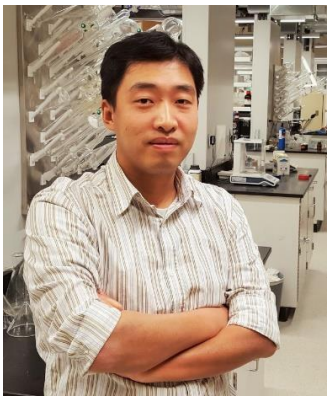
CANAL: Efficient and Versatile Annulation to Build Diverse (Macro)Molecular Ladders as Microporous Membranes and Antiaromatic Molecules

In the pursuit of unusual ladder-shaped (macro)molecular structures with unique properties, we developed Catalytic Arene-Norbornene AnnuLation (CANAL) to synthesize rigid ladder polymers from readily available norbornenes and aryl bromides. Efficient CANAL polymerization produced ladder polymers with molecular weights up to 1 MDa, various functionalities, and contorted conformations, despite the formed strained ring in each repeat unit. These ladder polymers exhibited high surface areas, high microporosity (pore width < 1 nm), and surprisingly high thermal stability up to 400 °C without detectable T_g. Membranes were fabricated as promising materials for gas separations and understanding gas transport in glassy polymers. Switching the substrates from norbornenes to oxanorbornenes, CANAL also allowed us to synthesize unusual π-systems containing antiaromatic cyclobutadienoids from readily accessible building blocks. These extended conjugated ladder molecules exhibit tunable degrees of antiaromaticity, which in turn affect their bonding, frontier orbital levels, and optoelectronic properties.



Yan Xia received his undergraduate degree from Peking University ('02) and MSc from McMaster University ('05). He then obtained his PhD in Chemistry from Caltech in 2010, working on cyclic and bottlebrush polymers. After working at Dow Chemical and postdoc at MIT, he joined the chemistry faculty at Stanford in the summer of 2013. His research interest lies in the design, synthesis, and manipulation of organic materials and polymers, driven by new synthetic capability, rational molecular design, and curiosity. He is a recipient of Terman Fellowship (2014), ARO Young Investigator Award (2015), 3M Non-Tenured Faculty Award (2016), NSF CAREER Award (2016), Thieme Chemistry Journals Award (2017), and Cottrell Scholar Award (2017).