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Electronic Properties of Metal-Phthalocyanine-Based 2D Conjugated Covalent Organic Frameworks

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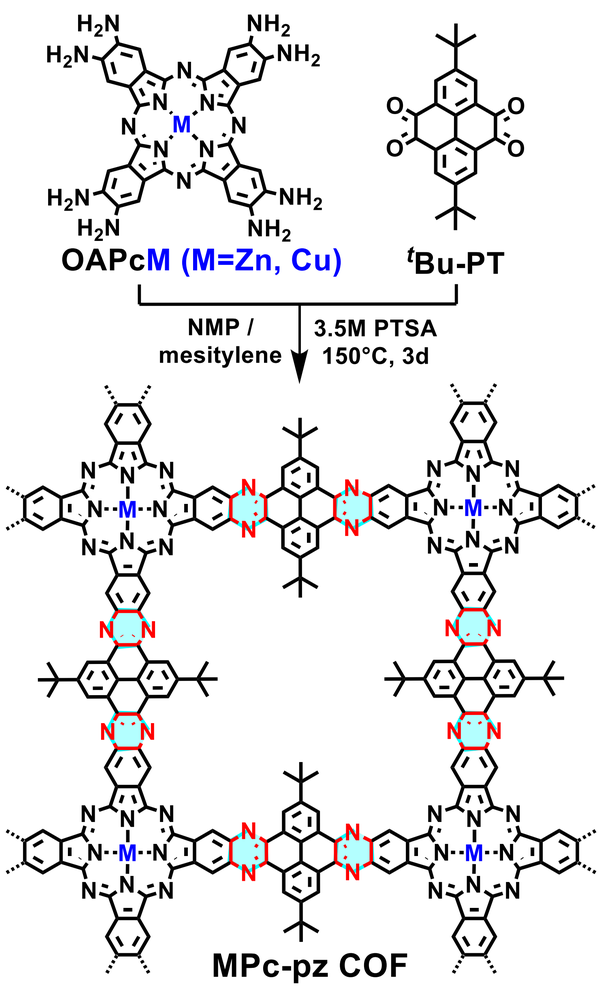
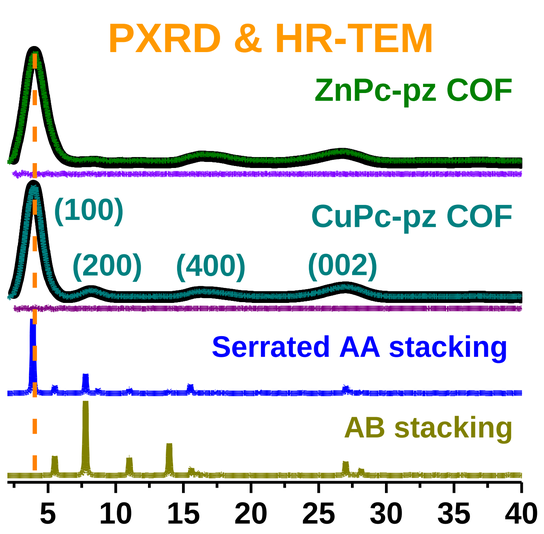
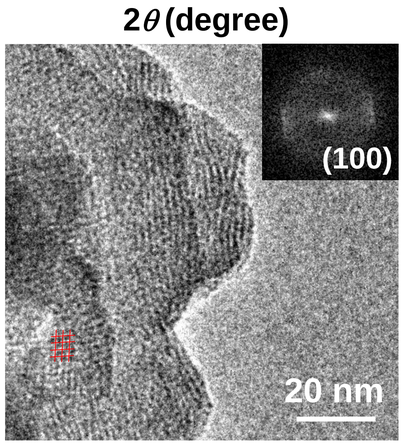
2D conjugated covalent organic frameworks (2D *c*-COFs) are emerging as a unique class of semiconducting 2D framework materials for (opto)electronics and energy storage and conversion.[1] However, understanding the intricate interplay between their chemical structures and electronic properties remains elusive. We have demonstrated two metal−phthalocyanine-based pyrazine-linked 2D *c*-COFs (MPc-pz, M = Cu or Zn) as *p*-type semiconductors with optical band gap of ~1.2 eV and charge mobility up to ~5 $cm^2/(Vs)$.[2] Hall effect measurements and terahertz spectroscopy in combination with density functional theory calculations confirm that varying metal center from Cu to Zn has a negligible effect on the charge transport behaviors. After reversible *p*-type doping with I_2, the doping-defined 2D *c*-COF displays enhanced conductivity by 3 orders of magnitude.[3] Remarkably, charge mobility also increased upon doping, which can be traced to increased scattering time for free charge carriers, indicating that scattering mechanisms limiting the mobility are mitigated by doping. Our works provide a rational approach to ascertain structure-electronic property relationships in COFs, and highlight the potential of 2D *c*-COFs to display high conductivities and mobilities.

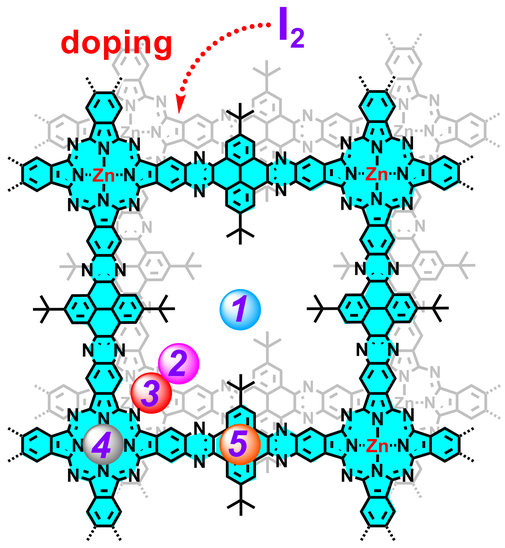
Synthesis and crystal structure of MPc-pz COF

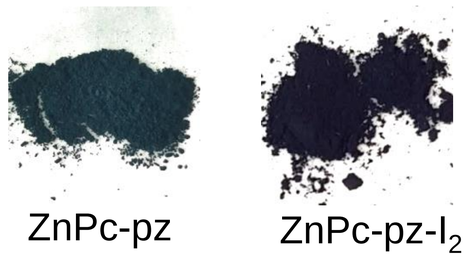


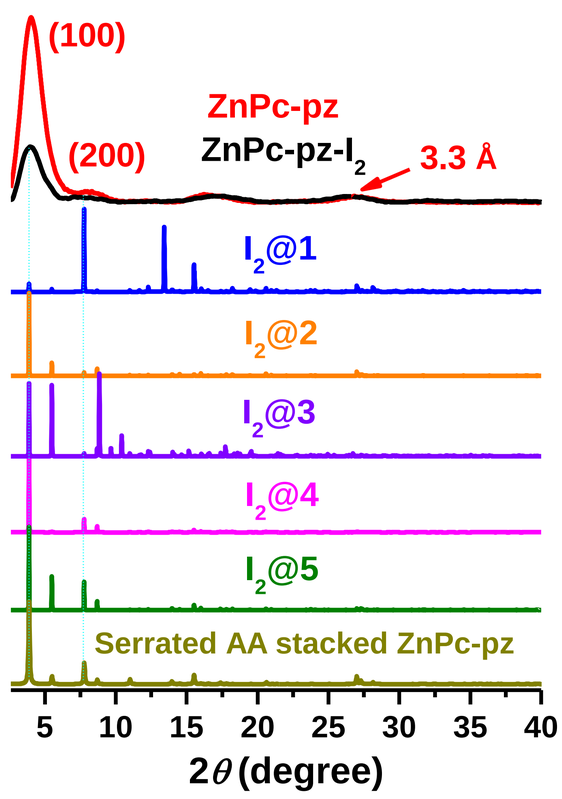




p-type doping of ZnPc-pz COF





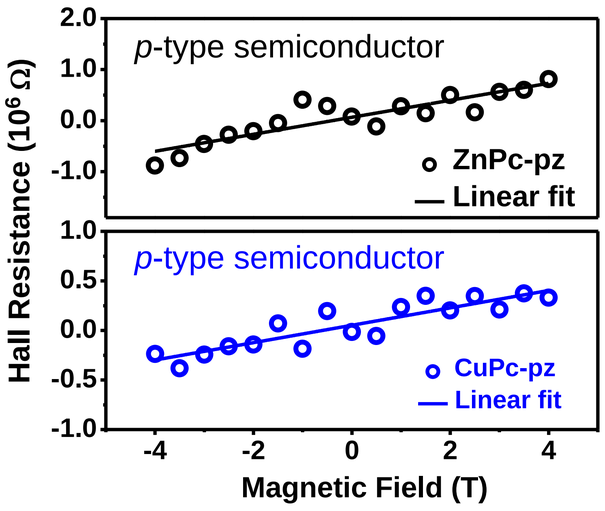


~9 wt% I_2 adsorbed in the framework (I_2@2).

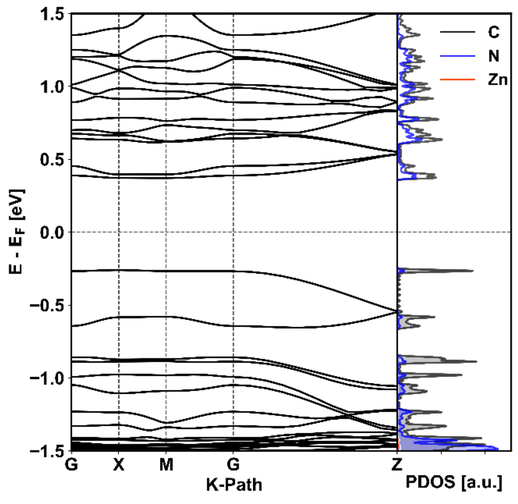
Reversible doping-dedoping without chemical reaction.

Charge transport of MPc-pz COF

Hall effect (n, μ, σ)



Band structure (m^*)



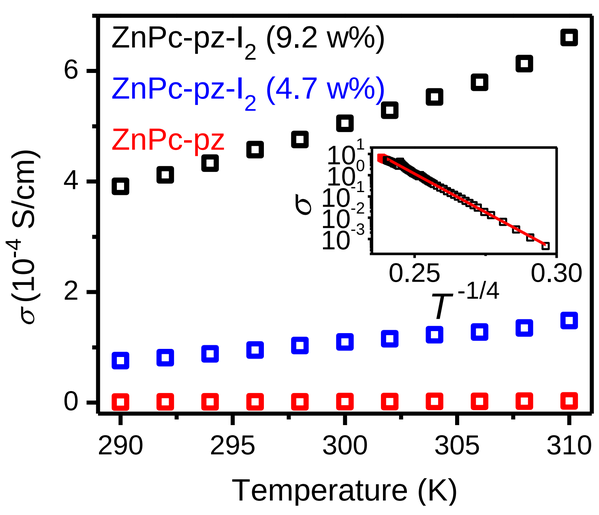
The metal center (Cu/Zn) has a negligible effect:

σ=~5×10^{-7} S/cm, n=~10^{12} cm^{-3}, τ=~30 fs, m_h*=~2.3 m_0.

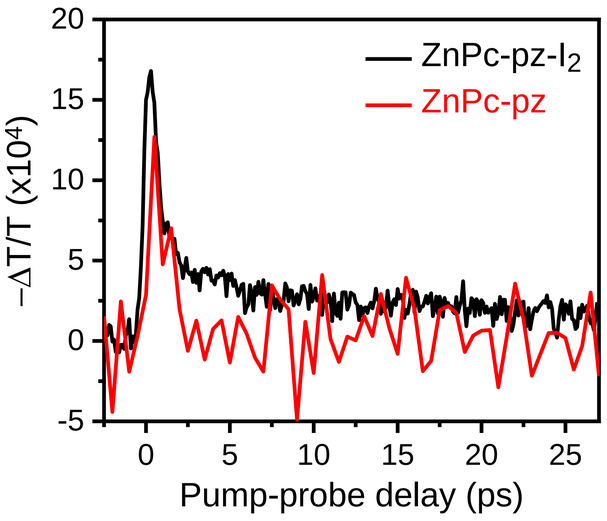
Anisotropic charge transport. μ=~4.8 cm^2/Vs (M=Zn).

Charge transport of doped ZnPc-pz COF

Electrical conductivity (σ)



Teraherz spectroscopy (τ, μ)



Formation of electron donor (ZnPc-pz)−acceptor (I_2) pairs:

σ=~3×10^{-4} S/cm, n=~10^{14} cm^{-3}, τ=~66 fs, m_h*=~2.1 m_0.

μ=~22 cm^2/Vs (M=Zn).

CONTACT PERSON

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REFERENCES

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[2] M. Wang, M. Ballabio, M. Wang, H.-H. Lin, B. P. Biswal, X. Han, S. Paasch, E. Brunner, P. Liu, M. Chen, M. Bonn, T. Heine, S. Zhou, E. Canovas, R. Dong, X. Feng, *J. Am. Chem. Soc.*, 141 (2019) 16810–16816.

[3] M. Wang, M. Wang, H.-H. Lin, M. Ballabio, H. Zhong, M. Bonn, S. Zhou, T. Heine, E. Cánovas, R. Dong, X. Feng, *J. Am. Chem. Soc.*, 142 (2020), 21622−21627.

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