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Fully Conjugated Three-Dimensional Thiazole-Based Covalent Organic Framework Exhibiting Hierarchical Microtubular Architecture

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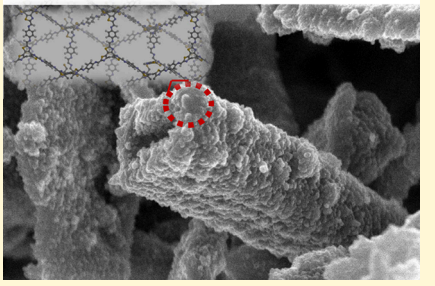
ABSTRACT: In this work, we report the synthesis of a pseudotetrahedral cyclooctatetraene building block based on a thiazole heterocycle ($COTz(CHO)_4$). The development of this building block required a challenging and carefully optimized synthetic strategy and represents a significant advance in the field of fully conjugated three-dimensional organic materials, as it constitutes one of the first examples of a thiazole-based heterocycle incorporated into three-dimensional frameworks. Polycondensation with *p*-phenylenediamine affords a highly crystalline covalent organic framework (COF) with permanent porosity, as confirmed by Rietveld refinement. The resulting material exhibits a high surface area and significant micropore volume. Morphological characterization by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) reveals a microtubular architecture. Furthermore, broad UV−vis absorption, strong photoluminescence, and an optical band gap of approximately 2.0 eV render the COTz-1P COF a promising candidate for future optoelectronic and photonic applications.



Three-dimensional covalent organic frameworks (3D COFs) have emerged as a distinctive class of porous crystalline materials whose spatially extended architectures offer unique physicochemical properties. Unlike their 2D counterparts, which rely on $\pi-\pi$ stacking of 2D polymer sheets to generate long-range order, 3D COFs typically exhibit intrinsically rigid, covalently connected networks defined by directional bond formation between building blocks in all three dimensions. The resulting structural diversity, combined with the possibility of tailoring pore environments and topologies, has positioned 3D COFs as promising platforms for a wide range of applications.

Since the first report by El-Kaderi et al.,[1] these materials have been widely explored and implemented in different fields, including gas storage and separation,[2−5] dye removal,[6,7] ion exchange,[8] drug delivery,[9] and catalysis.[10,11] However, due to the absence of a fully conjugated skeleton as a consequence of the typically sp^3 hybridized carbon atoms in the defining building blocks, extended electronic delocalization and potential optoelectronic applications of these frameworks have been limited.

One strategy to overcome this limitation is to design nonplanar conjugated molecular building blocks mimicking 3D building blocks such as tetrahedra. Recently, saddle-type pseudotetrahedral heterocyclic variants of cyclooctatetraenes have been implemented in COFs featuring diamond-like topologies.[12−15] These building blocks feature integrated thiophenes directly attached to the [8]annulene system. In order to allow the formation of COFs, functional groups are either directly attached[13] or connected through extended aromatic systems.[12,14,15] Here, we present a cyclooctatetraene-based COF building block composed of four conjugated thiazole units. Owing to the inherent saddle-shaped geometry imposed by the central [8]annulene core, this building block enables the formation of fully conjugated three-dimensional COFs as well as interpenetrated networks. The installation of aldehyde functional groups enables the formation of imine linkages, which serve as the connective nodes within the reticular framework.

Electron-deficient and chemically robust thiazole moieties incorporated into 2D COFs have been shown to impart favorable optoelectronic properties, enabling applications such as water splitting[16] and photocatalysis.[17] In 3D COFs, introducing thiazoles *via* postsynthetic modification of imine

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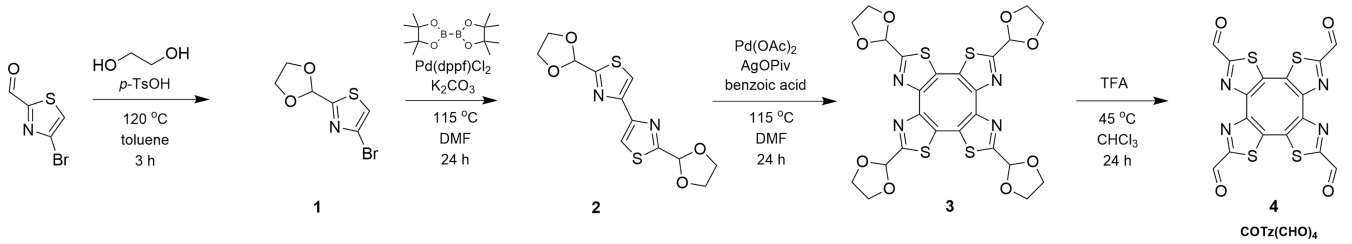
Scheme 1. Schematic Synthesis Route for the COTz(CHO)$_4$ Building Block



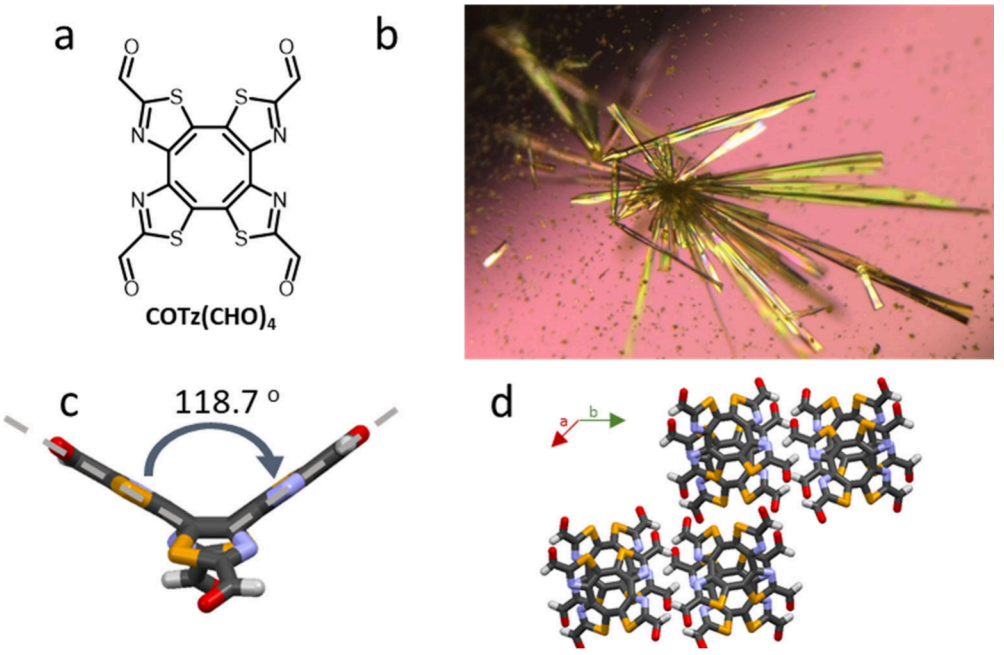


Figure 1. (a) Chemical structure of the COTz(CHO)$_4$ building block. (b) Optical microscopy image of representative single crystals obtained by slow evaporation of DCM/cyclohexane, showing a well-defined needle-like morphology. (c) Molecular structure derived from SC-XRD, highlighting the saddle-shaped conformation of the building block. (d) Crystal lattice viewed along the c-axis, highlighting the offset stacking of COTz(CHO)$_4$ in the packing arrangement.

linkages has been reported as an effective strategy for tuning optoelectronic properties.[18] However, this approach does not ensure complete conversion of imine bonds into thiazole linkages, which can be a limitation when aiming to modify an interpenetrated 3D COF. In contrast, the direct incorporation of thiazole units into COF building blocks has been less explored, primarily due to the challenging synthesis and limited reactivity of these heterocycles. Only a few examples have been reported to date, mainly based on thiazole−benzene fused motifs that give rise to either linear linkers[19−21] or trigonal-planar building blocks[17] that generate 2D COFs. In this context, the synthesis and characterization of fully conjugated three-dimensional COFs constructed from thiazole-containing building blocks represent a significant advance and open new horizons for this emerging class of electron-deficient materials.

To access the structurally complex saddle-type thiazole building block, a suitable synthetic strategy was developed (see Supporting Information, Linker Synthesis). The initial approaches focused on the design of thiazole-based cyclooctatetraene (COTz) systems bearing aldehyde functional groups attached to phenyl rings. Alternative routes, such as introducing the aldehydes in the final step onto a preformed COTz *via* a Vilsmeier reaction,[22] or carrying unprotected aldehyde groups throughout the synthetic pathway,[12] proved unsuccessful. Likewise, protection of the aldehydes using classical protecting groups, such as acetals or thioacetals, did not yield satisfactory results.

Consequently, efforts were redirected toward the synthesis of the COTz core with protected aldehyde groups directly attached, analogous to our previous work on cyclooctatetrathiophene-based building blocks.[13] During the palladium-catalyzed dehydrogenative cyclodimerization of diheteroaryl precursors, it was observed that commonly used solvents such as toluene hindered the reaction, likely due to interactions with the thiazole heterocycles. Replacing this aromatic solvent with a more inert alternative, dimethylformamide (DMF), enabled the successful synthesis of the thiazole-based cyclooctatetraene. Furthermore, the commonly employed protecting group neopentyl glycol (2,2-dimethylpropane-1,3-diol) was replaced with ethylene glycol (ethane-1,2-diol), as the former could not be efficiently removed during the deprotection step.

Starting from a prefunctionalized thiazole heterocycle (4-bromo-2-formylthiazole), the first step involved protection of the aldehyde group using ethylene glycol and *p*-toluenesulfonic acid (*p*-TsOH) as a catalyst, affording compound **1** (Scheme 1). With the aldehyde protected, a one-pot two-step Suzuki-cross-coupling was carried out using bis(pinacolato)diboron and Pd(dppf)Cl$_2$, yielding compound **2**. To form the central cyclooctatetraene (COT) core, a previously reported[22] Pd(OAc)$_2$/Ag(OPiv)-catalyzed dehydrogenative cyclodimeriza-

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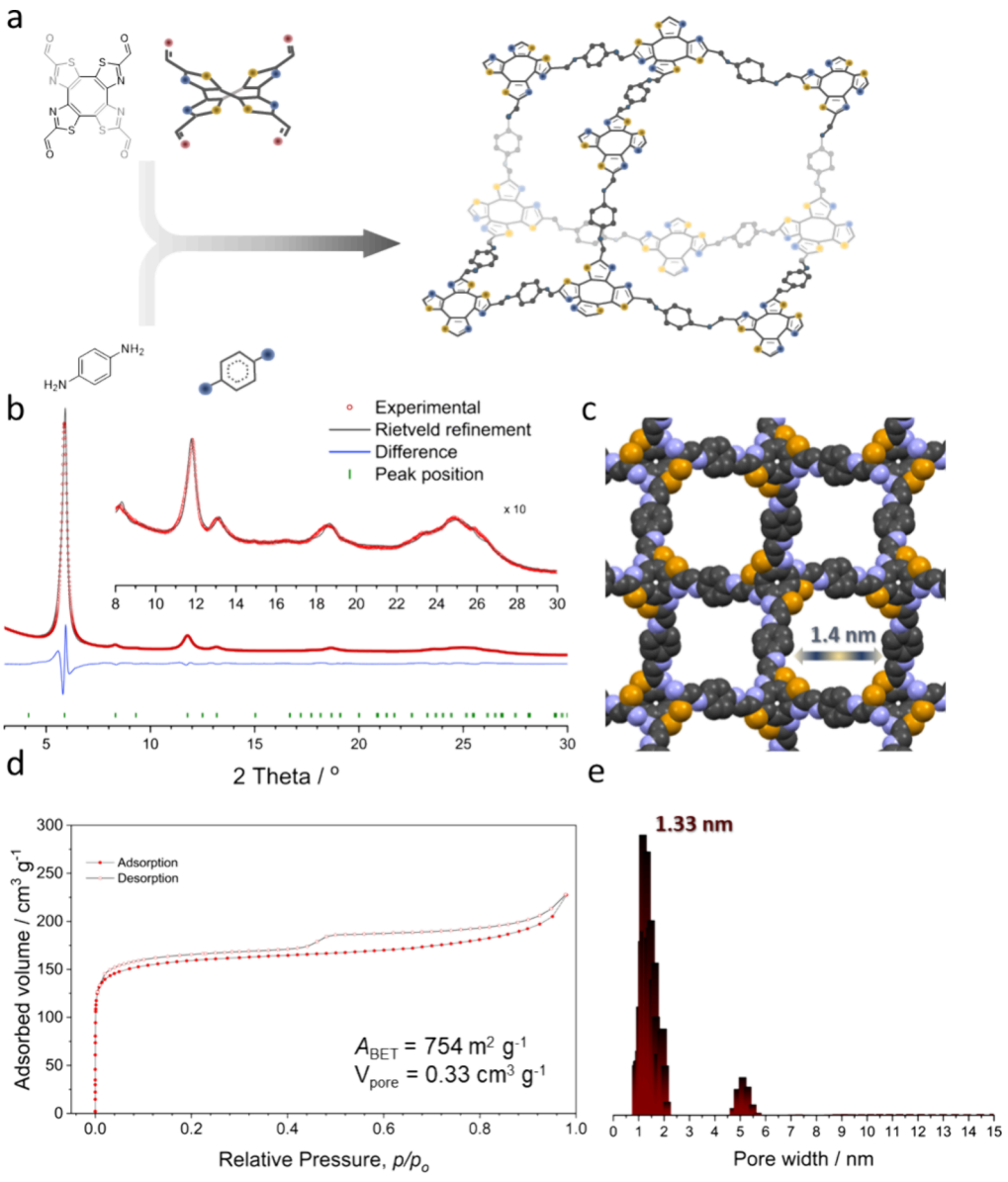

Figure 2. (a) Schematic representation of the COTz-1P COF formation through the condensation of the tetrahedral building block $COTz(CHO)_4$ and *p*-phenylenediamine (PPD). (b) Experimental PXRD pattern (red dots), calculated pattern after Rietveld refinement (black line), and difference between experimental and calculated data (blue). Inset: 10-fold magnification of the PXRD pattern from 2 theta 8° to 30° to visualize the less intense reflections. (c) Refined structural simulations indicate that the COF adopts a diamond-type (dia) topology featuring square-shaped pores when viewed along the *c*-axis and exhibits a 7-fold interpenetrated framework (dia-c7). (d) Type I(b) nitrogen sorption isotherm recorded at 77 K with the NLDFT-based pore size distribution modeled for cylindrical pores. (e) Pore size distribution of COTz-1P presenting a maximum at 1.33 nm.

tion was performed. A key modification was implemented in this step: toluene, the solvent typically used in such dehydrogenation reactions, was replaced by *N*,*N*-dimethylformamide (DMF) to avoid the formation of undesired side products arising from the reactivity of compound **2** with toluene. The use of DMF effectively suppressed side reactions and afforded compound **3** in good yield. Finally, deprotection of the aldehyde groups was achieved using trifluoroacetic acid (TFA) at 55 °C, yielding the target $COTz(CHO)_4$ building block as a bright yellow powder. The successful synthesis and purity of the building block were confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectrometry (MS) (see the Supporting Information). This four-step route provides an efficient and modular approach to access functionalized cyclooctatetrathiazoles in overall good yields.

To confirm the expected pseudotetrahedral saddle-shape of the linker (Figure 1a), single crystals of $COTz(CHO)_4$ (compound **4**) were grown and examined by single-crystal X-ray diffraction (SC-XRD). Crystals suitable for structure elucidation were obtained through slow solvent evaporation of a dichloromethane (DCM) solution layered with cyclohexane in a 10 mL glass vial (see the Supporting Information for experimental details). The resulting bright yellow crystals displayed a well-defined needle-like morphology with uniform dimensions (Figure 1b) The structure was solved in the monoclinic space group *C2/c* with unit cell parameters a = 27.4820(7) Å, b = 8.57151(7) Å, c = 19.2314(5) Å, and α =

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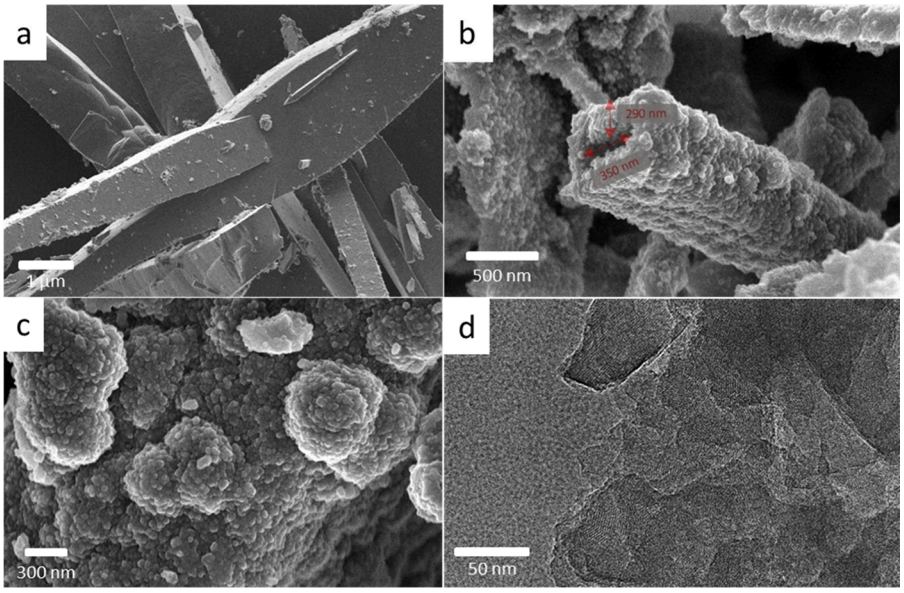

Figure 3. (a) SEM image of molecular crystals of the COTz(CHO)$_4$ linker, displaying microrod morphology. (b) SEM image of the COTz-1P COF showing the microtubular morphology; red arrows indicate the hollow core and wall dimensions. (c) High-magnification SEM image highlighting the granulated surface texture of the microtube walls. (d) TEM image revealing the presence of multiple intergrown crystalline domains within the hollow rod morphology.

90°, β = 132.842(4)°, γ = 90°. The solid-state molecular structure clearly confirms the nonplanar, saddle-shaped conformation of the building block (Figure 1c), defined by an angle of 118.7° between the aldehyde groups on opposite sides of the eight-membered ring. This geometry further propagates into a wave-like packing motif in the molecular crystal, in which the [8]annulene−thiazole moieties adopt an offset arrangement within the lattice (Figure 1d). The carbonyl oxygen atoms are repelled by the thiazole nitrogen lone pairs and all point toward the endocyclic sulfur atoms. Complete crystallographic and refinement data are provided in the Supporting Information.

The COTz-1P COF was synthesized *via* a Schiff-base condensation between COTz(CHO)$_4$ and *p*-phenylenediamine (PPD) in a 1:2 molar ratio under solvothermal conditions (Figure 2a). Solvent screening revealed that a 1:1 mixture of benzyl alcohol and 1,4-dioxane provided the best results regarding crystallinity. Additionally, aniline was introduced as a modulator to further enhance framework order. This modulator strategy has been previously demonstrated as an effective approach for promoting crystallinity and even enabling single-crystal growth in 3D COFs.[23] In our earlier work on fully conjugated 3D COFs,[13] we also showed that the introduction of reaction modulators significantly improved long-range order. In this context, the presence of an excess of a terminal amine improves the reversibility of imine bond formation (*via* competing reactions), facilitating dynamic error correction during framework assembly, and ultimately favoring the growth of highly crystalline COF structures.

Powder X-ray diffraction (PXRD) analysis of COTz-1P revealed a set of well-defined low-angle reflections at 2 theta = 5.86°, 8.19°, 11.82°, and 13.09°, which can be indexed to the (020), (220), (040), and (240) crystallographic planes, respectively (Figure 2b). The observation of several high-angle reflections between 20° and 30° 2 theta further corroborates the high crystallinity of the material. Structural modeling was carried out starting with the tetragonal $I4_1$ space group and a diamond-type topology with 7-fold interpenetration (dia-c7) (Figure 2c and Supporting Information section 7). The proposed structural model reproduces all major features of the experimental pattern and was validated through Rietveld refinement (R_{wp} = 8.51%), which yielded good agreement between the calculated and observed intensity distributions. The refined lattice constants are $a = b$ = 30.11 Å, c = 4.44 Å and $\alpha = \beta = \gamma$ = 90°. The close correspondence between experimental and simulated patterns supports the validity of the assigned topology and space group. The presence of broadened reflections is consistent with nanoscale domain sizes and possible local distortions of the soft lattice, as also suggested by TEM analysis (Supporting Information). Collectively, the PXRD data confirm that COTz-1P crystallizes as a highly ordered, multidomain framework consistent with the proposed interpenetrated dia-c7 architecture.

Nitrogen sorption analysis was performed at 77 K (Figure 2d) upon prior activation of the material with supercritical CO_2 at 40 °C and 100 bar pressure. The type I(b) isotherm of the COTz-1P exhibits a pronounced uptake at low relative pressures and a Brunauer−Emmett−Teller surface area of 754 m^2 g^{-1} with a total pore volume of 0.33 cm^3 g^{-1}, characteristic of a predominantly microporous framework. The steep initial rise is followed by a gradual increase in adsorbed volume across intermediate pressures, indicating the presence of additional textural mesoporosity that contributes to gas uptake beyond the micropore regime. The slight hysteresis observed between the adsorption and desorption branches points to capillary condensation within mesopores or interparticle voids. Collectively, these features confirm that the material combines well-defined microporosity with supplementary mesoporous contributions. The pore-size distribution profile (Figure 2e) displays a dominant and well-defined population of ultramicropores and micropores centered between approximately 1 and 2 nm, with a maximum at 1.33 nm, indicating that the material possesses a highly uniform and tightly distributed intrinsic pore network. This narrow distribution is consistent

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with a well-ordered framework in which the pore apertures arise directly from the periodicity of the organic linkers and the connectivity of the lattice. In addition to this primary microporous domain, a secondary and significantly less intense feature appears around 4−5 nm in the pore size distribution. The presence of this minor mesoporous contribution suggests the existence of additional textural voids, likely originating from interparticle packing effects, modest structural defects, or partial aggregation.

Scanning electron microscopy (SEM) reveals a striking morphological correlation between the precursor linker and the resulting COF crystallites. The addition of the COTz-$(CHO)_4$ precursor as a suspension under the above-mentioned conditions, followed by solvothermal COF formation, suggests that a template-assisted mechanism governs framework growth. As shown in Figure 3a, single crystals of the cyclo-octatetrathiazole COTz$(CHO)_4$ linker exhibit a pronounced anisotropic habit, forming high-aspect-ratio microrods driven by the strong directionality of its supramolecular self-assembly. Notably, this anisotropic morphology is largely preserved in the resulting COF crystallites (Figure 3b), despite the substantial chemical transformation occurring during framework formation. Such morphological inheritance is consistent with previous reports where preorganized aggregates or seeds direct anisotropic COF growth paths.[24,25] These studies demonstrate that kinetically favored growth along a pre-established structural axis can dominate over isotropic polymerization in reticular frameworks.[26] We therefore propose that the reaction proceeds *via* kinetically controlled anisotropic growth, in which imine condensation and framework propagation are preferentially accelerated along the stacking axis of the preassembled linker rods, while lateral growth is comparatively suppressed. The evolution of these primary rod-like crystallites into the observed microtubular structures is attributed to a thermodynamically driven inside-out Ostwald ripening process.[27−30] In this scenario, under solvothermal conditions, the metastable inner cores of the initially solid aggregates, possessing higher surface energy and defect density, undergo selective dissolution and redeposition onto the more crystalline exterior shell. As annotated in Figure 3b, the resulting tubes exhibit a hollow core with characteristic wall thicknesses of 290 nm and outer diameters of 350 nm. Furthermore, high-magnification SEM imaging shows that the external walls of these microtubes possess a distinct granulated texture (Figure 3c). This hierarchical morphology is further elucidated by high-resolution transmission electron microscopy (HRTEM), which reveals that the COF architecture is composed of multiple crystalline domains (Figure 3d). This cooperative mechanism, combining linker-directed anisotropic assembly and condensation with subsequent morphological ripening, underscores the critical role of precursor geometry in defining the macroscopic architecture of the 3D fully conjugated COTz-1P COF.

The optical properties of the synthesized COTz-1P COF were characterized using powder samples. The normalized UV−vis spectrum (Figure 4a) displays a broad and intense absorption feature ranging from the UV to about 600 nm, which is attributed to $\pi-\pi^*$ transitions within the extended conjugated framework. The gradual onset and smooth curvature of the absorption edge suggest a wide distribution of electronic states and moderate exciton delocalization, a phenomenon frequently observed in porous organic materials with extended aromatic domains.[31,32] This is further quantified

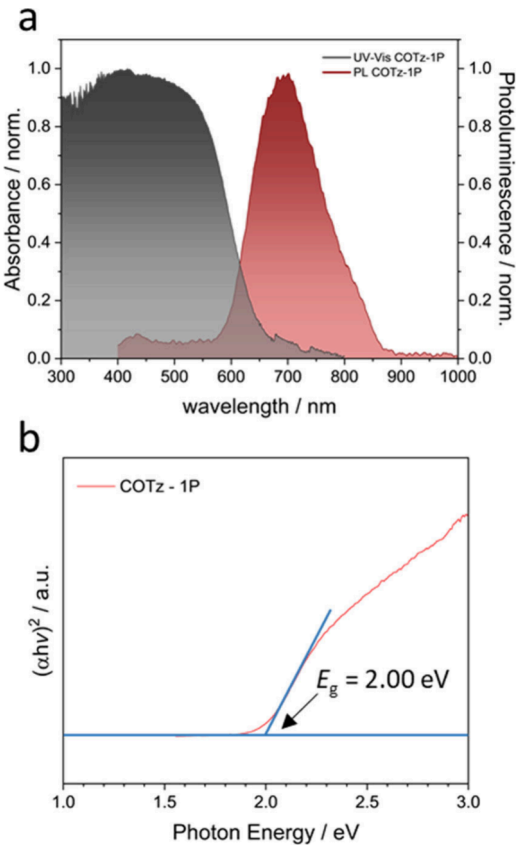

Figure 4. (a) UV−vis absorption (black) and photoluminescence (red) spectra of the COTz-1P COF as a bulk material. (b) Band gap determination *via* Tauc plot for COTz-1P COF, assuming a direct band gap.

by the Tauc plot (Figure 4b), which reveals a direct optical band gap of E_g = 2.00 eV. The PL spectrum reveals a pronounced emission band centered at approximately 710 nm. The substantial Stokes shift, measured from the absorption onset to the PL maximum, indicates significant excited-state relaxation. This likely involves structural reorganization or the localization of excitons at low-energy sites prior to radiative decay, behavior characteristic of COFs where strong interunit coupling or planarization stabilizes emissive states.[33,34] The intense red emission underscores the potential of COTz-1P for photonic applications requiring deep-red or near-infrared (NIR) output.

The optical band gap was estimated from a Tauc plot constructed using the direct-allowed transition formalism $(\alpha h\nu)^2$ versus photon energy (Figure 4b). A well-defined linear region is observed near the absorption edge, enabling reliable extrapolation to yield an optical band gap of 2.00 eV. The direct-gap behavior inferred from the Tauc analysis suggests that the lowest-energy transition in COTz-1P is optically allowed and does not require phonon participation, a feature advantageous for applications involving light harvesting or emission. Overall, the combined absorption, emission, and Tauc analyses confirm that COTz-1P is a direct-gap semiconductor exhibiting strong visible-light absorption and efficient red photoluminescence, making it a promising candidate for optoelectronic and photonic device integration. The comparison between the optical properties reported in this work and those of previously described COFs constructed from analogous thiophene building blocks[13] (Figure S16)

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provides a clear illustration of the influence of heterocycle structure on the optoelectronic behavior of fully conjugated frameworks. In the thiophene-based analog, the optical band gap is substantially larger - by approximately 0.32 eV - than that of the thiazole-containing COF presented here. This difference highlights the ability of thiazole units, owing to their more electron-deficient character and enhanced donor−acceptor polarization in the lattice, to stabilize low-lying excited states and thereby narrow the optical gap of the framework. Consequently, the use of thiazole motifs in COF construction appears to be particularly advantageous for applications where reduced band gaps are desirable, such as photocatalytic hydrogen evolution,[20,35] broadband light harvesting,[21] and near-infrared photonics.[36]

In this study, we have demonstrated the development of a COF linker based on a cyclooctatetrathiazole backbone bearing aldehydes directly attached to the heterocycle. The synthesis of this building block was challenging due to the low reactivity of the thiazole moiety, requiring the exploration of a broad spectrum of synthetic strategies and modifications to previously reported synthetic pathways. The crystallographic characterization of the $COTz(CHO)_4$ building block established a pronounced molecular saddle shape, which served as the basis for the construction of a 3D conjugated COF featuring diamond-type topology.

The solvothermal co-condensation of the $COTz(CHO)_4$ node with a compact linear linker, *i.e.*, *p*-phenylenediamine, in the presence of modulator agents, led to a highly crystalline 3D conjugated COF with an exceptionally high surface area and a microtubular morphology. The optical properties obtained with UV−vis and photoluminescence measurements support the extension of the conjugated system within the lattice, resulting in red-shifted optical features. The decreased optical band gap compared to related cyclooctatetraene-based COFs makes the COTz-1P COF a promising candidate for applications where these characteristics are key, such as photocatalysis, light harvesting or near-IR photonics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.6c00101.

Synthetic procedures, single-crystal characterization data, NMR and MS spectra, crystallographic data for the $COTz(CHO)_4$ building block, SEM and TEM images, UV−vis absorption and PL spectra, optical band gap comparison, and structural analysis for COTz-1P COF (PDF)

Crystallographic information file for $COTz(CHO)_4$ (CIF)

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Author Contributions

I.M.-A. conducted the synthesis and characterization of the final building block and its synthetic intermediates, prepared single crystals for analysis, synthesized and optimized the COTz-1P COF, performed optical analyses, and wrote the original draft, with contributions to review and editing. J.S. carried out single-crystal X-ray diffraction (SC-XRD) analysis and structure refinement. M.D. performed Rietveld refinement of the COTz-1P COF and acquired high-resolution transmission electron microscopy (HRTEM) images. T.X. conducted optical analyses and contributed to the molecular design of the COTz-1P COF model. I.H. and T.B. conceived the project, contributed resources, and were responsible for supervision, project administration, funding acquisition, and manuscript review and editing.

Notes

The authors declare no competing financial interest.

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