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RPPR Final Report

as of 06-Apr-2023

Agency Code: 21XD

Proposal Number: 69029SM

Agreement Number: W911NF-17-1-0126

INVESTIGATOR(S):

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Report Date: 14-Oct-2021

Date Received: 29-Mar-2023

Final Report for Period Beginning 15-Mar-2017 and Ending 14-Jul-2021

Title: 2D Conjugated Polymers from Stable Free Radical Building Blocks

Begin Performance Period: 15-Mar-2017

End Performance Period: 14-Jul-2021

Report Term: 0-Other

Submitted By: Dmitrii Perepichka

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 2

STEM Participants: 4

Major Goals: The goal of this project is to develop 2D organic polymers with unique optoelectronic and magnetic properties resulting from 2D electron confinement of unpaired electrons. Achieving this goal was envisaged through pursuing four interrelated objectives:

- (i) synthesis of reactive multidentate monomers;
- (ii) establishing 2D polymerization under dynamic equilibrium conditions and structural characterization of the resulting layered materials;
- (iii) preparation of individual 2D polymer sheets by (a) exfoliation of the bulk materials and (b) surface templated synthesis;
- (iv) characterization of electrical and magnetic properties of 2D polymers.

Accomplishments: 1) Three types of reactive monomer based on TANG (trioxazatriangulene), TANGO (trioxazatriangulene), PTM (perchlorinated triphenylmethyl radical) have been designed and synthesized. Their polymerization using dynamic solvothermal polymerization, surface template polymerization and selective thermolysis was demonstrated.

2) 2D polymers with neutral PTM radical (see ref. 11 in Dissemination) and TANG radical-cation (see ref. 5 in Dissemination) have been synthesized. The effect of unpaired electrons interactions on their electrical and magnetic properties have been experimentally characterized (with support of Density Functional Theory calculations).

3) Two new dynamic covalent polymerization reactions for synthesis of conjugated (aldol condensation, see ref. 2 in Dissemination) and non-conjugated (boronate ester metathesis, see ref. 10 in Disseminations) 2D polymers have been developed.

4) Formation of individual 2D polymer (several hundred nm size) have been accomplished by exfoliation of layered materials (synthesized in solvothermal synthesis) and by on-surface polymerization (with TANG/TANGO monomers). In the latter case, angle-resolved X-ray photoelectron spectroscopy was used to prove the existence of Dirac cone intersection resembling that in graphene, in organic 2D polymers (ref. 6 in Dissemination)

5) Unusual and efficient luminescence was discovered in TANGO (triplet emission/phosphorescence, ref. 4 in Dissemination) and PTM monomer (doublet emission, ref. 8 in Dissemination). These properties will be further explored in details in resulting 2D polymers in the follow-up project.

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Training Opportunities: This project has provided training opportunities for 6 post-doctoral fellows, 2 PhD students and 2 undergraduate research trainees. Most of these trainees have received competitive fellowships/awards, published their research in peer-reviewed journals.

Post-doctoral researchers:

Dr. Yoko Otsuka, 04/2018-08/2018, worked on dynamic covalent polymerization and synthesis of PTM monomers. Co-authored 1 paper in this project (ref. 11). Recruited as a research engineer at CEA-LETI (France)

Dr. Thaksen Jadhav, 05/2018-08/2019, FQRNT fellowship (05/2018-05/2019); worked on synthesis on developing developed Aldohol dynamic polymerization for preparation of COF. Also applied this reaction to polymerization of an open-shell monomer (perchlorotriphenylmethyl-tricarbaldehyde). Co-authored 3 papers in this project (refs. 2, 7, 11). Obtained FRQNT post-doctoral scholarship. Now post-doctoral researcher at KAUST.

Dr. Yuan Fang, 05/2018-01/2021, works on interfacial synthesis of 2D polymers. Co-authored 4 papers in this project (refs. 3, 4, 5, 7). Obtained NSERC post-doctoral fellowship. Recruited as Full Professor at U Suzhou (China).

Dr. Lakshmi Vellanki, 05/2018-09/2019 (now Assistant Prof at NIT, India); worked on synthesis and characterization of triangulene-based COF. Co-authored 1 paper in this project (refs. 5, 7). Obtained FRQNT visiting scholarship. Recruited as an Assistant Professor at NIT-Karnataka (India)

Dr. Kiran Unikela, 03/2019 – 08/2020. Worked on synthesis of triangulene radical monomers for 2D polymers. Recruited as a Lead Scientist at GSK India.

Dr. Afshin Dadvand, 06/2019 – 12/2021. Measured conductivity of 2D polymers and their applications in energy storage. Co-authored 2 papers in this project (ref. 5). Recruited as an engineer Wolfspeed, NC (USA)

Graduate Students:

Ehsan Hamzehpoor, 09/2018-03/2023, worked on synthesis of TANGO/TANG based 2D polymers, developed a new dynamic polymerization chemistry for synthesis of 2D polymers, helped with XPS analyses of all 2D polymers developed in this project; discovered unusual phosphorescent properties in TANGO monomers. Co-authored 5 papers in this project (refs. 1, 2, 4-8, 10, 11). Obtained FRQNT doctoral and Banting post-doctoral awards.

Chenghao Liu, 09/2018-present, worked on 2D polymers based on PTM radicals; discovered the efficient luminescence (doublet emission) in the PTM monomer; helped with computational and TEM analyses of many 2D polymers prepared in this project. Co-authored 5 papers in this project (refs. 2, 5, 7, 8, 11). Obtained Vanier doctoral scholarship.

Undergraduate Students:

Akaela Michaels-Gualtier, 06-08/2018, URAP student, worked on scale synthesis of PTM radical monomers. Co-authored 1 paper in this project (ref. 11).

William Patterson, 09/2018-08/2019, Honors project, then URAP summer student, worked on synthesis of vinylene-linked 2D polymers. Co-authors 1 paper in this project (ref. 7).

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Results Dissemination: 11) C.-H. Liu, Y. Sakai-Otsuka, R. Richardson, M.R. Niazi, E. Hamzehpoor, T. Jadhav, A. Michels-Gualteri, Y. Fang, M. Murugesu, D. F. Perepichka,* A 2D Perchlorinated sp²-Carbon Network, Cell Rep. Phys. Sci. 2022, 3, 100858
10) E. Hamzehpoor, A. Jonderian, E. McCalla, D.F. Perepichka,* Synthesis of Boroxine and Dioxaborole Covalent Organic Frameworks via Transesterification and Metathesis of Pinacol Boronates, J. Amer. Chem. Soc. 2021, 143, 13274
9) M. Souto*, D. F. Perepichka*, Electrically Conductive Covalent Organic Frameworks: Bridging the Fields of Organic Metals and 2D Materials, J. Mater. Chem. C 2021, 9, 10668
8) C.-H. Liu, E. Hamzehpoor, D. F. Perepichka*, 90% Quantum Yield Pure-Red Doublet Emission from Stable, Colorless, Iodinated Triphenylmethane Solid, Angew. Chem. Int. Ed. 2020, 59, 23030.
7) T. Jadhav, Y. Fang, C.-H. Liu, A. Dadvand, E. Hamzehpoor, W. Patterson, A. Jonderian, R. Stein, D. F. Perepichka,* Transformation between 2D and 3D Covalent Organic Frameworks via Reversible [2+2] Cycloaddition, J. Am. Chem. Soc. 2020, 19, 8862.
6) G. Galeotti, F. De Marchi, E. Hamzehpoor, O. MacLean, M. R. Rao, Y. Chen, L. V. Besteiro, D. Dettmann, L. Ferrari, F. Frezza, P. M. Sheverdyayeva, R. Liu, A. K. Kundu, P. Moras, M. Ebrahimi, M. C. Gallagher,* F. Rosei,* D. F. Perepichka,* G. Contini*, Synthesis of a mesoscale ordered 2D pi-conjugated polymer with semiconducting properties, Nat. Mater. 2020, 19, 874.
5) V. Lakshmi, C.-H. Liu, M. R. Rao, Y. Chen, Y. Fang, A. Dadvand, E. Hamzehpoor, Y. Sakai-Otsuka, R. S. Stein, D. F. Perepichka*, A Two-Dimensional Poly(azatriangulene) Covalent Organic Framework with Semiconducting and Paramagnetic States, J. Am. Chem. Soc. 2020, 142, 2155.
4) E. Hamzehpoor, D. F. Perepichka,* Crystal Engineering of Room Temperature Phosphorescence in Organic Solids, Angew. Chem. Int. Ed. 2020, 59, 9977.
3) D. Cui, Y. Fang, O. MacLean, D. F. Perepichka*, F. Rosei*, S. Clair*, Covalent organic frameworks from a monomer with reduced symmetry: polymorphism and Sierpinski triangles, Chem. Commun. 2019, 55, 13586.
2) T. Jadhav, Y. Fang; W. Patterson; C.-H. Liu, E. Hamzehpoor, D. F. Perepichka*, 2D Poly(arylene vinylene) Covalent Organic Frameworks via Aldol Condensation of Trimethyltriazine, Angew. Chem. Int. Ed. 2019, 58, 13753.
1) F. De Marchi, G. Galeotti, M. Simenas, M. C. Gallagher, E. Hamzehpoor, O. MacLean, R. M. Rao, Y. Chen, D. Dettmann, G. Contini, E. E. Tornau, M. Ebrahimi, D. F. Perepichka,* F. Rosei*, Temperature-induced molecular reorganization on Au(111) driven by oligomeric defects, Nanoscale 2019, 19, 19468.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Yoko Otsuka

Person Months Worked: 5.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Thaksen Jadhav

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Yuan Fang

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Person Months Worked: 15.00
Project Contribution:
National Academy Member: N

Funding Support:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Vellanki Lakshmi

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Kiran Unikela

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Staff Scientist (doctoral level)

Participant: Afshin Dadvand

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Ehsan Hamzehpoor

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Cheng-Hao Liu

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Undergraduate Student

Participant: Akaela Michaels-Gaultier

Person Months Worked: 3.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Undergraduate Student

Participant: William Patterson

Person Months Worked: 12.00

Funding Support:

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Date Submitted: 1/22/20 12:00AM

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Publication Location:

Article Title: Supramolecular Assemblies on Surfaces: Nanopatterning, Functionality, and Reactivity

Authors: Dominic P. Goronzy, Maryam Ebrahimi, Federico Rosei, , Yuan Fang, Steven De Feyter, Steven L. Tait,

Keywords: self-assembled molecular networks, on-surface polymerization, two-dimensional polymers, supramolecular assemblies, scanning tunneling microscopy, molecular electronics, graphene nanoribbons

Abstract: Understanding how molecules interact to form large scale hierarchical structures on surfaces holds promise for building designer nanoscale constructs with defined chemical and physical properties. Here, we describe advances in this field and highlight upcoming opportunities and challenges. Both direct intermolecular interactions and those that are mediated by substrates are discussed. Scanning probe microscopies have assumed defining roles in the field of molecular organization on surfaces delivering deeper understanding of interactions, structures, and local potentials. The emergence of graphene and the resulting impetus to explore 2D materials have broadened the field, as surface-confined reactions of molecular building blocks provide access to such materials as 2D polymers and graphene nanoribbons.

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Article Title: Temperature-induced molecular reorganization on Au(111) driven by oligomeric defects

Authors: F. De Marchi, G. Galeotti, M. Simenas, M. C. Gallagher, E. Hamzehpoor, O. MacLean, R. M. Rao, Y. Cf

Keywords: triangulene, self-assembly, on-surface polymerization

Abstract: Here we study the self-assembly of an oxygen-bridged tribromo-substituted triphenylamine, on the Au (111) surface by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) techniques, combined with density functional theory (DFT), and Monte Carlo simulations. At room temperature we observe the long-range self-assembly of intact molecules stabilized by Br-Br halogen bonding interactions. Annealing at 100°C results in the dissociation of C-Br bonds, followed by the formation of TBTANG dimers and trimers. Partial dehalogenation of the molecules induces a dramatic change in the self-assembled structure. Dimerization of as little as ten percent of the monomers is sufficient to induce local changes, whereas higher percentages (35%) are necessary to obtain surface-wide reorganizations. Annealing the surface to 200°C completes the dehalogenation process and yields a disordered polymeric phase.

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Article Title: 2D Poly(arylene vinylene) Covalent Organic Frameworks via Aldol Condensation of Trimethyltriazine

Authors: Thaksen Jadhav, Yuan Fang, William Patterson, Cheng-Hao Liu, Ehsan Hamzehpoor, Dmitrii F. Perepic

Keywords: 2D materials, aldol reaction, covalent organic frameworks, polymers, pi-conjugation

Abstract: Designing structural order in electronically active organic solids remains a great challenge in the field of materials chemistry. Now, 2Dpoly(arylene vinylene)s prepared as highly crystalline covalent organic frameworks (COFs) by basecatalyzed aldol condensation of trimethyltriazine with aromatic dialdehydes are reported. The synthesized polymers are highly emissive (quantum yield of up to 50%), as commonly observed in their 1D analogues poly(phenylene vinylene)s. The inherent well-defined porosity (surface area ca. 1000 m² g⁻¹, pore diameter ca. 11 c for the terephthaldehyde derived COF-1) and 2D structure of these COFs also present a new set of properties and are likely responsible for the emission color, which is sensitive to the environment. COF-1 is highly hydrophilic and reveals a dramatic macroscopic structural reorganization that has not been previously observed in framework materials

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Article Title: A Two-dimensional Polyazatriangulene; Covalent Organic Framework with Semiconducting and Paramagnetic States

Authors: V. Lakshmi, C.-H. Liu, M. R. Rao, Y. Chen, Y. Fang, A. Dadvand, E. Hamzehpoor, Y. Sakai-Otsuka, R. S

Keywords: 2D polymers, triangulene, doping, conducting polymers, magnetic polymers

Abstract: We report a series of highly emissive azatriangulenetrione (TANGO) solids in which the luminescent properties are controlled by engineering the molecular packing by adjusting the steric size of substituents. The co-alignment of 'phosphorogenic' carbonyl groups within the π -stacks results in an almost pure triplet emission in HTANGO, TCTANGO, TBTANGO and TITANGO, while their rotation by $\sim 60^\circ$ in the sterically hindered tBuTANGO leads to an almost pure singlet emission. Despite strong π -interactions, aggregation-induced quenching and triplet-triplet annihilation are avoided in HTANGO and TCTANGO which display efficient phosphorescence in the solid state. To our knowledge, HTANGO with the solid-state phosphorescence quantum yield of 42% at room temperature is the most efficient phosphor composed of the 1st/2nd row elements only

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Volume: 59 **Issue:** **First Page #:** 9977
Date Submitted: 10/3/20 12:00AM **Date Published:**
Publication Location:

Article Title: Crystal Engineering of Room Temperature Phosphorescence in Organic Solids

Authors: E. Hamzehpoor, D. F. Perepichka

Keywords: Organic Room Temperature Phosphorescence, Crystal engineering, Azatriangulene, J-aggregation, pi- Stacking

Abstract: We report a series of highly emissive azatriangulenetrione (TANGO) solids in which the luminescent properties are controlled by engineering the molecular packing by adjusting the steric size of substituents. The co-alignment of 'phosphorogenic' carbonyl groups within the π -stacks results in an almost pure triplet emission in HTANGO, TCTANGO, TBTANGO and TITANGO, while their rotation by $\sim 60^\circ$ in the sterically hindered tBuTANGO leads to an almost pure singlet emission. Despite strong π -interactions, aggregation-induced quenching and triplet-triplet annihilation are avoided in HTANGO and TCTANGO which display efficient phosphorescence in the solid state. To our knowledge, HTANGO with the solid-state phosphorescence quantum yield of 42% at room temperature is the most efficient phosphor composed of the 1st/2nd row elements only

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Article Title: Transformation between 2D and 3D Covalent Organic Frameworks via Reversible $2+2$ Cycloaddition

Authors: Thaksen Jadhav, Yuan Fang, Cheng-Hao Liu, Afshin Dadvand, Ehsan Hamzehpoor, William Patterson,

Keywords: 2D polymers, covalent organic frameworks, cross-linking, ion conductivity

Abstract: We report the first transformation between crystalline vinylene-linked two-dimensional (2D) polymers and crystalline cyclobutane-linked three-dimensional (3D) polymers. Specifically, absorption-edge irradiation of the 2D poly-(arylenevinylene) covalent organic frameworks (COFs) results in topological $[2+2]$ cycloaddition cross-linking of the π -stacked layers in 3D COFs. The reaction is reversible, and heating to 200°C leads to a cycloreversion while retaining the COF crystallinity. The resulting difference in connectivity is manifested in the change of mechanical and electronic properties, including exfoliation, blueshifted UV-vis absorption, altered luminescence, modified band structure, and different acid-doping behavior. The Li-impregnated 2D and 3D COFs show a significant room-temperature ion conductivity of 1.8×10^{-4} S/cm and 3.5×10^{-5} S/cm, respectively. Even higher room-temperature proton conductivity of 1.7×10^{-2} and 2.2×10^{-3} S/cm was found for H_2SO_4 -treated 2D and 3D COFs.

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Publication Location:

Article Title: Synthesis of mesoscale ordered two-dimensional π -conjugated polymers with semiconducting properties

Authors: G. Galeotti, F. De Marchi, E. Hamzehpoor, O. MacLean, M. Rajeswara Rao, Y. Chen, L. V. Besteiro, D.

Keywords: 2D polymers; on-surface synthesis; Dirac cone materials; triangulene

Abstract: Two-dimensional materials with high charge carrier mobility and tunable band gaps have attracted intense research effort for their potential use in nanoelectronics. 2D π -conjugated polymers constitute a promising subclass because the band structure can be manipulated by varying the molecular building blocks while preserving key features such as Dirac cones and high charge mobility. The major barriers to the application of two-dimensional π -conjugated polymers have been the small domain size and high defect density attained in the syntheses explored so far. Here, we demonstrate the fabrication of mesoscale ordered two-dimensional π -conjugated polymer kagome lattices with semiconducting properties, Dirac cone structures and flat bands on Au (111). This material has been obtained by combining a rigid azatriangulene precursor and a hot dosing approach, which favours molecular diffusion and eliminates voids in the network.

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Article Title: 90% Quantum Yield Pure-Red Doublet Emission from Stable, Colorless, Iodinated Triphenylmethane Solid

Authors: C. Liu, E. Hamzehpoor, Y. Sakai-Otsuka, T. Jadhav, D. F. Perepichka

Keywords: iodine · luminescence · radicals · photochemistry · structure elucidation

Abstract: Reported here is red luminescence in off-white tris(iodoperchlorophenyl)methane (3I-PTMH) crystals which is characterized by a high photoluminescence quantum yield (PLQY 91%) and color purity (CIE coordinates 0.66, 0.34). The emission originates from the doublet excited state of the neutral radical 3I-PTMR, which is spontaneously formed and becomes embedded in the 3I-PTMH matrix. The radical defect can also be deliberately introduced into 3I-PTMH crystals which maintain a high PLQY with up to 4% radical concentration. The immobilized iodinated radical demonstrates excellent photostability (estimated half-life >1 year under continuous irradiation) and intriguing luminescent lifetime (69 ns). TD-DFT calculations demonstrate that electron-donating iodine atoms accelerate the radiative transition while the rigid halogen-bonded matrix suppresses the nonradiative decay.

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Paper Title: Design and Synthesis of Two-Dimensional π -Conjugated Polymers

Authors: Dmitrii Perepichka

Acknowledged Federal Support: Y

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Conference Location: Orlando, FL

Paper Title: On-Surface Assembly and Reactivity of Oligo/Polythiophenes

Authors: Dmitrii Perepichka

Acknowledged Federal Support: **Y**

Partners

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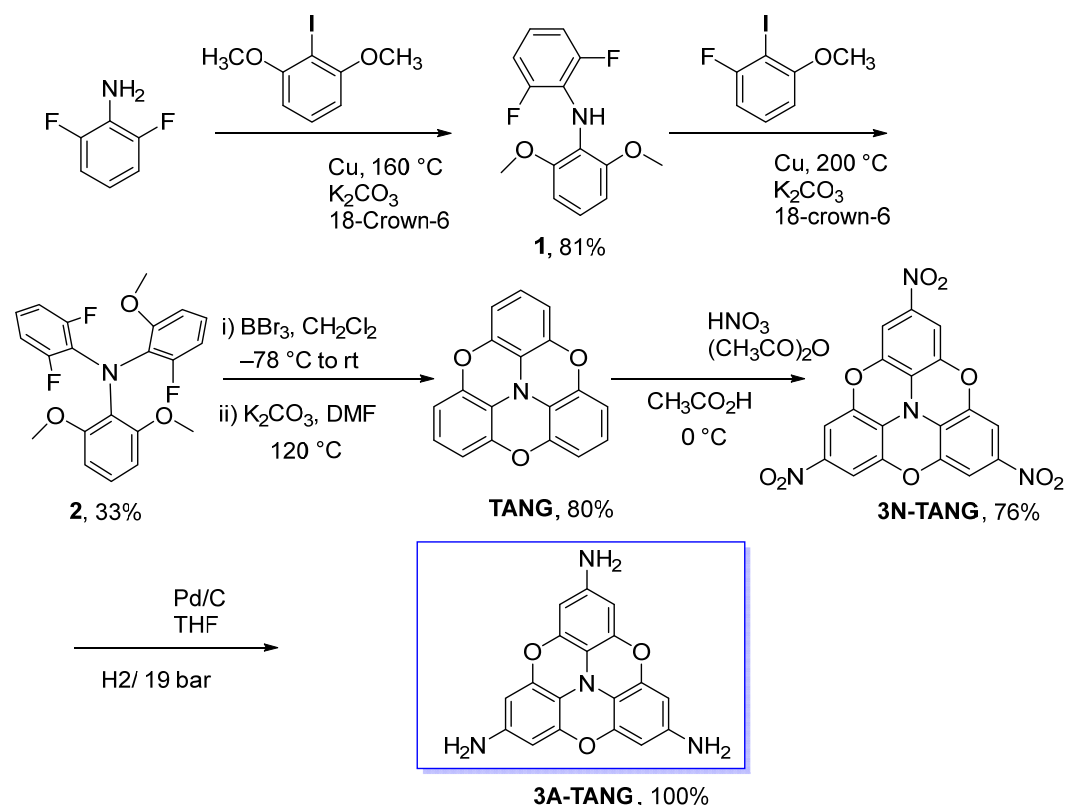
Signature: Dmytro Perepichka

Signature Date: 3/29/23 7:56PM

“2D Conjugated Polymers from Stable Free Radical Building Blocks”

- 1) Three families of reactive monomer based on **TANG** (trioxazatriangulene), **TANGO** (trioxazatriangulene), **PTM** (perchlorinated triphenylmethyl radical) have been designed and synthesized. Their polymerization using dynamic solvothermal polymerization, surface template polymerization and selective thermolysis was demonstrated.
- 2) 2D polymers with **TANG** radical-cation (and neutral **PTM** radical nodes have been synthesized. The effect of unpaired electrons interactions on their electrical and magnetic properties have been experimentally characterized (with support of Density Functional Theory calculations).
- 3) Two new dynamic covalent polymerization reactions for synthesis of conjugated (aldol condensation, see ref. 2 in Dissemination) and non-conjugated (boronate ester metathesis) 2D polymers have been developed.
- 4) Formation of individual 2D polymer (several hundred nm size) have been accomplished by exfoliation of layered materials (synthesized in solvothermal synthesis) and by on-surface polymerization (with TANG/TANGO monomers). In the latter case, angle-resolved X-ray photoelectron spectroscopy was used to prove the existence of Dirac cone intersection resembling that in graphene, in organic 2D polymers.
- 5) Unusual and efficient luminescence was discovered in TANGO (triplet emission/phosphorescence) and PTM monomer (doublet emission). These properties will be further explored in details in resulting 2D polymers in the follow-up project.

1) Synthesis of reactive monomers.



Scheme 1. Synthesis of **TANG** and amino-functionalized **3A-TANG** monomer.¹

2,6-Difluoro-N-(2,6-dimethoxyphenyl)aniline 1. The mixture of 2,6-difluoroaniline (0.82 g, 6.35 mmol), 2-iodo-1,3-dimethoxybenzene¹ (2.01 g, 7.62 mmol), K₂CO₃ (2.63 g, 19.1 mmol), copper powder (0.61 g, 9.53 mmol) and 18-crown-6 (0.17 g, 0.64 mmol) were dissolved in 1,2-dichlorobenzene (8.0 mL). The mixture was stirred at 160 °C for 15 h. The insoluble materials were filtered off, and the solids were washed with ethylacetate (50 mL). The obtained crude was concentrated under reduced pressure and purified by silica gel column chromatography (CH₂Cl₂:hexane = 1:3, *R_f* = 0.18) and recrystallized in CH₂Cl₂/hexane mixture to give **1** (1.37 g, 5.16 mmol) in 81% yield as white crystalline solid. HRMS: *m/z* calculated for C₁₄H₁₃F₂NO₂: 265.0914; found *m/z*: C₁₄H₁₄F₂NO₂: 266.0987 (M+H); ¹H NMR (400 MHz, CDCl₃, PPM): δ = 6.97 (t, *J* = 8.3 Hz, 1H), 6.85 – 6.68 (m, 3H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.47 (1H, bs), 3.77 (s, 6H); ¹³C NMR (101 MHz, CDCl₃, PPM): δ = 155.99 (d, *J*_{C-F} = 6.6 Hz), 153.57 (d, *J*_{C-F} = 6.6 Hz), 152.43, 122.47, 120.90, 118.98 (t, *J*_{C-F} = 9.5 Hz), 111.21 – 110.77 (m), 104.60, 56.05.

2,6-Difluoro-N-(2,6-dimethoxyphenyl)-N-(2-methoxy-6-fluorophenyl)aniline 2. The mixture of **1** (1.0 g, 3.77 mmol), 3-fluoro-2-iodo-anisole² (1.14 g, 4.52 mmol), 18-crown-6 (0.1g, 0.38 mmol), K₂CO₃ (1.56 g, 11.3 mmol) and copper powder (0.44 g, 6.97 mmol) were dissolved in mesitylene (10.0 mL). The mixture was stirred at 200 °C for 54 h. The insoluble materials were filtered off, and the solids were washed with ethylacetate (50 mL) and the solvent was concentrated under reduced pressure. The obtained crude

¹ V. Lakshmi, C.-H. Liu, M. R. Rao, Y. Chen, Y. Fang, A. Dadvand, E. Hamzehpoor, Y. Sakai-Otsuka, R. S. Stein, D. F. Perepichka, *J. Am. Chem. Soc.* **2020**, *142*, 2155.

product was purified by silica gel column chromatography (CH_2Cl_2 :hexane = 1:1, R_f = 0.25) to obtain **2** (0.49 g, 33%) as a white solid. HRMS: m/z calculated for $\text{C}_{21}\text{H}_{18}\text{F}_3\text{NO}_3$: 389.1239; found m/z : $\text{C}_{21}\text{H}_{19}\text{F}_3\text{NO}_3$: 390.1311 ($\text{M}+\text{H}$); ^1H NMR (400 MHz, CDCl_3 , PPM): δ = 7.07 (t, J = 8.3 Hz, 1H), 6.97 (td, J = 8.3, 6.1 Hz, 1H), 6.93 – 6.84 (m, 1H), 6.76 (t, J = 8.9 Hz, 2H), 6.68 – 6.61 (m, 2H), 6.56 (d, J = 8.3 Hz, 2H), 3.59 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3 , PPM): δ = 160.18, 159.86 (d, $J_{\text{C-F}}$ = 6.1 Hz), 157.72, 157.39 (d, $J_{\text{C-F}}$ = 6.0 Hz), 156.53 (d, $J_{\text{C-F}}$ = 13.4 Hz), 156.46, 126.10, 125.93 (d, $J_{\text{C-F}}$ = 4.4 Hz), 125.40, 124.04 (d, $J_{\text{C-F}}$ = 10.3 Hz), 122.46 (t, $J_{\text{C-F}}$ = 9.9 Hz), 111.21 (d, $J_{\text{C-F}}$ = 23.6 Hz), 109.00, 108.86 – 108.64 (m), 106.32, 57.00, 56.71.

Trioxaazatriangulene TANG. Triarylamine **2** (0.75 g, 1.93 mmol) was dissolved in dry CH_2Cl_2 (45 mL). BBr_3 (9.63 mL, 9.63 mmol) was added to the solution at -78°C . The mixture was slowly warmed up to room temperature and further stirred for 12 h. The reaction mixture was poured into water and extracted with ethyl acetate (15 mL). The combined organic phase was washed with brine, dried over Na_2SO_4 , filtered off, and concentrated under reduced pressure to give 0.51 g of the crude demethylated product as a white solid. Without further purification, this solid was dissolved in DMF (45 mL), K_2CO_3 (1.01 g, 7.34 mmol) was added and the mixture was stirred at 120°C for 24 h. The resulting solution was filtered off and washed with CH_2Cl_2 (30 mL), and the filtrate was concentrated under reduced pressure. The obtained solid was dissolved in CH_2Cl_2 (30 mL). After addition of 1 M HCl aq. (30 mL), the mixture was extracted with CH_2Cl_2 (10 mL) and washed with brine. The organic phase was dried over Na_2SO_4 , filtered off, and concentrated under reduced pressure. The obtained crude product was dissolved in CH_2Cl_2 and purified by silica gel column chromatography (CH_2Cl_2 : hexane = 1:3, R_f = 0.64) to give pure **TANG** (0.45 g, 80%) as a pale-yellow solid. The ^1H and ^{13}C NMR spectra matched those reported previously.²

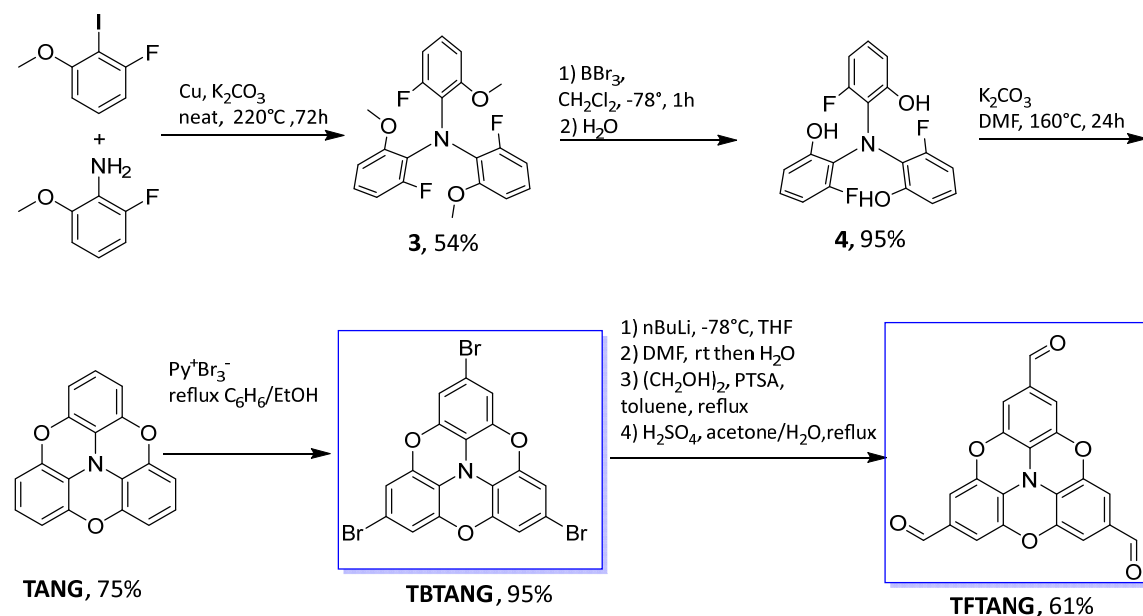
4,4',4''-Trinitro-2,2':6',6'',6-trioxytriphenylamine 3N-TANG. **TANG** (109.7 mg, 0.38 mmol) was added slowly to the stirred 69-71% HNO_3 (1.2 mL) in a round bottom flask placed in the ice bath. After 5 min, a mixture of $(\text{CH}_3\text{CO})_2\text{O}$ and $\text{CH}_3\text{CO}_2\text{H}$ (0.35 mL + 0.65 mL) was added slowly.³ The mixture was stirred for 45 min and then added additional 1.5 mL of $\text{CH}_3\text{CO}_2\text{H}$. The red colored mixture was poured into ice. The precipitate was filtered and washed with excess water. The solid **5** was crystallized from 1,4-dioxane and collected as red solid (123 mg) in 76% yield. HRMS: m/z calculated for $\text{C}_{18}\text{H}_6\text{N}_4\text{O}_9$: 422.0140; found m/z : $\text{C}_{18}\text{H}_7\text{N}_4\text{O}_9$: 422.0137 (M^+); ^1H NMR (400 MHz, DMSO, PPM): δ = 7.48 (6H, s). ^{13}C was not measured due to the poor solubility in basic D-solvents such as CDCl_3 , CD_2Cl_2 and DMSO.

4,4',4'''-Triamino-2,2':6',6'',6-trioxytriphenylamine 3A-TANG. In a hydrogenator reactor (Biotage), dry tetrahydrofuran (4 mL), **3N-TANG** (30 mg, 0.071 mmol) and a catalytic amount of 10% Pd/C were added. The mixture was purged with nitrogen and under 19 bar hydrogen pressure at room temperature for 36 h. The catalyst was filtered from the reaction mixture in the glove box and washed with 1,4-dioxane. The solvent was removed by distillation under inert conditions and the product **3A-TANG** was used as such without further purification. HRMS: m/z calculated for $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_3$: 332.0909; found m/z : $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_3$: 332.0904 (M^+). *Note 1:* $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was used as a reducing agent as well as stabilizing reagent to avoid oxidation of the triamino-TANG (and doping of the growing COF). The $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was dried in vacuum at 90°C (0.1 mbar) for 3h. The structural and spectroscopic features of so produced TANG-COF was indistinguishable from the **TANG-COF** prepared by without hydrazine, protected from air using Schlenk and glove-box. *Note 2:* **3A-TANG** is extremely unstable towards oxidation. It was prepared immediately

² Kuratsu, M.; Kozaki, M.; Okada, K. *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 4056.

³ Plietich, O.; Schilling, C. I.; Tolev, M.; Nieger, M.; Richert, C.; Muller, T.; Brase, S. *Org. Biomol. Chem.* **2009**, *7*, 4734.

prior to the synthesis of **TANG-COF** each time and used without purification/characterization an assumption of full hydrogenation of all nitro groups.



Scheme 2. Improved synthesis of **TANG** and **TBTANG** and **TFTANG** monomers.

Tris(2-fluoro-6-methoxyphenyl)amine (3). A mixture of 2-fluoro-6-methoxyaniline (2.00 g, 14.17 mmol), 3-fluoro-2-iodoanisole (10.71g, 42.51 mmol), copper powder (1.80 g, 28.34 mmol) and K_2CO_3 (5.87g, 42.51 mmol) was added into a 15 mL Pyrex high-pressure tube from ChemGlass. The mixture was further degassed and purged with N_2 for 5 min. The reaction was then stirred up to 220°C for 72 h. The resulting crude mixture (solid at room temperature) was slowly dissolved in 100 ml of aqueous HCl (1M) and 100 ml CH_2Cl_2 . The obtained crude was extracted with CH_2Cl_2 (3x100ml), washed with brine, dried over anhydrous Mg_2SO_4 , and concentrated under the vacuum. The residue was purified by column chromatography (SiO_2 , hexanes/ CH_2Cl_2 6:4) to afford the desired **1** (2.98 g, 54%) as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 6.98 (td, $J = 8.3, 6.0$ Hz, 3H), 6.69-6.62 (m, 6H), 3.59 (s, 9H). ^{13}C -NMR (126 MHz, CDCl_3) δ 159.82, 157.86, 156.39, 125.81 (d, $J = 10.8$ Hz), 123.95 (d, $J = 10.8$ Hz), 108.78 (d, $J = 21.6$ Hz), 56.84. ^{19}F NMR (376 MHz, CDCl_3) δ -122.91.

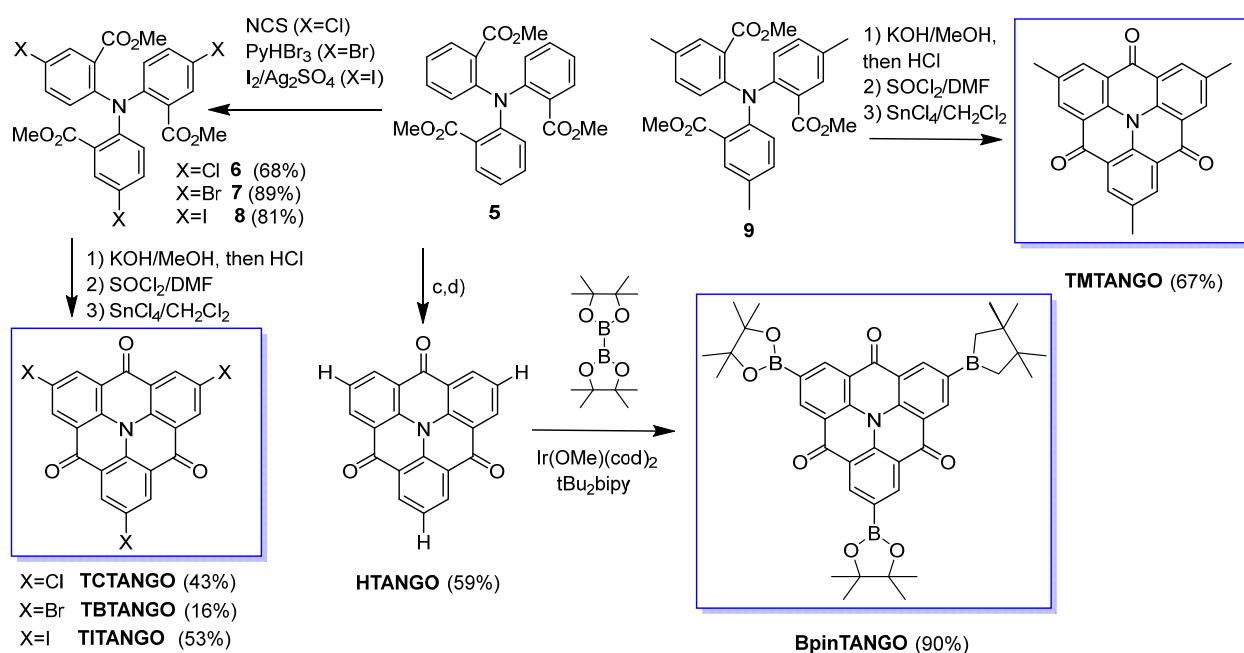
2,2':2''-nitriлотris(3-fluorophenol) (4) To a solution of **3** (1.00 g, 2.57 mmol) dissolved in dry CH_2Cl_2 (30 mL) was added dropwise of BBr_3 (3.2 g, 12.83 mmol) at -78°C and stirred for 1h. The reaction was then left to slowly warm up to room temperature and stirred for 12 h. After the reaction completion (checked by TLC), the reaction was quenched with H_2O . The crude was extracted with chloroform, washed with brine, and dried under vacuum to give the compound **4** as a white solid (0.85 g, 95%), used without further purification for the next step. ^1H NMR (500 MHz, CDCl_3) δ 7.08 (td, $J = 8.3, 5.8$ Hz, 1H), 6.72 (t, $J = 9.0$ Hz, 2H), 6.40 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.71, 159.76, 154.86, 127.68 (d, $J = 10.8$ Hz), 121.20 (d, $J = 13.9$ Hz), 112.61, 108.44 (d, $J = 21.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -120.79.

2,2':6',2'':6'',6-trioxotriphenylamine (TANG): **4** (0.80 g, 2.3 mmol) was dissolved in dry DMF (30 mL) and added K_2CO_3 (1.6 g, 11.5 mmol). The reaction mixture was slowly brought up to 150°C for 24 h. The solvent

was then evaporated by vacuum distillation. The obtained crude was purified on a silica gel column using a gradient (0-15%) ethyl acetate/hexane to afford the desired compound **TANG** (0.50 g, 75%) as a pale-yellow solid. ^1H NMR (500 MHz, C_6D_6) δ 6.25 (m, 9H). ^{13}C NMR (126 MHz, C_6D_6) δ 142.36, 127.89, 116.81, 111.13. The ^1H - and ^{13}C -NMR spectra matched those reported previously.²

4,4',4'''-Tribromo-2,2':6',2'':6'',6-trioxytriphenylamine (TBTANG). **TANG** (0.50 g, 1.74 mmol) and pyridinium tribromide (8.35 g, 26.1 mmol) were dissolved in 100 mL 3:2 (v:v) solution of Benzene: EtOH. The mixture was then refluxed at 90 °C overnight, during which a yellow precipitate was formed. After cooling to room temperature, the crude was filtered out and washed with EtOH, affording **TBTANG** as a yellow solid (0.87 g, 95%) which was used without further purification for the next step. The extremely low solubility of the product in organic solvents precludes NMR characterization.

4,4',4'''-Trialdehyde-2,2':6',2'':6'',6-trioxytriphenylamine (TFTANG). To a solution of **TBTANG** (100 mg, 0.19 mmol) dispersed in dry THF (2 mL) was added n-Butyllithium (0.25 mL, 2.5 M in hexanes, 0.63 mmol) at -78 °C (acetone/dry ice bath). After two hours, dry DMF (85 mg, 1.16 mmol) was added into the reaction mixture and the reaction was brought up to room temperature over 1h and continued stirring at room-temperature for an extra 1h. The reaction was then quenched with water and the resulting orange crude was filtrated out washed with excess water, acetone, successively, to give **TFTANG** as a red solid (65 mg, 92%). The crude was then redispersed in toluene in which excess ethylene glycol (0.3 mL, 5.43 mmol), followed by a catalytic amount of 4-toluenesulfonic acid monohydrate (6 mg, 0.035 mmol) was added. Then the reaction was brought to reflux and stirred until all the crude solids have disappeared (ca. 4 h). The reaction mixture was cooled down to room temperature, quenched with 10 ml of with 5% w/w aq. sodium hydroxide, and extracted with toluene. The organic phase was dried over anhydrous potassium carbonate and the solvent was evaporated under vacuum. The residue was then purified using flash column chromatography using 1% triethylamine in 15% EtOAc/toluene. The resulting acetal (60 mg, 69%) was unstable and partially converted back to insoluble **TFTANG** after columns chromatography. Then solvent of this acetal fraction was evaporated under vacuum and to the acetal/TATANG mixture was then added concentrated hydrochloric acid (1 mL), acetone (15 mL), and water (1 mL). The reaction mixture was brought to reflux for 1h and during which light orange crystals of **TFTANG** crashed out of the solution. The reaction mixture was then cooled down to room temperature and was filtered out to afford a final yield with (43 mg, 97%). The final yield of **TFTANG** was 61%. ^1H NMR (500 MHz, DMSO, 100°C) δ 9.71 (s, 1H), 7.06 (s, 2H). ^{13}C NMR (101 MHz, DMSO, 100°C) δ 190.03, 141.88, 133.97, 119.29, 113.22.



Scheme 3. Synthesis of **TANGO** derivatives.⁴

Trimethyl 2,2',2''-nitritotribenzoate (**5**) was synthesized according to literature.⁵ All TANGO derivatives were synthesized as described below. HTANGO, TCTANGO, TBTANGO and TITANGO used in photoluminescence studies were additionally purified by Soxhlett extraction (i-PrOH, THF and CHCl₃) and subject to fractional vacuum sublimation (at least twice or until their emission spectra and photoluminescence quantum yield remain unchanged).

4H-benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-4,8,12-trione (HTANGO):⁶ **5** (1.50 g, 3.60 mmol) and KOH (2.02 g, 36 mmol) were dissolved in MeOH (40 ml) and H₂O (10 ml). After stirring at 60 °C for 24 h, the solution was diluted with H₂O (100 ml) and acidified (pH~3) with aq. HCl (1M). The resulting precipitate was filtered off, excessively washed with H₂O and dried under vacuum to give the triacid as a pale-yellow powder (0.98 g, 73 %) which was used without further purification and characterization for the next step. The resulting triacid (0.98 g, 2.6 mmol), SOCl₂ (10 ml), and DMF (0.5 ml) were stirred in dry CH₂Cl₂ (30 mL) at 40°C for 3 h. SnCl₄ (0.30 ml, 2.6 mmol) was then added and the solution was stirred at 40°C for further 20 h. The yellow precipitate was filtered off and stirred in aq. NaOH (1 M, 50 mL) for 30 min. After filtration the residue was excessively washed with H₂O and acetone and dried to yield **HTANGO** (499 mg, 59%). The residue was then transferred to a sublimation chamber and sublimed under vacuum to give pure crystalline powder of **HTANGO**. APCI-MS calcd. for C₂₁H₁₀NO₃ [MH]⁺ 324.0655, found 324.0661; extremely low solubility of the product in organic solvents precluded NMR characterization.

Trimethyl 6,6',6''-nitritotris(3-chlorobenzoate) (6): **5** (2.00 g, 4.77 mmol) in 75ml acetonitrile was brought to reflux and NCS (2.23g, 16.70 mmol) was added portionwise in 3 hours. Reaction stirred overnight under

⁴ E. Hamzehpoor, D. F. Perepichka, *Angew. Chem. Int. Ed.* **2020**, 59, 9977.

⁵ Z. Fang, T.-L. Teo, L. Cai, Y.-H. Lai, A. Samoc, M. Samoc, *Org. Lett.* **2008**, 11, 1.

⁶ J. E. Field, D. Venkataraman, *Chem. Mater.* **2002**, 14, 962.

reflux conditions. The solvent was evaporated, and the crude was washed with brine and dried under vacuum. Residue was purified by column chromatography (SiO₂, hexanes/EtOAc 9:1) to provide **6** as a pale-yellow solid (1.69g, 68.0%) ESI-MS (toluene) calcd. for C₂₄H₁₈O₆NCl₃Na [M]⁺ 544.0097, found 544.0110; ¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 2.5 Hz, 3H), 7.33 (dt, *J* = 8.7, 2.2 Hz, 3H), 6.98 (d, *J* = 8.7 Hz, 3H), 3.45 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 165.92, 144.88, 132.42, 130.80, 129.35, 128.83, 127.16, 52.16.

2,6,10-Trichloro-4H-benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-4,8,12-trione (TCTANGO): 6 (1.64 g, 3.15 mmol) and KOH (1.76 g, 31.5 mmol) were dissolved in MeOH (40 mL) and H₂O (10 mL). After stirring at 60°C for 24 h, the solution was diluted with H₂O (100 mL) and acidified (pH~3) with aq. HCl (1 M). The resulting precipitate was filtered off, excessively washed with H₂O, and dried under vacuum to give the triacid as a pale-yellow powder (1.35 g, 89%) which was used without further purification and characterization for the next step. The triacid (1.35 g, 2.81 mmol), SOCl₂ (10ml), and DMF (0.1 ml) were stirred in dry CH₂Cl₂ (30 mL) at 40°C for 3 h. SnCl₄ (0.33 mL, 2.81 mmol) was then added and the solution was stirred at 40°C for further 20 h. The yellow precipitate was filtered off and stirred in aq. NaOH (1 M, 50 mL) for 30 min. After filtration the residue was excessively washed with H₂O and acetone and dried to yield a yellow powder (0.51 g, 43%). The residue was then transferred to a sublimation chamber and sublimed under vacuum to give pure TCTANGO. APCI-MS calcd. for C₂₁H₇Cl₃NO₃ [MH]⁺ 425.9486, found 425.9478; extremely low solubility of the product in organic solvents precluded NMR characterization.

Trimethyl 6,6',6''-nitrilotris(3-bromobenzoate) (7): To a solution of **5** (1.50g, 3.6 mmol) in 100ml EtOH/Benzene (v/v 1:1) was added 17.10 g (5 eq, 53.6 mmol) pyridinium tribromide and stirred under reflux for 6 hours. The solvent was evaporated, and the crude was dissolved in ethyl acetate, washed with brine and dried under vacuum residue was purified by column chromatography (SiO₂, hexanes/EtOAc 4:1) to provide **7** as a pale-yellow solid (2.10 g, 89%). APCI-MS calcd. for C₂₄H₁₉Br₃NO₆ [M]⁺ 653.8757, found 653.8751; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 2.5 Hz, 3H), 7.42 (dd, *J* = 8.7, 2.5 Hz, 3H), 6.87 (d, *J* = 8.7 Hz, 3H), 3.40 (s, 9H).; ¹³C NMR (101 MHz, CDCl₃) δ 165.74, 145.25, 135.34, 133.71, 129.13, 127.48, 116.81, 52.15.

2,6,10-Tribromo-4H-benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-4,8,12-trione (TBTANGO): 7 (1.5g, 2.3 mmol) and KOH (1.29g, 23mmol) were dissolved in MeOH (40 mL) and H₂O (10 mL). After stirring at 60°C for 24 h, the solution was diluted with H₂O (100 mL) and acidified (pH~3) with aq. HCl (1 M). The resulting precipitate was filtered off, excessively washed with H₂O, and dried under vacuum to give the triacid as a pale-yellow powder (1.05, 75%) which was used without further purification and characterization for the next step. The triacid (1.00 g, 1.63 mmol), SOCl₂ (10ml), and DMF (0.5ml) were stirred in dry CH₂Cl₂ (30 mL) at 40°C for 3 h. SnCl₄ (497 mg, 0.22 mL, 1.91 mmol) was then added and the solution was stirred at 40 °C for further 20 h. The yellow precipitate was filtered off and stirred in aq. NaOH (1 M, 50 mL) for 30 min. After filtration the residue was excessively washed with H₂O and acetone and dried to yield TBTANGO as a yellow powder (148 mg, 16%). The residue was then transferred to a sublimation chamber and sublimed under vacuum to give pure TBTANGO. APCI-MS calcd. for C₂₁H₇Br₃NO₃ [MH]⁺ 557.7971, found 557.7966; extremely low solubility of the product in organic solvents precluded NMR characterization.

Trimethyl 6,6',6''-nitrilotris(3-iodobenzoate) (8): To a solution of **5** (2.00 g, 4.77 mmol) in 100 ml EtOH was added iodine (4.12 g, 16.2 mmol) and silver sulfate (4.45 g, 14.2 mmol) and stirred in room temperature for 4 hours. The reaction mixture was washed with sodium thiosulfate (0.1 M) and the dried

under vacuum and the residue was purified by column chromatography (SiO₂, hexanes/EtOAc 5:1) to provide **8** as a pale-yellow solid (3.10 g, 81%). APCI-MS: calcd. for C₂₄H₁₉I₃NO₆ [MH]⁺ 797.8341, found 797.8315; ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 2.2 Hz, 3H), 7.66 (dd, *J* = 8.7, 2.2 Hz, 3H), 6.78 (d, *J* = 8.6 Hz, 3H), 3.44 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 165.64, 145.79, 141.22, 139.59, 129.32, 127.66, 87.08, 52.16.

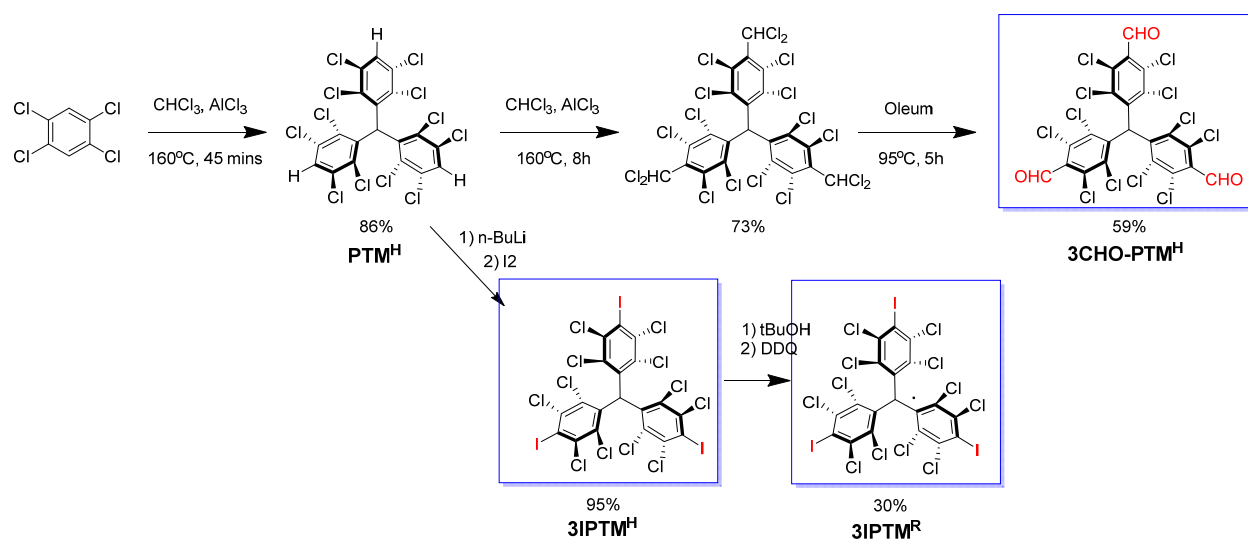
2,6,10-Triiodo-4H-benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-4,8,12-trione (TITANGO): **8** (3.00 g, 3.76 mmol) and KOH (2.11 g, 36.7mmol) were dissolved in MeOH (40 mL) and H₂O (10 mL). After stirring at 60°C for 24 h, the solution was diluted with H₂O (100 mL) and acidified (pH~3) with aq. HCl (1 M). The resulting precipitate was filtered off, excessively washed with H₂O, and dried under vacuum to give the triacid as a pale-yellow powder (2.32 g, 82%) which was used without further purification and characterization for the next step. The resulting triacid (2.32 g, 3.07 mmol), SOCl₂ (10 ml), and DMF (0.1 ml) were stirred in dry CH₂Cl₂ (30 mL) at 40°C for 3 h. SnCl₄ (0.36 mL, 1.62 mmol) was then added and the solution was stirred at 40°C for further 20 h. The yellow precipitate was filtered off and stirred in aq. NaOH (1 M, 50 mL) for 30 min. After filtration the residue was washed with copious amount of H₂O and acetone and dried to give TITANGO as a yellow powder (1.14 g, 53%). The residue was then transferred to a sublimation chamber and sublimed under vacuum to give pure TITANGO. APCI-MS calcd. for C₂₁H₆I₃NO₃ [M]⁺ 701.7555, found 701.7533; extremely low solubility of the product in organic solvents precluded NMR characterization.

Trimethyl 6,6',6''-nitrilotris(3-methylbenzoate) (9): A mixture of methyl 2-amino-5-methylbenzoate (2.00g, 12.11 mmol) and methyl 2-iodo-5-methylbenzoate (7.35g, 26.64 mmol), K₂CO₃ (16.73g, 121.07 mol), Cu (0.77 g, 12.11 mmol) and CuI (2.31 g, 12.11 mmol) in diphenylether (25 mL) was heated at 230 °C under argon for 48 h. The solvent was removed under reduced pressure and the residue was extracted with water 200ml and ethyl acetate (3x 100ml). The organic layer was evaporated under reduced pressure and the residue was chromatographed on silica gel using 4 : 1 hexane–ethyl acetate as eluent to give **9** (1.26 g, 3.38 mmol, 27%) as a yellow solid, ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 2.2 Hz, 1H), 7.16 (dd, *J* = 8.3, 2.2, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 3.40 (s, 3H), 2.32 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 168.02, 144.83, 132.87, 132.79, 131.09, 127.09, 125.76, 51.61, 20.56.

2,6,10-Trimethyl-4H-benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-4,8,12-trione (TMTANGO): **9** (1.00 g, 2.17 mmol) and KOH (2.55 g, 45.5 mmol) were dissolved in MeOH (20mL) and H₂O (20 mL). The reaction was refluxed for 18h and then the solution was diluted with H₂O (100 mL) and acidified (pH~3) with aq. HCl (1M). The resulting precipitate was filtered, excessively washed with H₂O, and dried under vacuum to give the triacid as a pale-yellow powder (0.90 g, quantitative) which was used without further purification and characterization for the next step. The resulting triacid (0.90 g, 2.14 mmol), SOCl₂ (10 ml), and DMF (0.5ml) were stirred together at 40°C for 3 h. SnCl₄ (0.30 ml, 2.6 mmol) and in dry CH₂Cl₂ (30 mL) was then added and the solution was stirred at 40°C for further 20 h. The yellow precipitate was filtered off and stirred in aq. NaOH (1M, 50 mL) for 30 min. After filtration the residue was excessively washed with H₂O and acetone and dried to yield **TMTANGO** (510 mg, 67%). The residue was then transferred to a sublimation chamber and sublimed under vacuum to give pure crystalline powder of **TMTANGO**. ¹H NMR (500 MHz, CDCl₃) δ 8.86 (2H), 2.72 (s, 3H). low solubility of the product in organic solvents precluded CNMR characterization.

2,6,10-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-4,8,12-trione(BpinTANGO): A mixture of (1,5- cyclooctadiene)(methoxy)iridium(I) dimer

(0.031 g, 0.062 mmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (0.033 g, 0.12 mmol), bis(pinacolato)diboron (0.71 g, 2.80 mmol) and **HTANGO** (0.20 g, 0.62 mmol) was added in 20 mL of dry cyclohexane. The mixture was then purged with Argon for 10 min and heated up to 90 °C for 10 h. After cooling to room temperature, the deep-red reaction mixture was added to 10 ml of methanol and stirred for 10 min. The orange precipitate was vacuum filtered, washed with 2×5 ml of cold methanol, and recrystallized twice from methanol (25 ml) to afford pure **BpinTANGO** (0.40 g, 90%) as dark yellow powder. ESI-MS calcd. for C₃₉H₄₃B₃NO₉ [MH]⁺ 702.3211, found 702.3225; ¹H NMR (500 MHz, CDCl₃) δ 9.44 (s, 1H), 1.46 (s, 7H). ¹³C NMR (126 MHz, CDCl₃) δ 176.41, 141.16, 140.19, 139.60, 134.86, 122.82, 84.80, 24.99.



Scheme 4. Synthesis of functionalized **PTM** monomers.⁷

Tris(2,3,5,6-tetrachlorophenyl)methane (PTM^H). 1,2,4,5-Tetrachlorobenzene (3.00 g, 13.9 mmol) and aluminum chloride (223 mg, 1.87 mmol) were charged in a dry glass pressure vessel. Dry chloroform (150 µL, 1.87 mmol) was subsequently added. The vessel is heated at 160°C for 45 minutes. Upon cooling to room temperature, ice and 1N aq. HCl (10 mL) were added to the reaction mixture and it was stirred overnight. The mixture was extracted with chloroform (2×50 mL), washed with 2% aq. sodium bicarbonate (50 mL), water (2×50 mL). The organic layer was dried over sodium sulfate and evaporated. The crude product was recrystallized in a chloroform, DCM, and hexanes mixture (1:1:2). The mother liquor was evaporated, and recrystallized in diethyl ether and hexanes (1:1) before flash column chromatography in hexanes to obtain pure **PTM^H** (1.06g, 86%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.65 (s, 3H), 6.98 (s, 1H).

Tris(2,3,5,6-tetrachloro-4-(dichloromethyl)phenyl)methane. PTM^H (100 mg, 0.15 mmol) and aluminum chloride (24 mg, 0.18 mmol) were charged in a dry glass pressure vessel. Dry chloroform (2.72 g, 22.8 mmol) was subsequently added. The vessel is heated at 160°C for 8 hours. Upon cooling to room

⁷ C.-H. Liu, E. Hamzehpoor, Y. Sakai-Otsuka, T. Jadhav, D. F. Perepichka, *Angew. Chem. Int. Ed.* **2020**, 59, 23030.

temperature, ice and 1N aq. HCl (10 mL) were added to the reaction mixture. The mixture was extracted with chloroform (2×50 mL), washed with 2% aq. sodium bicarbonate (50 mL), water (2×50 mL). The organic layer was dried over sodium sulfate and evaporated. The product was recrystallized in hexanes and DCM mixture (1:1) to obtain pure product (101 mg, 73%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.63 (s, 3H), 7.11 (s, 1H).

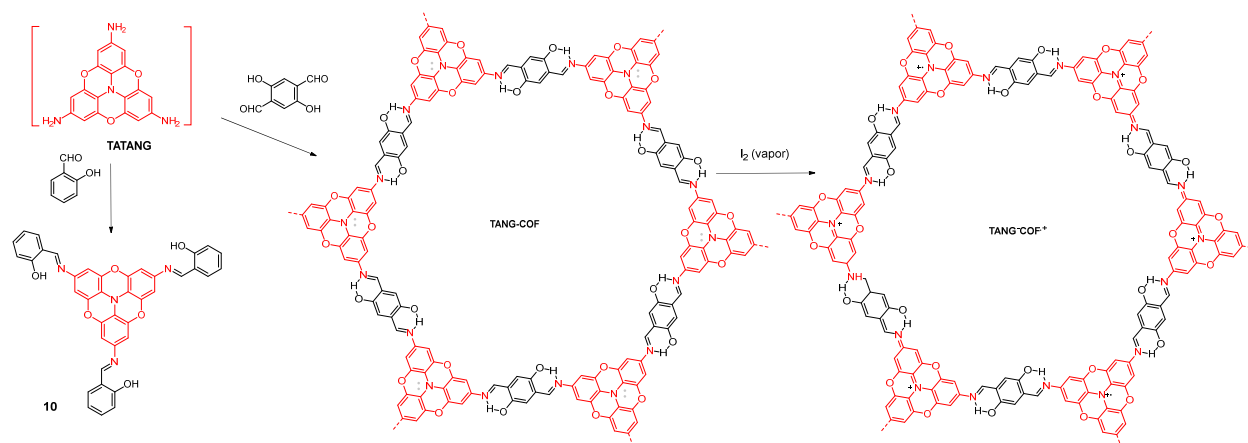
Tris(2,3,5,6-tetrachloro-4-formylphenyl)methane (3CHO-PTM^H). Tris(2,3,5,6-tetrachloro-4-(dichloromethyl)phenyl)methane (607 mg, 0.670 mmol) and 7 mL of oleum was added to a 50 mL round bottom flask equipped with a reflux condenser. The mixture was heated at 95 °C for 5 hours. Upon cooling, the mixture was poured onto ice and the precipitate was filtered and washed with water. The crude product was subjected to flash column chromatography in hexanes and DCM mixture (1:1.5) to obtain pure **3CHO-PTM^H** (361 mg, 59%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 10.35 (s, 3H), 7.12 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 187.2, 140.7, 135.9, 135.0, 134.1, 133.6, 132.9, 57.2. APCI-HRMS (m/z): calculated 740.6710 (M-H), found 740.6262.

Tris(4-iodo-2,3,5,6-tetrachlorophenyl)methane (3I-PTM^H) was synthesized with a procedure modified from literature.⁶ In a dry and degassed 100 mL two-neck round-bottom flask, dodecachlorotriphenylmethane (402 mg, 0.61 mmol) and 16 mL of dry THF were charged under argon. The solution was cooled to -78 °C by using acetone/dry ice cooling bath. *n*-BuLi(2.5M in Hexane)(1.46 mL, 3.65 mmol) was slowly added to the solution, and the mixture was stirred at -78 °C for 2h. Afterwards, iodine (1.55 g, 6.1 mmol) dissolved in 8 mL of dry and degassed THF were transferred to the reaction mixture by a cannula and the resulting mixture was slowly warmed to room temperature and stirred overnight. A saturated sodium thiosulfate solution (100 mL) was added to the mixture to quench the reaction, then THF was evaporated. The precipitate was filtered and washed with excess amount of warm water, acetone, hexane and chloroform to afford **3I-PTM^H** as an off-white solid (599 mg, 95%). HRMS, APCI positive mode: calculated m/z for C₁₉HCl₁₂I₃ [M]⁺: 1035.3387; found m/z: 1035.3379. ¹H NMR (500 MHz, THF, solvent suppression mode): δ (ppm) 6.99 (1H, s). ¹³C NMR (200 MHz, THF-d₈): δ (ppm) 139.8, 138.3, 137.9, 132.9, 132.1, 135.4, 57.6.

Tris(4-iodo-2,3,5,6-tetrachlorophenyl)methyl radical (3I-PTM^R). In a dry 100 mL two-neck round-bottom flask, **3I-PTM^H** (100 mg, 0.097 mmol) and 50 mL of THF (distilled from HPLC grade) were charged and the solution was stirred until complete dissolution. Tetrabutylammomium hydroxide (55 wt% aqueous solution) (139 mg, 0.54 mmol) was added to the mixture under argon atmosphere and in the dark. The mixture was stirred at room temperature overnight. 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) (60.5 mg, 0.27 mmol) was then added to the flask, where the mixture was stirred at room temperature for 45 min. Silica gel was added to the mixture and then solvent was removed by rotary evaporator. The resulting solid was subjected to flash chromatography immediately (hexane/THF(HPLC grade) = 9/1). The solvent in the collected fraction was removed. Methanol (HPLC grade, 5 mL) was added and the solid was filtered to obtain **3I-PTM^R** as a deep-red solid (30 mg, 30%). HRMS, APCI positive mode: m/z calculated for C₁₉Cl₁₂I₃ [M]⁺: 1034.3310; found m/z: 1034.3289.

2a. Synthesis of radical-cationic 2D COF based on TANG building block.

Using the in-situ prepared (see above) **TA-TANG** monomer, we synthesized (aza)triangulene-based covalent organic framework (TANG-COF) by polycondensation with dihydroxyterephthalaldehyde under solvothermal conditions (Scheme 5). High crystallinity and permanent porosity of the layered two-dimensional (2D) structure were established by powder X-ray diffraction (PXRD), electron microscopy (Fig. 1) and BET measurements. The rigid, electron-rich TANG building block together with intramolecular hydrogen bonding enables strong π -electron inter-actions manifested in broad absorptions across the visible and NIR region (Eg ~ 1.2 eV, Fig. 2). The high HOMO of TANG-COF (-4.8 eV) level enables facile p-doping resulting in electrical conductivity (up to 10^{-2} S/cm) and paramagnetic behavior with spin concentration $\sim 10\%$. See ref. 1 for further details.



Scheme 5. Synthesis of **TANG-COF** by dynamic polycondensation with dihydroxyterephthalic aldehyde. The model compound **10** was prepared to aid in characterization of the COF. The doped **TANG-COF $^{+\bullet}$** was prepared by exposure to iodine vapor.

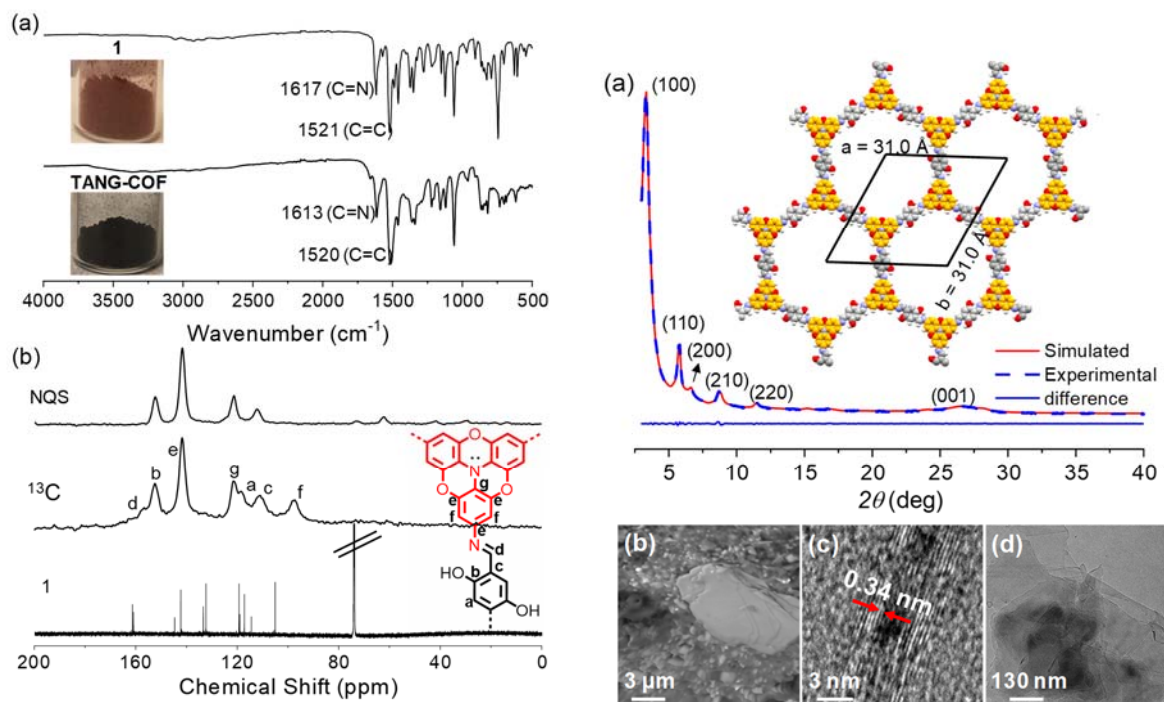


Fig. 1. (left panel) (a) IR (photographs in inset) and (b) ^{13}C NMR spectra of **TANG-COF**, and **10** (in C2D2Cl4). (right panel) (a) PXRD pattern for **TANG-COF** (inset shows the simulated structure); (b) SEM image of as-prepared COF powder and (c,d) TEM images of exfoliated COF nanosheets.

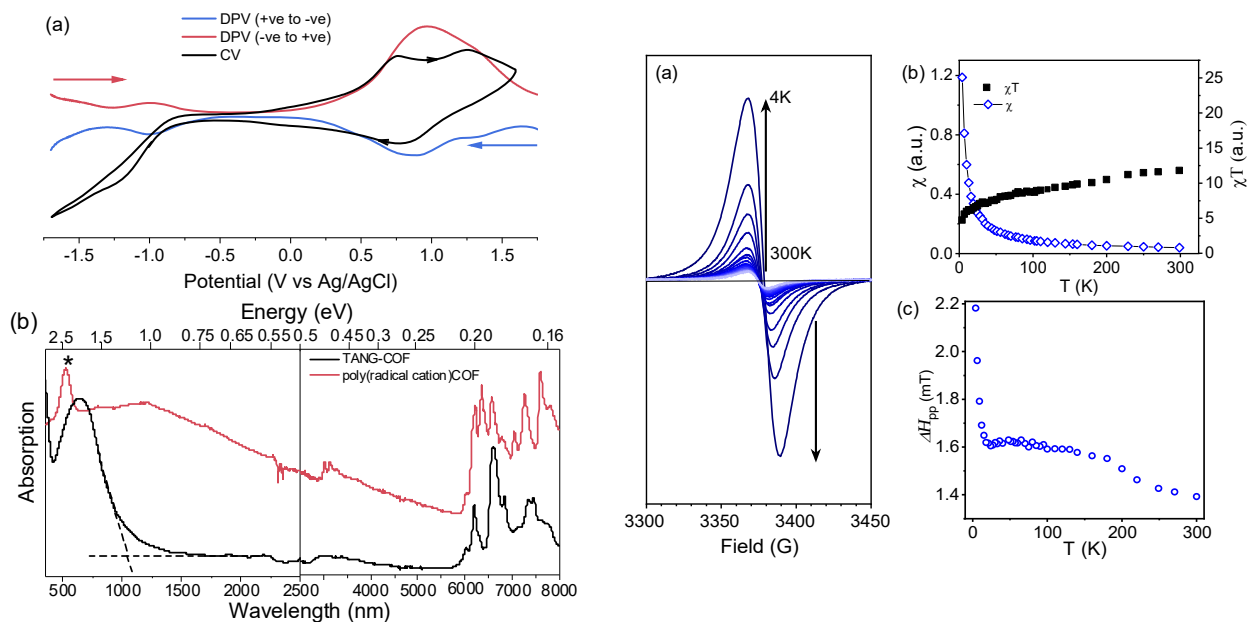


Fig 2. (left panel) a) Electrochemistry of **TANG-COF** (20 mV/s; 0.1 M Bu_4NPF_6 , in CH_3CN); (b) optical extinction spectra for the pristine (black, KBr pellet) and iodine-doped COF (red, nujol suspension), acquired separately in the Vis-NIR and mid-IR regions. (right panel) a) ESR spectra of the iodine-doped **TANG-COF** at different temperatures; (b) temperature dependence of the spin susceptibility and (c) ESR linewidth.

2b. Synthesis of paramagnetic 2D polymer with PTM repeat unit (P^2PTM)

We synthesized 2D covalent organic polymer with perchlorotriphenylmethyl (radical) nodes by through dehalogenative thermolysis polymerization of **3I-PTM^H** (Fig. 3). The resulting C–C-linked **P²PTM** is black layered solid (Fig. 3) was characterized by NMR, Raman and FTIR spectroscopies (Fig. 4), and PXRD (Fig. 5g). Exfoliated, layered 2D sheets can be imaged with TEM and AFM (Fig. 5d,e). N₂ adsorption experiment reveals a permanent porosity with a surface area of 150 m²/g and chloroform dynamic vapor sorption shows a specific adsorption of one chloroform molecule per **P²PTM** unit cell, in line with modeling (Fig. 5a,b). DFT calculations predict degenerate Mott-insulating anti-ferromagnetic and ferromagnetic states while the semi-metallic closed-shell configuration is less stable by ~ 1 eV. Experimentally, **P²PTM** is a low bandgap black solid with moderate electrical conductivity ($\sim 4 \times 10^{-4}$ S cm⁻¹), gate-modulated ambipolar charge transport and paramagnetic behavior down to 1.9 K (Fig. 6). See ref. 7 for further details.

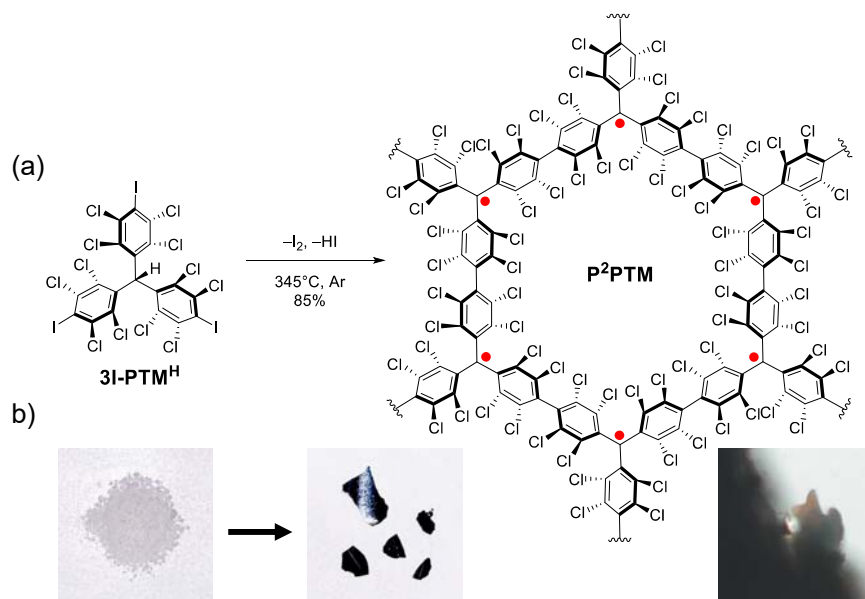


Fig. 3. Synthesis of **P²PTM** by thermolysis of **3I-PTM^H** (photographs of the monomer and the polymer shown on the bottom).

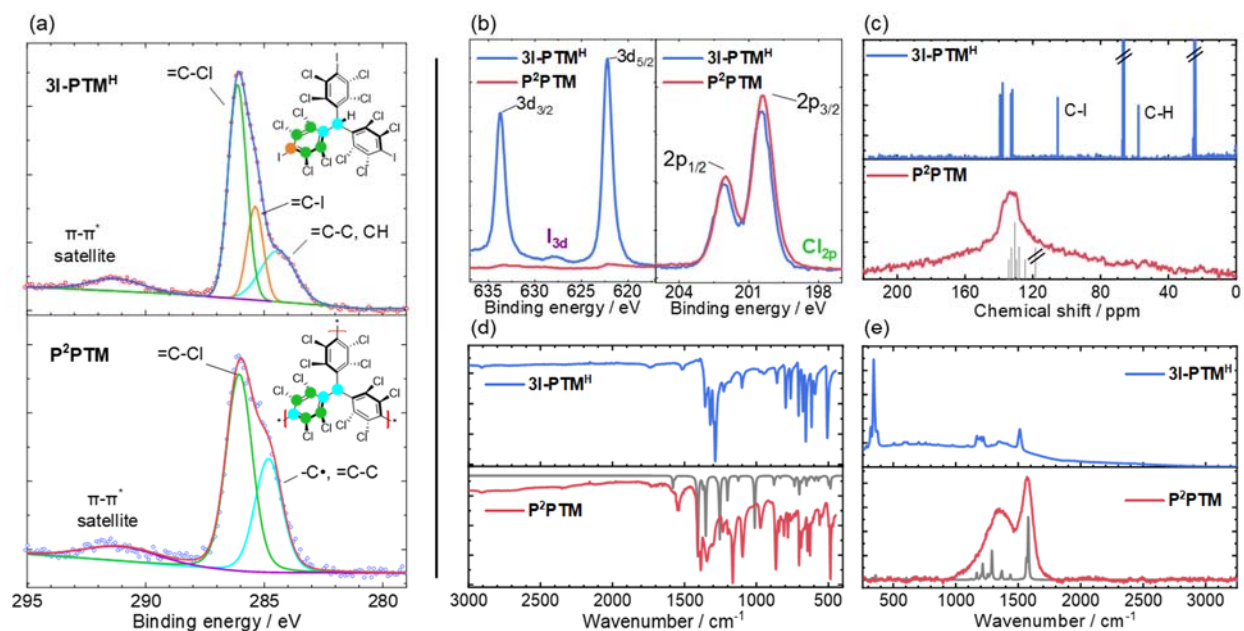


Fig. 4. Chemical characterization of P^2PTM , compared against the monomer 3I-PTM^{H} . (a) C1s XPS of 3I-PTM^{H} and P^2PTM . (b) I3d (left) and Cl2p (right) XPS of 3I-PTM^{H} and P^2PTM . (c) ^{13}C NMR of 3I-PTM^{H} in THF- d_8 and direct excitation magic angle spinning ^{13}C NMR of P^2PTM in solid state (crossed peaks for 3I-PTM^{H} is the solvent; crossed peak for DFT calculation is terminal aromatic carbon). (d) FTIR spectra of 3I-PTM^{H} and P^2PTM (e) Raman spectra of 3I-PTM^{H} and P^2PTM (laser wavelength = 785 nm). DFT-calculated (B3LYP/6-31G(d)) spectra for the PTM dimer are shown in (c, d, e) in grey.

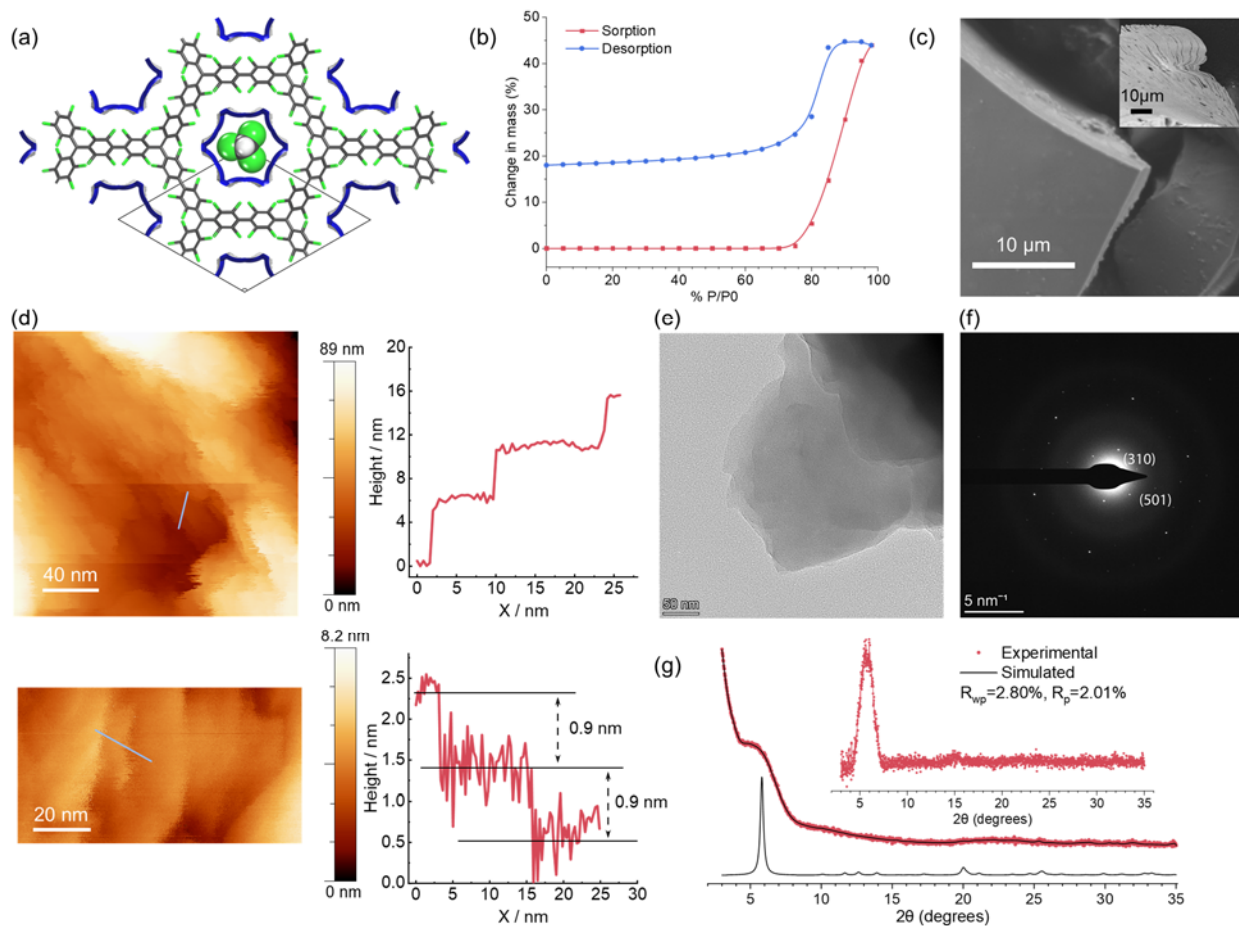


Fig. 5. Structural characterization of P^2PTM . (a) DFT calculated model of P^2PTM viewed from [001] plane, $a=b=17.2 \text{ \AA}$, $\gamma=120^\circ$, with its solvent accessible surface and a chloroform molecule. (b) Chloroform DVS isotherm of P^2PTM . (c) SEM of the P^2PTM surface (inset shows the layered structure at a broken edge). (d) AFM image of P^2PTM plates and the corresponding height profiles. (e) TEM (200 kV) of exfoliated P^2PTM . (f) Selected area electron diffraction of P^2PTM . (g) PXRD of compressed P^2PTM powder, inset shows the background deconvoluted pattern.

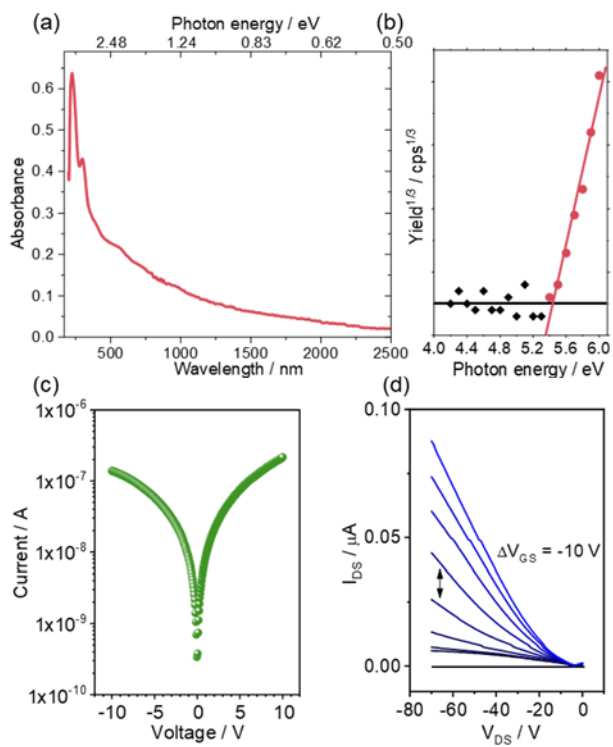


Fig. 6. Electronic properties of P^2PTM . (a) UV-Vis-NIR absorption spectrum from diffuse-reflectance measurements; (b) photoelectron spectroscopy in air (PESA); (c) two-probe electrical conductivity; (d) FET output characteristics of P^2PTM .

3a. New boronate metathesis dynamic covalent polymerization for 2D boroxine/dioxaborole COFs.

Boroxine and dioxaborole are the first and the most studied synthons of COFs. Despite their wide application in the design of functional COFs over the last 15 years, their synthesis still relies on the original Yaghi's condensation of boronic acids (with itself or with polyfunctional catechols), some of which are difficult to prepare, poorly soluble, or unstable in the presence of water. We developed a new synthetic approach to such COFs based on transesterification of pinacol aryl boronates (ArBpin) with methyl boronic acid (MBA) and methylboryl-protected catechols (Fig. 7). The ArBpin and MBA-protected catechols are easy to purify, highly soluble, and bench-stable. Unlike the conventional condensation which eliminates water by-products, the by-product of the metathesis (MBA pinacolate). We show the generality of this approach by synthesis of seven known boroxine/dioxaborole COFs whose crystallinity is better or equal to those reported by conventional condensation. We also apply metathesis polymerization to obtain two new COFs, Py4THB and B2HHTP, whose synthesis was previously precluded by their insolubility and hydrolytic instability, respectively, of the boronic acid precursors (Scheme 6). See ref. 8 for further details.

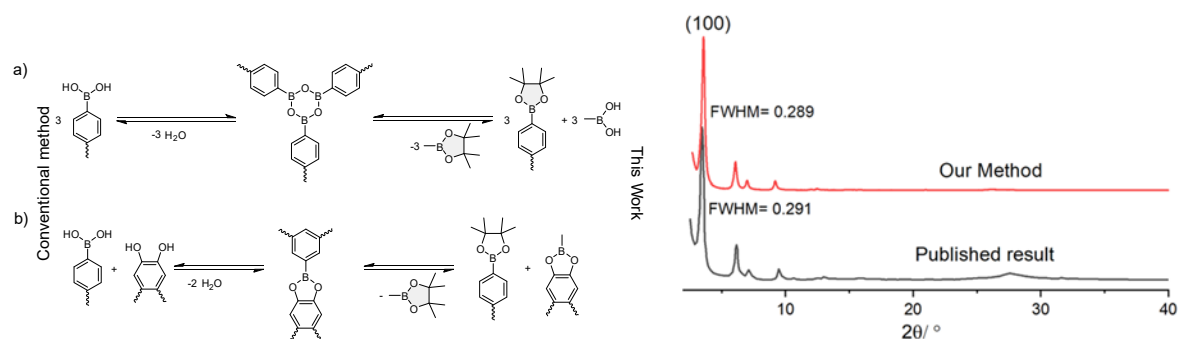
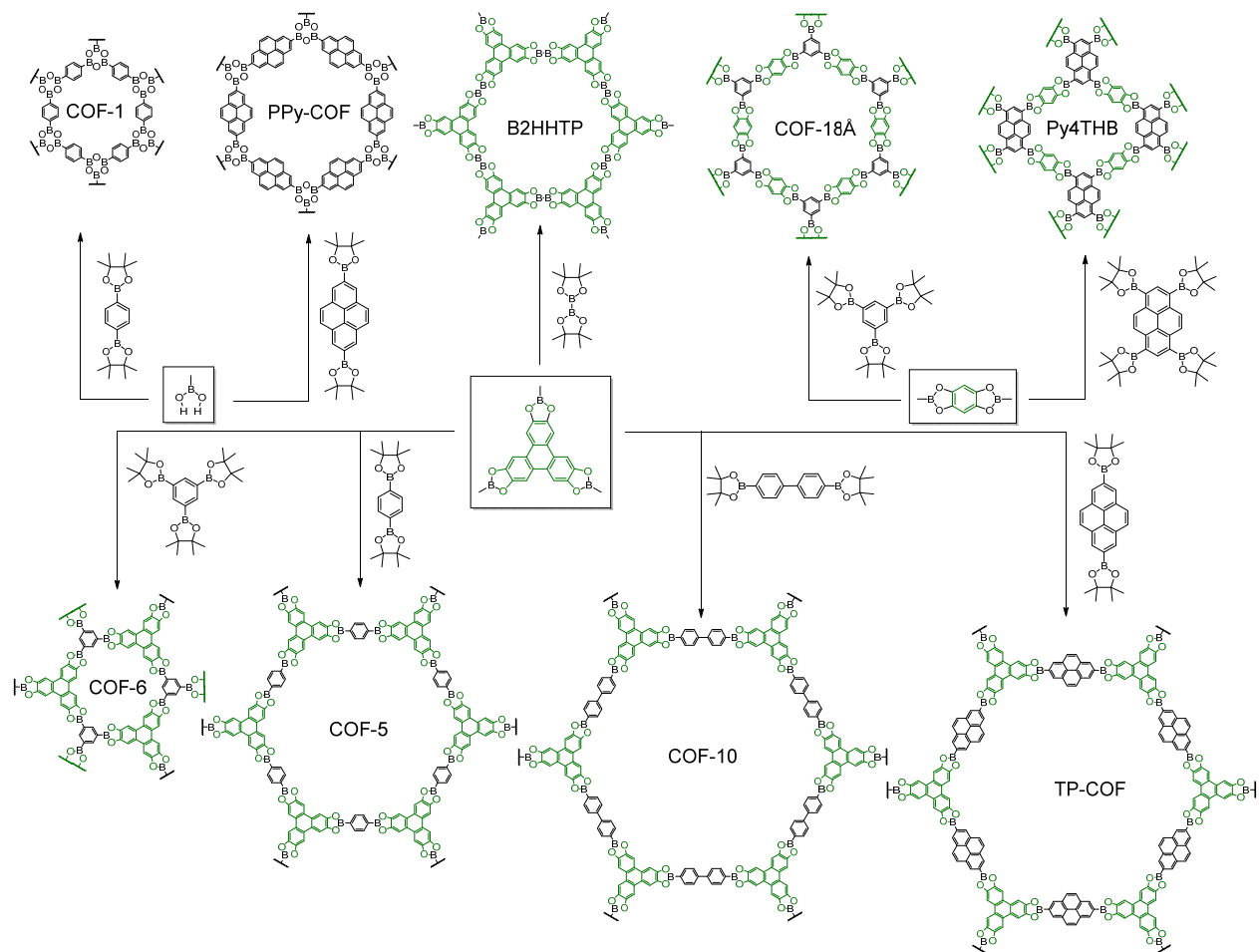


Fig. 7. (left) New transesterification/metathesis method for synthesis of boroxine/dioxaborole COFs in comparison to the conventional polycondensation. (right) PXRD of COF-5 prepared by conventional and metathesis polymerization showing similar order/crystallinity of both samples.

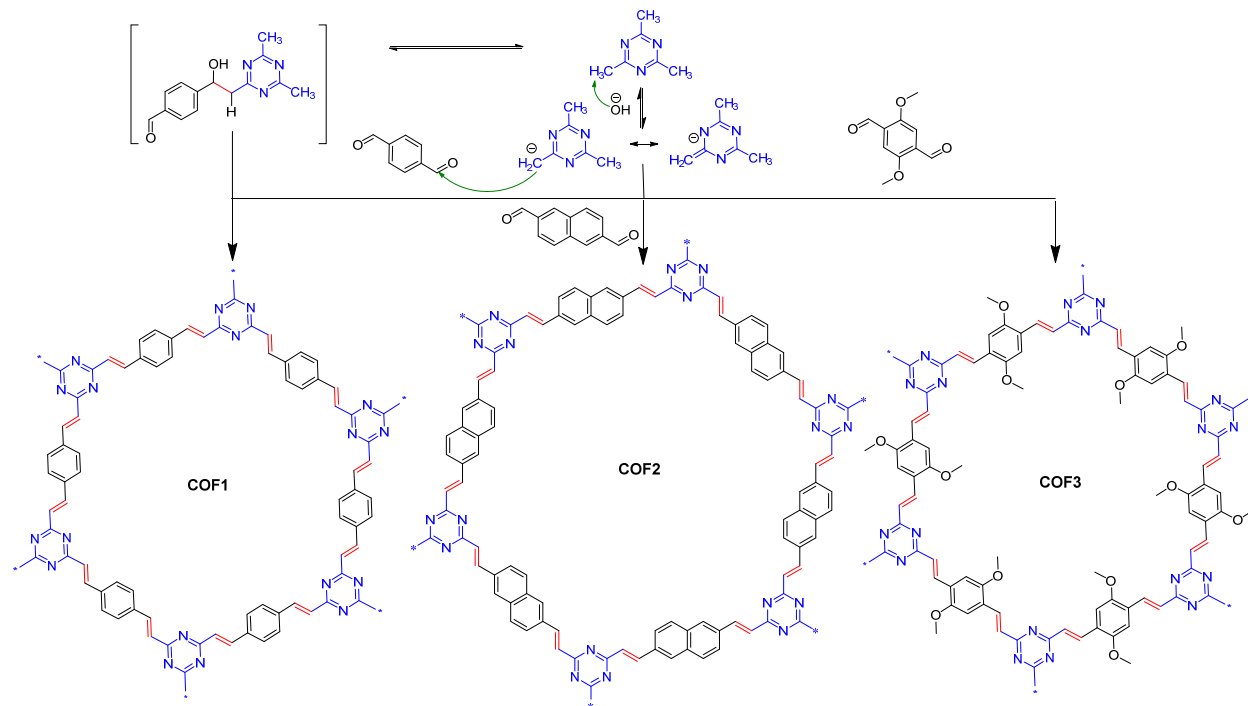
⁸ E. Hamzehpoor, A. Jonderian, E. McCalla, D.F. Perepichka, *J. Amer. Chem. Soc.* **2021**, *143*, 13274.



Scheme 6. Scope of the COF synthesis via transesterification and metathesis reactions.

3b. New aldol-type dynamic covalent polymerization for 2D polyarylenevinylene conjugated polymers.

In order to achieve higher chemical stability of 2D polymers and better electronic communication between their node (comparing to the imine and boronate-linked COF described above), we developed a new dynamic aldol condensation reaction between aromatic dialdehydes and trimethyltriazine (Scheme 7). The structure of these polymers was established by solid state ^{13}C NMR, Raman and FTIR (Fig. 8). The PXRD confirms excellent crystallinity of the resulting COFs (Fig. 9a,c). The crystallinity/order of these highly hydrophilic COFs further improves upon swelling in water which was attributed to solvation of triazine nitrogen and planarization of 2D sheets (Fig. 9d,e). See refs. 9,10 for further details.



Scheme 7. Synthesis of conjugated C-C linked COFs via aldol condensation of trimethyltriazine (dioxane / ethanol / 1 M aq. NaOH, 100 °C/3 days).

⁹ T. Jadhav, Y. Fang; W. Patterson; C.-H. Liu, E. Hamzehpoor, D. F. Perepichka, *Angew. Chem. Int. Ed.* **2019**, *58*, 13753.

¹⁰ T. Jadhav, Y. Fang, C.-H. Liu, A. Dadvand, E. Hamzehpoor, W. Patterson, A. Jonderian, R. Stein, D. F. Perepichka, *J. Am. Chem. Soc.* **2020**, *142*, 8862

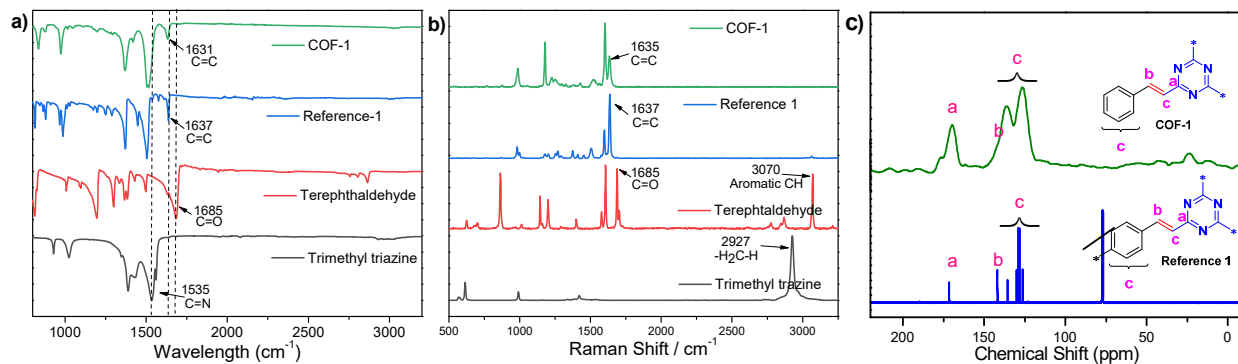


Fig. 8. (a) Comparison of the IR and Raman spectra of **COF-1** (green), reference **1** (blue), terephthalaldehyde (red) and trimethyltriazine (black); and (b) ^{13}C CP-MAS NMR spectra of **COF-1** (green, solid state), reference **1** (blue, CDCl_3 solution).

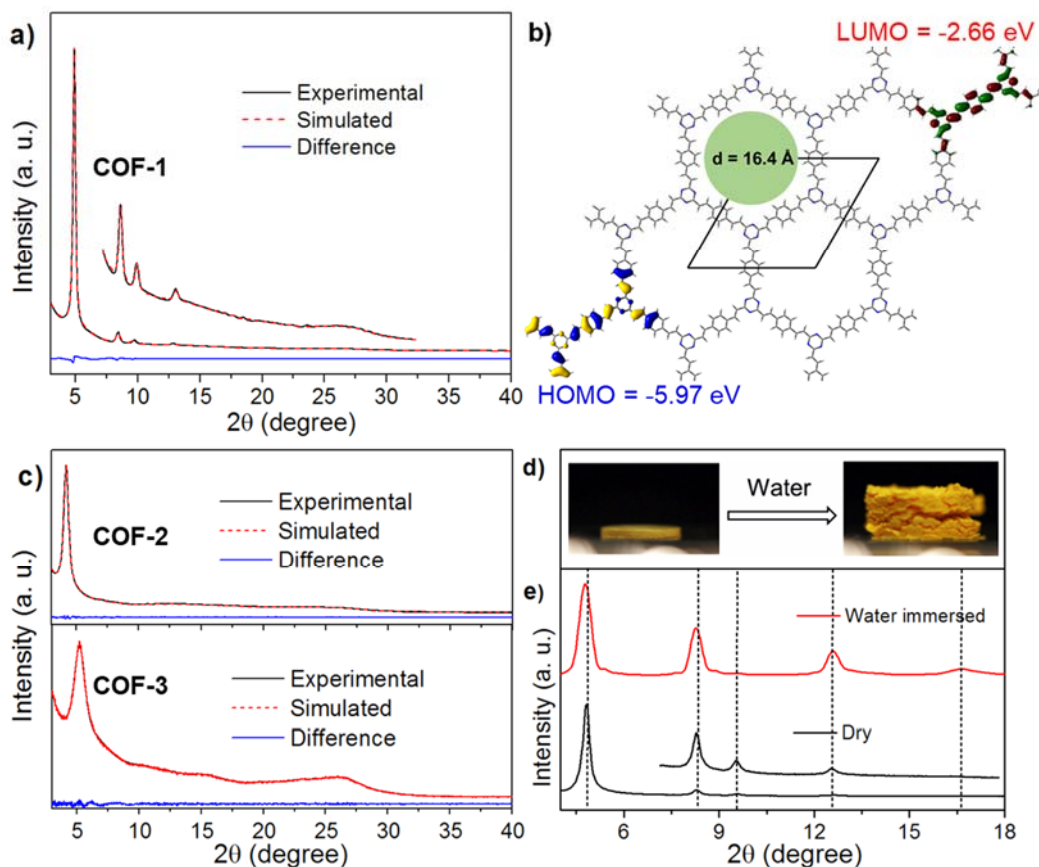
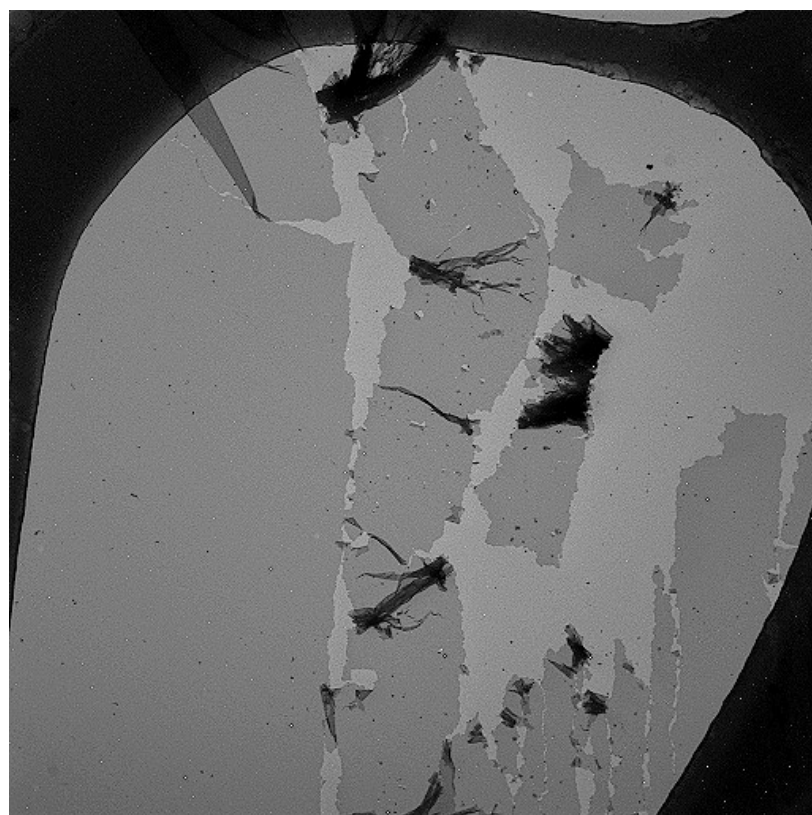


Fig. 9. (a, c) PXRD patterns and Pawley refinement of **COF-1** (Rwp = 1.95%, Rp = 1.55%), **COF-2** (Rwp = 2.00%, Rp = 1.48%) and **COF-3** (Rwp = 2.29%, Rp = 1.78%). (b) DFT optimized (B3LYP/6-31G(d)) model of **COF-1** with superimposed HOMO and LUMO topologies. Bottom left and top right displaying HOMO and LUMO structures, respectively. (d) Photograph showing swelling effect on dry **COF-1** pallette; before adding water drops (left) and after adding water drops (right). (e) Comparison of PXRD patterns of dry and water immersed **COF-1**.

4a. Synthesis of individual 2D polymer sheets by on-surface polymerization.

COFs prepared by solvothermal polymerization are obtained as polycrystalline powders consisting of stacked 2D sheets. We have developed¹⁰ a convenient method for exfoliating the COFs without damage to the sheet induce by convention sonication-assisted exfoliation. The method consists of gentle stirring of the COF in conc. H₂SO₄ or oleum (depending on basicity of the COF), followed by dilution with water and separation of non-exfoliated particles by centrifugation. Fig. 10 below shows large (several microns) sheets of C=C linked triazine 2D polymer P²PV (shown as COF-1 in Scheme 7). The AFM height analysis of such samples (not shown) suggest that they consist of 2-10 layers of 2D polymers (~1-5 nm thickness).



500 nm

FOV 6720 nm

Fig. 10. TEM image of exfoliated **P²PV** by ultrasonication in pure H₂SO₄ for 3 hours.

4b. Preparation of exfoliated 2D polymer sheets from COFs.

Although preparation of true single-layer 2D polymers by exfoliation is possible, it is a tedious process and manipulation of the resulting (solution-dispersed) 2D layers is complicated and might not be compatible with most device fabrication approaches. To solve this problem, we have also developed a fundamentally different approach to 2D polymers using surface-templated polymerization of halogenated monomers. The P²TANG polymer was synthesized by subliming halogenated TBTANG monomer on Au(111) substrate held at 200°C. Performing this reaction on clean surface in ultra-high vacuum allowed for the state-of-art characterization of P²TANG by Scanning Tunnelling Microscopy (STM) (collaboration with the group of Federico Rosei, INRS-University of Quebec and Giorgio Contini, CNR-Rome) and Angle-Resolved X-ray Photoelectron Spectroscopy. For the first time, these measurement revealed mesoscale order in on-surface synthesized 2D polymer and proved the existence of Dirac cone in its band structure. See ref. 11 for further information.

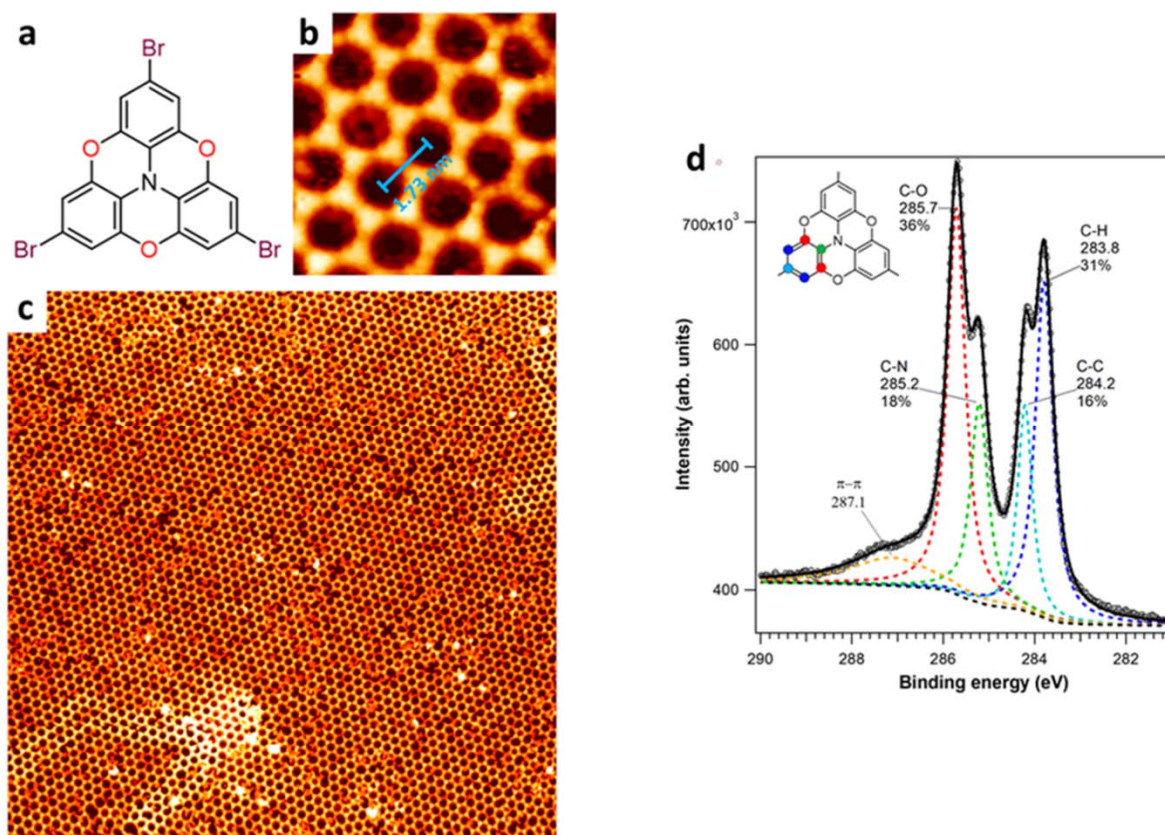


Fig. 11: a) TBTANG molecular structure. b) 15x15 nm² and c) 90x90 nm² STM images of TBTANG dosed on Au(111) kept at 210 °C (It= -0.99nA, Vt= -1.12V). d) C 1s XPS spectra (photon energy 450 eV) of P²TANG/Au(111) at 210 °C, the color scheme of the TBTANG molecules indicates the correspondence of C atoms and spectral components.

¹¹ G. Galeotti, F. De Marchi, E. Hamzehpoor, O. MacLean, M. R. Rao, Y. Chen, L. V. Besteiro, D. Dettmann, L. Ferrari, F. Frezza, P. M. Sheverdyaeva, R. Liu, A. K. Kundu, P. Moras, M. Ebrahimi, M. C. Gallagher, F. Rosei, D. F. Perepichka, G. Contini, *Nat. Mater.* **2020**, *19*, 874.

5) Unusual Luminescent Properties discovered in 2D polymer precursors.

During the project we have serendipitously discovered highly unusual solid state emission properties in monomer precursors. Specifically, highly efficient room-temperature phosphorescence (quantum yield >40% for HTANGO, a record-high value for heavy-atom free solids) has been established in TANGO series.¹²

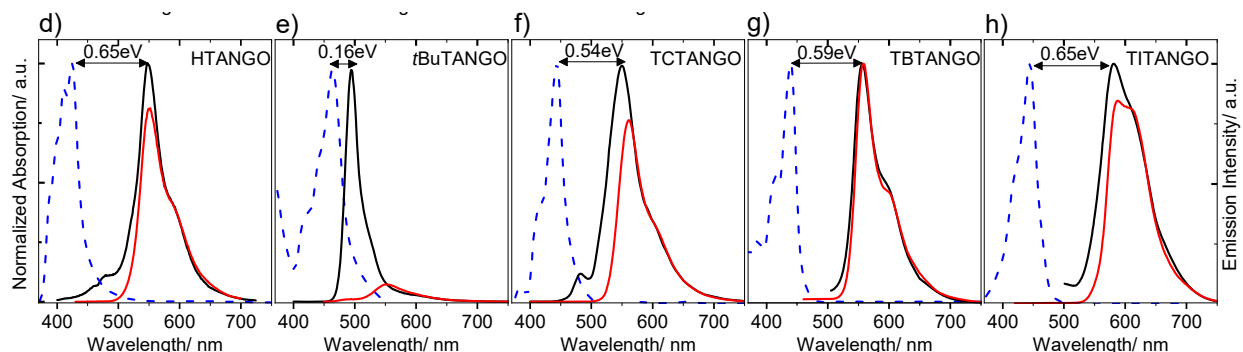


Fig 12. d-h) Solid state absorption (blue), steady state (black) and delayed (0.2 ms, red) emission of TANGO solids at room temperature. The arrows in (d-h) show Stokes shifts.

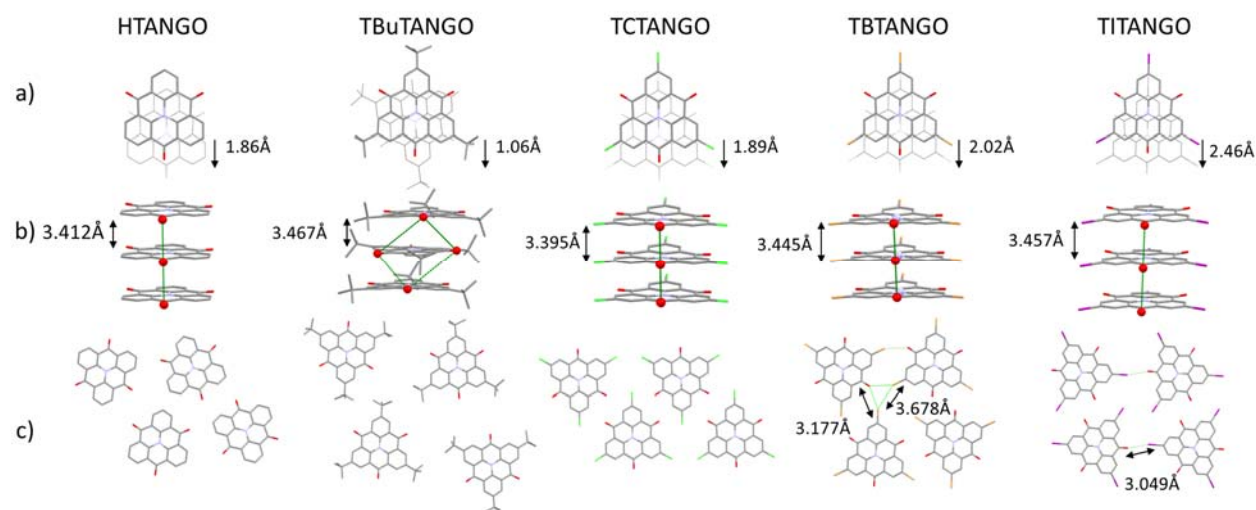


Fig. 13. X-ray crystallographic structure of TANGO derivatives. The rotation of TBTANGO derivative within its pi-stack is the reason for its drastically different luminescent properties (fluorescence).

¹² E. Hamzehpoor, D. F. Perepichka, *Angew. Chem. Int. Ed.* **2020**, 59, 9977.

We have also discovered unusual and highly efficient red luminescence if the solid monomer **3I-PTM^H** (Fig. 14).¹³ This property was shown to be a result of doping of the **3I-PTM^H** crystal with corresponding radical **3I-PTM^R**. The latter is a doublet-emitter with unusually long fluorescence lifetime, high color purity and very high photostability. The results will become the basis for the further development of luminescent 2D polymers with unusual multiplicity.

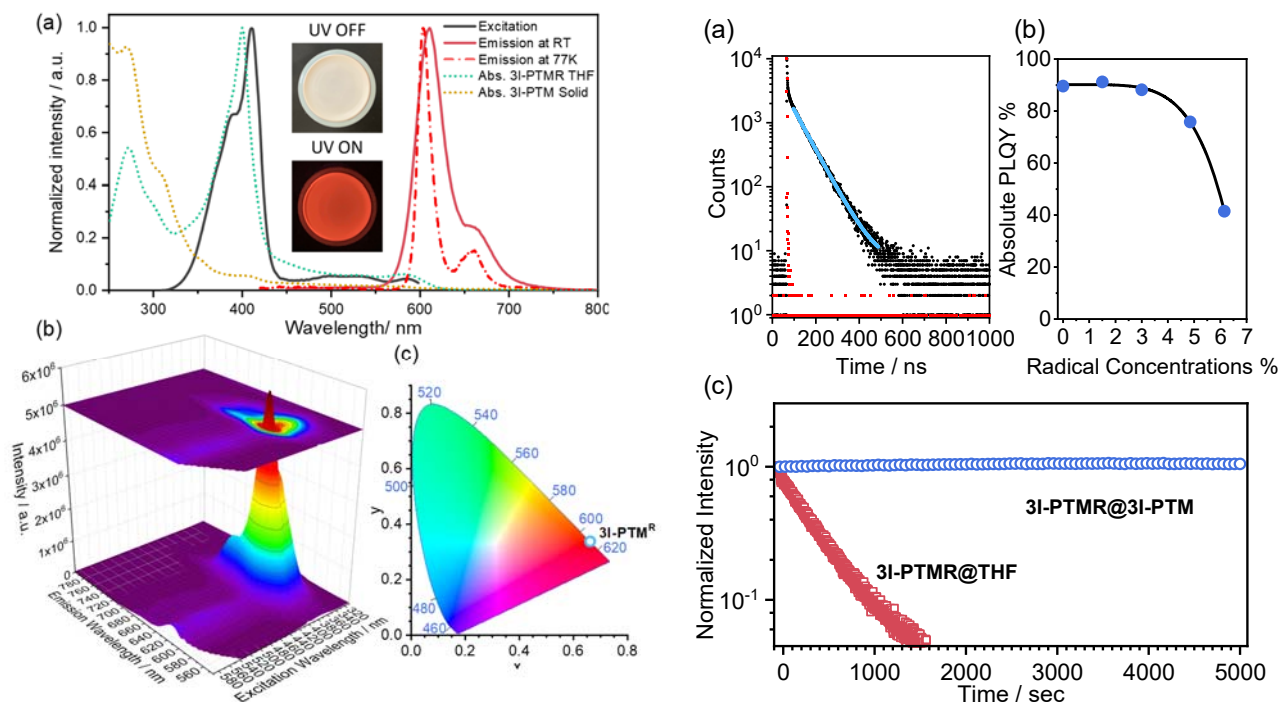


Fig. 14. (left) a) Absorption, excitation, and emission spectra of **3I-PTM^R@3I-PTM^H** and **3I-PTM^R** in THF; the inset shows photos of **3I-PTM^R@3I-PTM^H**. (b) 2D intensity contour plot of excitation and emission wavelength of **3I-PTM^R@3I-PTM^H**. (c) CIE 1931 coordinates of **3I-PTM^R@3I-PTM^H**. (right) a) **3I-PTMR@3I-PTM** emission kinetics at room temperature; red points represent the IRF. (b) PLQY dependence on concentration of **3I-PTM^R** in **3I-PTM^H** matrix. (c) Photobleaching studies of **3I-PTM^R@3I-PTM^H** and **3I-PTM^R** in THF in air under 400 nm irradiation.

¹³ C.-H. Liu, E. Hamzehpoor, Y. Sakai-Otsuka, T. Jadhav, D. F. Perepichka, *Angew. Chem. Int. Ed.* **2020**, 59, 23030.