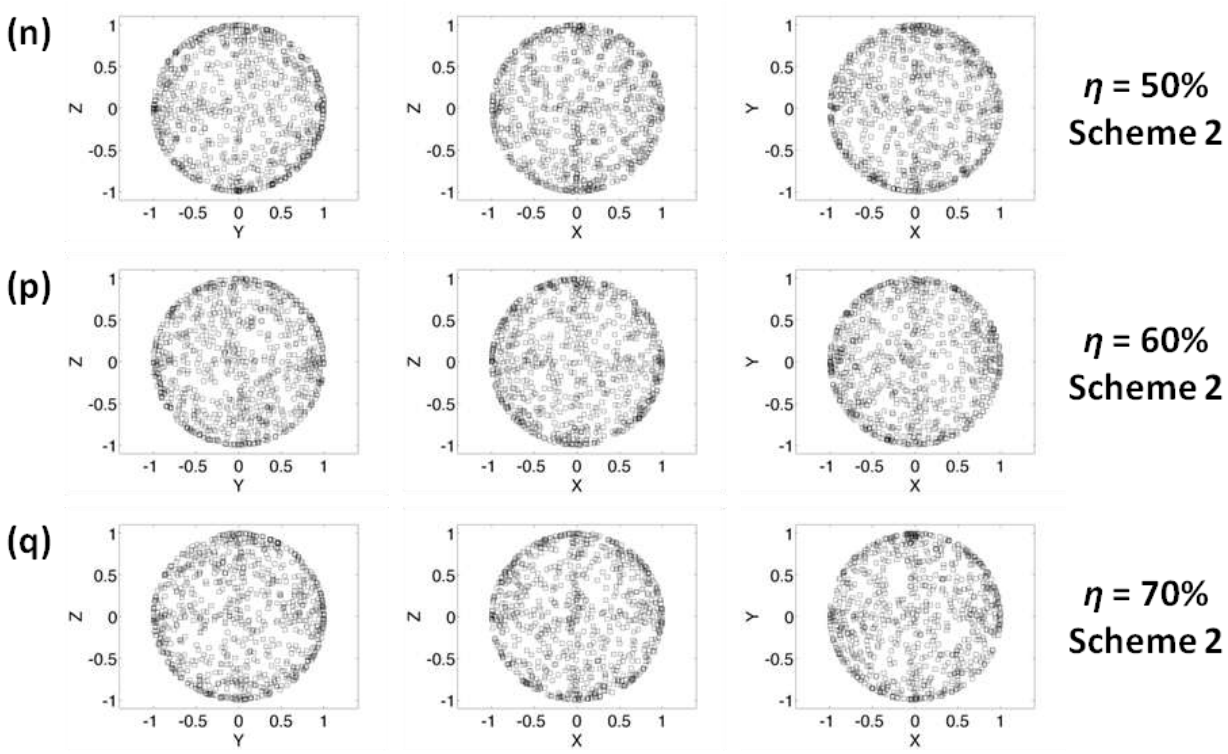


Figure S1. X, Y, and Z components of the orientation vectors of the monomeric DHI units for: **(a)** the pure DHI aggregate system (η = 0%), and **(b)-(q)** the cross-linked DHI systems at the various η values considered (10% ~ 70%) under cross-linking **Schemes 1 and 2**.

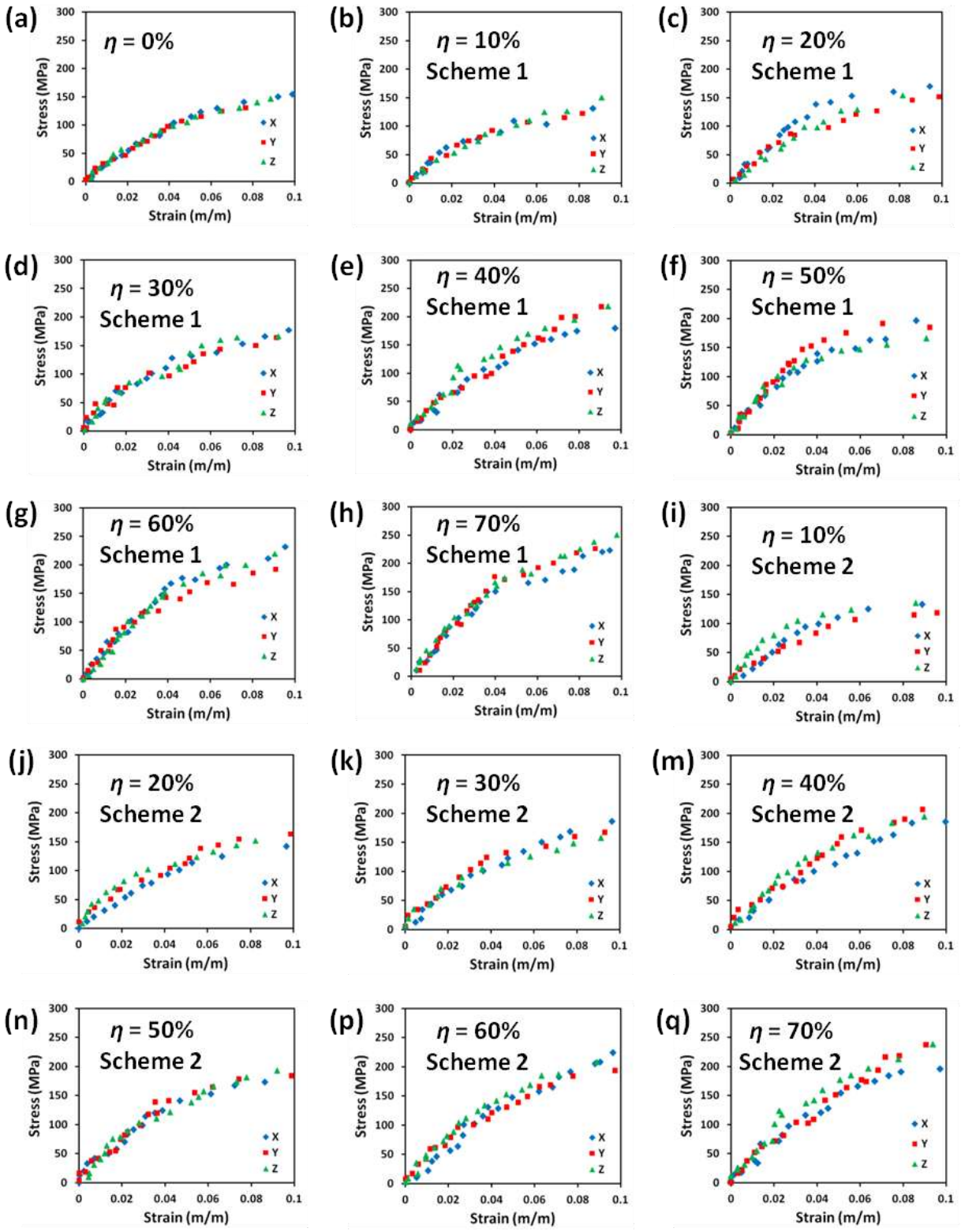


Figure S2. The stress-strain curves from the mechanical tensile test *in silico* for: **(a)** the pure DHI aggregate system, and **(b)-(q)** the cross-linked DHI systems at the various η values considered (10% ~70%) under cross-linking **Schemes 1 and 2**.

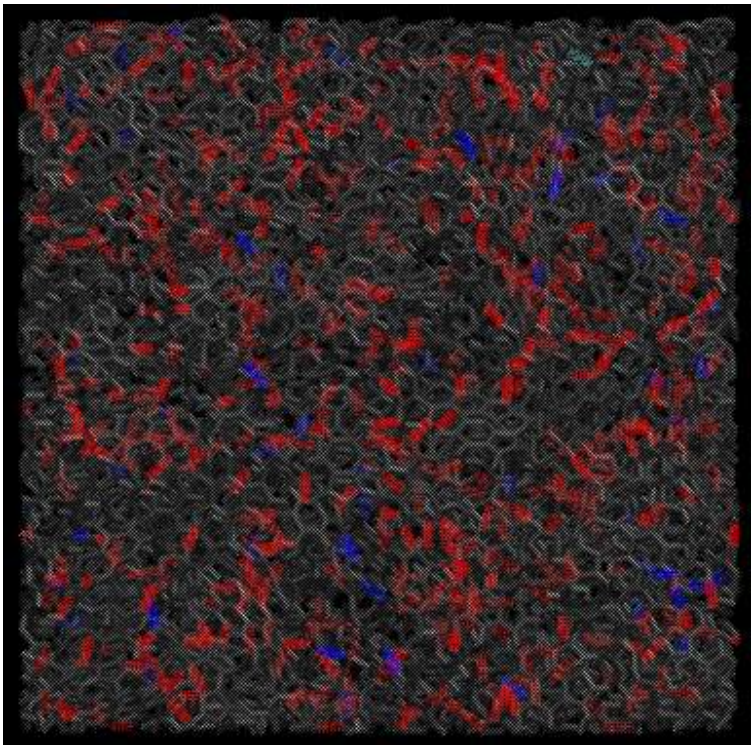


Figure S3. Simulation snapshot of the pure DHI aggregate system highlighting hydrogen bonds in red (O−H---O) and blue (N−H---N), while the bulk DHI melt is shown in grey.

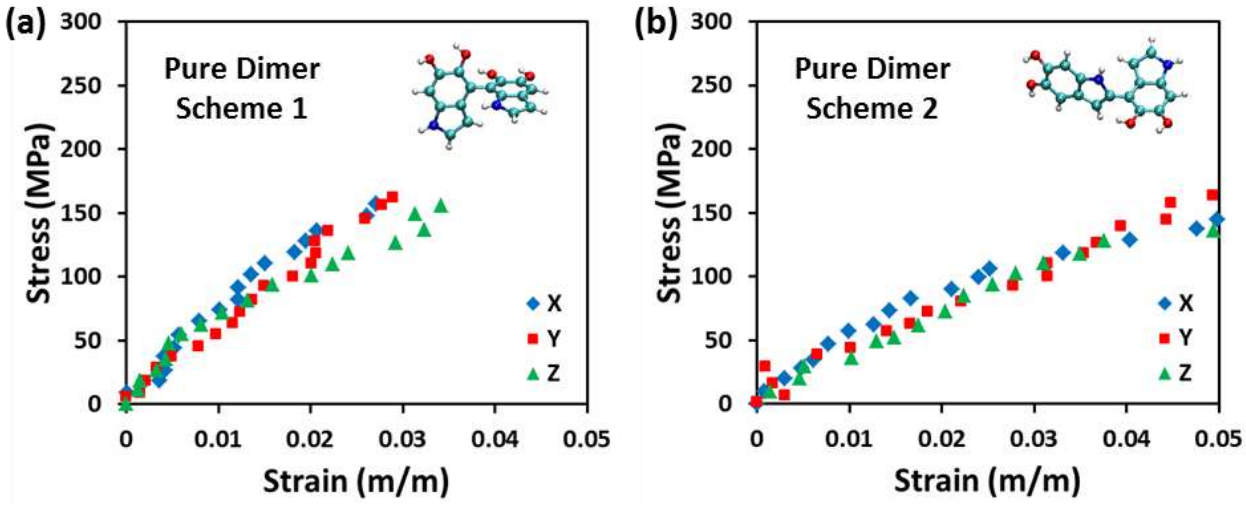


Figure S4. The stress-strain curves from the mechanical tensile test *in silico* for pure dimer systems formed under cross-linking **Schemes 1 (a) and 2 (b)**.