

Organic 2D crystal synthesis on water

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Polymerizing in two orthogonal direction with long range order toward freestanding crystalline film offers rationally synthesizable platform for molecular functional two dimensional (2D) material design. dynamic covalent chemistry opened the way to stitch building blocks into crystalline structure [1,2], however conventional solvothermal synthetic methodology is limiting the crystal size and the product morphology as powder. Water surface provides the clue how to propagate the polymerization not in bulk system but in space which offers two orthogonal direction [3]. Also "on water" synthesis revealed kinetically favorable conditions via catalyzing reaction of interfacial water molecules [4]. Here we combine dynamic covalent chemistry and on water synthesis as a glide path to achieve the large organic 2D crystal with bottom up synthesis. We demonstrate structurally well-defined porphyrin-backed four different chemistry such as boronate ester, imine, imide and amide bond. These resulting 2D films indicates the way to take one step nearer to the infinitely extended, structurally perfect, covalent network on flatland

References

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- [2] F. Uribe-Romo et al., *J. AM. CHEM. SOC.*, 131 (2009) 4570–4571
- [3] H. Sahabudeen et al., *Nature Commun.*, 7 (2016) 13461

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Figures

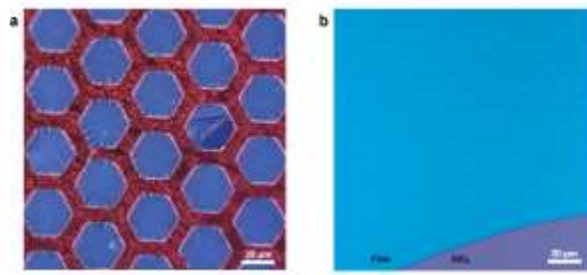


Figure 1: Optical microscopy images of synthesized 2D polymer film **a.** suspended over a copper grid and **b.** deposited on 300 nm SiO₂/Si.



Figure 2: **a.** Chemical structure of representative two 2D polymer. **b.** High resolution TEM image of P2D(PBB) film that shows a tetragonal pore packing. **c.** Monocrystalline square unit cell electron-diffraction pattern.