



OPEN Calcium-molybdenum-cobalt-2-methylimidazole trimetallic organic framework as a saturable absorber for passive mode-locked thulium–holmium doped fiber lasers

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Ultrafast fiber lasers operating in the 2 μm spectral region require robust and highly nonlinear saturable absorbers (SAs) to achieve stable mode-locking. This study demonstrates that a calcium-molybdenum-cobalt-2-methylimidazole (CaMoCo-MIM), a trimetallic organic framework (TMOF), functions as an efficient SA, enabling stable and self-starting mode-locking pulse in a thulium–holmium-doped fiber laser (THDFL). The CaMoCo-MIM exhibits excellent nonlinear optical performance, achieving a high modulation depth of 36.2%, surpassing many previously reported MOF-based SAs, as supported by the comparative data presented in this study. Stable soliton pulse generation was realized at a pump power of 307 mW, producing a central wavelength of 1895.21 nm, a 3 dB spectral bandwidth of 3.03 nm, and a pulse duration of 1.25 ps. A time-bandwidth product (TBP) of 0.316 indicates a nearly chirp-free pulse. Long-term operation over four hours confirmed robust stability with a constant repetition rate of 14.6 MHz. This TMOF establishes a high-modulation-depth SA in next-generation lasers.

Keywords calcium-molybdenum-cobalt-2-methylimidazole, trimetallic organic framework, saturable absorber, thulium-holmium doped fiber lasers, mode-locking pulse

Mode-locked fiber lasers have established themselves as among the most vital ultrafast lasers in contemporary photonics. Mode-locked fiber lasers serve as critical ultrafast sources, reliably producing periodic sequences of light pulses ranging from picoseconds to femtoseconds¹. Such lasers can deliver high peak powers² while maintaining exceptionally stable, well-defined repetition rates³, making them indispensable for high-speed optical measurements and nonlinear optical applications. Mode locking enables the creation of coherent pulse trains with high temporal consistency by maintaining a stable phase relationship between the longitudinal modes within the laser cavity. Owing to their waveguide-based architecture, all-fiber mode-locked lasers exhibit significant advantages over traditional solid-state counterparts, such as inherent alignment-free operation, enhanced mechanical stability, and cost efficiency⁴. Due to these advantages, mode-locked fiber lasers have emerged as compelling platforms for both academic research and real-world applications.

The gain medium is the primary factor that determines the operating wavelength of ultrafast fiber lasers. The emission bands of optical fibers doped with ytterbium, erbium, and thulium/holmium are around 1 μm , 1.5 μm , and 2 μm , respectively⁵. Recent years have seen a significant increase in research concerning 2 μm fiber lasers. Fiber lasers operating at 1 μm and 1.5 μm are already widely used in industrial processes and

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optical communications⁶. However, the 2 μm region is receiving increasing attention. This heightened interest arises from numerous inherent benefits, notably the protection against eye injury⁷, enhanced aqueous-phase absorption in biological tissues⁸, and elevated sensitivity for gas detection and environmental monitoring⁹. Furthermore, operation at longer wavelengths can alleviate specific nonlinear propagation effects in optical fibers, thereby supporting more stable pulse formation and higher pulse energies¹⁰. As a result, mode-locked fiber lasers have found expanding roles in applications such as precision micromachining, medical diagnostics and therapy, ultrafast spectroscopy, and remote sensing, underscoring their versatility and continued relevance as ultrafast laser platforms^{11–13}.

Thulium ions (Tm^{3+}) and holmium ions (Ho^{3+}) are excellent active dopants for fiber lasers operating around 2 μm . When both ions are incorporated into the same fiber, an efficient cross-relaxation and energy-transfer process significantly enhances pump utilization: laser diodes (LDs) operating near 1.55 μm can excite Tm^{3+} ions, which then transfer energy to Ho^{3+} ions via cross-relaxation and energy-transfer processes, overcoming the limited availability of efficient direct pump sources for Ho^{3+} and increasing the effective pump absorption and quantum efficiency¹⁴. This cooperative interaction improves system performance, reduces thermal load, and enables more compact laser designs. In addition, Tm^{3+} - Ho^{3+} co-doped fibers exhibit a broader emission and gain bandwidth around 2 μm compared to singly doped fibers, allowing greater wavelength tunability and flexibility for mid-infrared applications¹⁵. These characteristics make Tm - Ho co-doped fibers a promising platform for high-efficiency and broadband 2 μm fiber lasers¹⁶.

As nonlinear elements with intensity-dependent absorption, saturable absorbers (SAs) are often used to achieve passive mode-locking¹⁷. Ultrafast laser systems have widely used traditional SAs, such as semiconductor saturable absorber mirrors (SESAMs). However, their relatively low damage threshold¹⁸, limited operational bandwidth¹⁹, and high fabrication cost²⁰ have motivated the search for alternative SAs. Recently, metal-organic frameworks (MOFs) have emerged as promising options due to the unique way their structures function. MOFs are crystalline architectures constructed from organic ligands coordinated to metal ions or clusters. It is possible to tailor these networks to display desired physical and chemical characteristics²¹. They have various practical applications due to their large surface area and intrinsic high porosity, such as gas storage²², gas separation²³, catalysis²⁴, chemical sensing²⁵, and energy storage²⁶. More recently, these advantageous features have sparked growing interest in exploiting MOFs for nonlinear optical applications, particularly for use as SAs in fiber laser systems^{27–29}.

The majority of reported MOF SAs have been demonstrated in erbium-doped fiber lasers operating at 1.5 μm . It occurred despite the rapid progress in the development of MOF-based nonlinear optical materials³⁰. While these works have confirmed the feasibility of employing MOF for ultrafast pulse modulation, their extension to longer wavelengths has received comparatively limited attention. In particular, investigations of MOF-assisted mode-locking in the 2 μm spectral region remain scarce, especially in thulium-holmium doped fiber laser (THDFL) systems, where suitable SAs are still under active exploration³¹. This research gap is notable given that several MOF systems have exhibited broadband optical absorption extending into the near- and mid-infrared regions, suggesting their potential compatibility with 2 μm ultrafast laser operation³². Recent studies on zinc-, copper-, cobalt-, and nickel-based MOFs have demonstrated high modulation depths and strong third-order nonlinear optical responses, key parameters for achieving self-starting, stable passive mode-locking³³.

Furthermore, the inherently porous MOF architecture facilitates efficient thermal dissipation and moisture absorption, offering distinct advantages for managing heat accumulation and maintaining performance stability under high optical intensities³⁴. Strong absorption near 2 μm has also been reported for selected MOF structures, reinforcing their suitability for thulium- and holmium-doped fiber laser systems³⁵. In several instances, SAs derived from MOFs have demonstrated modulation depths exceeding those of conventional SAs, including topological insulators and transition-metal dichalcogenides, thereby mitigating spectral filtering-induced instabilities and facilitating scalable ultrafast performance³⁶. However, existing studies have primarily focused on a narrow subset of MOF compositions and metal centers, leaving the nonlinear optical behavior, long-term stability, and wavelength adaptability of many alternative MOF systems insufficiently explored³⁷. Improving the stability and pulse control of MOF-based SAs for the next generation of ultrafast fiber lasers needs ongoing study into new MOF designs and metal-ligand pairs that provide strong saturable absorption.

Motivated by this need, this study investigates the application of calcium-molybdenum-cobalt-2-methylimidazole (CaMoCo-MIM), a trimetallic organic framework (TMOF), for passive mode-locking in a THDFL operating at approximately 2 μm wavelength. In this work, MIM refers to 2-methylimidazole, an organic ligand that coordinates with metal ions to form the CaMoCo-MIM TMOF. The molecular structure consists of calcium (Ca), molybdenum (Mo), and cobalt (Co) metal centers, each coordinated to 2-methylimidazole ligands, forming a metal-organic coordination framework. The nitrogen atoms in the imidazole ring act as coordination sites, allowing strong bonding with the transition metal ions and facilitating the formation of a stable hybrid structure³⁸. The nonlinear optical absorption of CaMoCo-MIM mainly originates from the electronic structure of the transition metal ions and the conjugated organic ligand. The presence of Mo and Co ions introduces partially filled d-orbitals, which enable electronic transitions such as d-d transitions and metal-ligand charge transfer (MLCT)³⁹. Under high optical intensity, electrons are excited from the ground state to higher energy states, leading to state filling and saturation of available absorption centers. As excited states become occupied, further photon absorption is reduced, leading to saturable absorption. This combination of transition-metal electronic transitions and ligand-assisted charge transfer leads to strong nonlinear optical behavior, making CaMoCo-MIM a suitable saturable absorber for generating stable mode-locked pulses in fiber laser systems.

In this context, the advantages of the proposed CaMoCo-MIM SA are mainly due to its strong nonlinear optical response and effective pulse generation in the 2 μm spectral region. The CaMoCo-MIM SA exhibits an exceptionally high modulation depth of 36.2%. The large modulation depth promotes efficient pulse shaping and facilitates stable mode-locking operation in the THDFL⁴⁰. In addition, the laser-generated pulses had a time-

bandwidth product (TBP) of approximately 0.316, which is close to the sech^2 transform limit. Furthermore, this work represents one of the few reported demonstrations of a TMOF-based SA operating in near 2 μm fiber laser system, highlighting the potential of CaMoCo-MIM as a promising nonlinear optical material for ultrafast photonic applications in the eye-safe wavelength region.

Materials and methods

Synthesis and Characterization of CaMoCo-MIM Saturable Absorber

All trials were conducted using distilled water (DI). System Chemicals in Malaysia provided us with 99.00% pure calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and 99.50% pure ethanol, respectively. Acros Organics in the USA provided the ingredients, 2-methylimidazole (MIM) and cobalt nitrate tetrahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), with a purity of 99.00%. Sigma-Aldrich (USA) delivered 99.00% concentrations of ammonium bicarbonate and sodium molybdate dihydrate. All chemicals were utilised as packaged, with no further cleaning.

The CaMoCo-MIM TMOF was prepared via a simple wet-chemical precipitation method. Metal precursors totalling 0.06 mol in molar quantity were dissolved within 60 mL of deionized water at a molar ratio corresponding to Ca: Mo: Co = 3:2:1. The Ca: Mo: Co molar ratio was selected based on our previous study on bimetallic Ca/Co-MOFs, which used a 1:1 ratio⁴¹. In this work, the incorporation of Mo enabled the formation of a TMOF. This specific 3:2:1 ratio was chosen to maintain structural stability while leveraging the synergistic effects of all three metals. Notably, this is the first study to explore a TMOF for mode-locked laser applications, highlighting the novelty of our approach. In a separate step, 50 mL of DI water containing 0.01 mol of MIM was added to the metal precursor solution while stirring continuously. At the same time, 0.01 mol of ammonium bicarbonate solution was added to the combined metal-organic solution after it was dissolved in DI. To encourage framework formation, the resultant mixture was gently agitated for 4 days. The final product was obtained by centrifugation at 5000 rpm for 5 min, washed multiple times with ethanol and deionized water, and subsequently desiccated overnight at 80 °C in an oven. The synthesis of CaMoCo-MIM is illustrated in Fig. 1.

The morphology of the CaMoCo-MIM material, as shown in Fig. 2(a), which was deposited on the arc-shaped fiber, was examined using a Coxem EM-30AX PLUS scanning electron microscope (SEM). At a magnification of 500x, the SEM picture shows that the CaMoCo-MIM SA was efficiently deposited along the arc-shaped fiber surface, resulting in an almost uniform coating. Upon increasing the magnification to 2000x, irregularly shaped nanoparticles become clearly visible. The presence of clustered nanoparticulates indicates that the drop-casting deposition technique promotes particle aggregation on the fiber surface. This aggregation may be further enhanced by the curvature of the arc-shaped region, which can influence local particle distribution during solvent evaporation. Despite the observed aggregation, the coating remains well adhered to the fiber, with no evidence of large-scale delamination. Elemental mapping in Fig. 2(b) from further field emission scanning electron microscope (FESEM) analysis verifies the existence of silicon (Si), cobalt (Co), gold (Au), oxygen (O), carbon (C), calcium (Ca), and molybdenum (Mo). The detection of Si and O is primarily attributed to the SMF-28 arc-shaped fiber host, which is composed of silicon dioxide (SiO_2) and serves as the substrate for CaMoCo-MIM SA deposition. The high carbon content, predominantly covering the upper surface of the arc-shaped fiber, originates from 2-methylimidazole (MIM) with the chemical formula $\text{C}_4\text{H}_6\text{N}_2$. Meanwhile, the presence of Mo, Co, and Ca arises from their respective metal precursors used during synthesis. The detected Au signal is likely due to trace impurities during sample preparation. However, its atomic percentage is minimal, at only 0.35%, as shown in the energy-dispersive X-ray (EDX) spectra of Fig. 2(c). Carbon constitutes the highest atomic percentage at 57.68%, followed by O (29.87%), Si (7.13%), Mo (2.09%), Ca (1.97%), and Co (0.91%). Excluding the contribution from Au, the total atomic percentage amounts to 99.65%, indicating good compositional consistency of the deposited CaMoCo-MIM SA layer.

Fourier-transform infrared (FTIR) spectroscopy was utilized to analyze the coordination environment of the metal nodes and 2-methylimidazole, as depicted in Fig. 3. Typically, 2-methylimidazole (MIM) displays broad and prominent characteristic peaks within the range of 2200 to 3300 cm^{-1} , resulting from hydrogen bonding

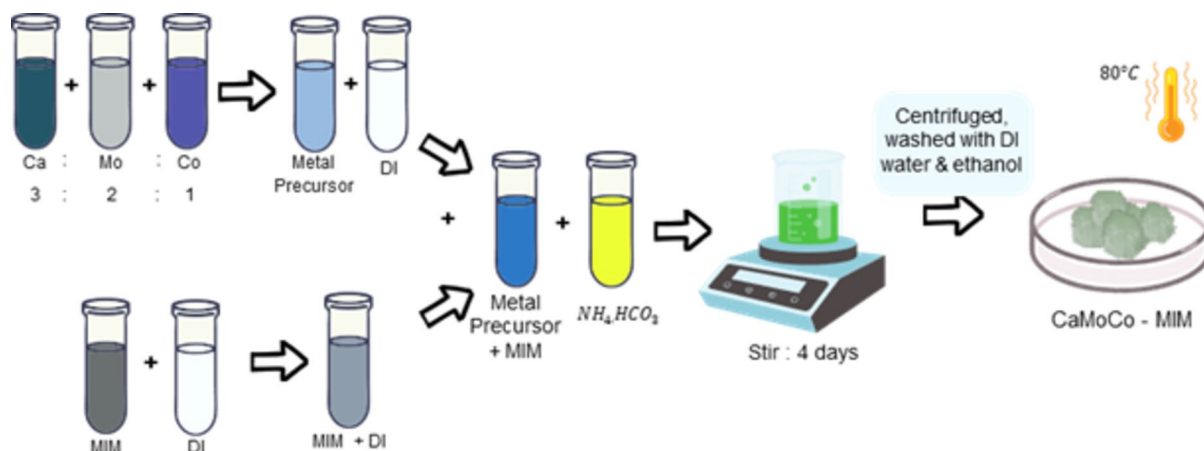


Fig. 1. Synthesis process of calcium-molybdenum-cobalt-2-methylimidazole (CaMoCo-MIM).

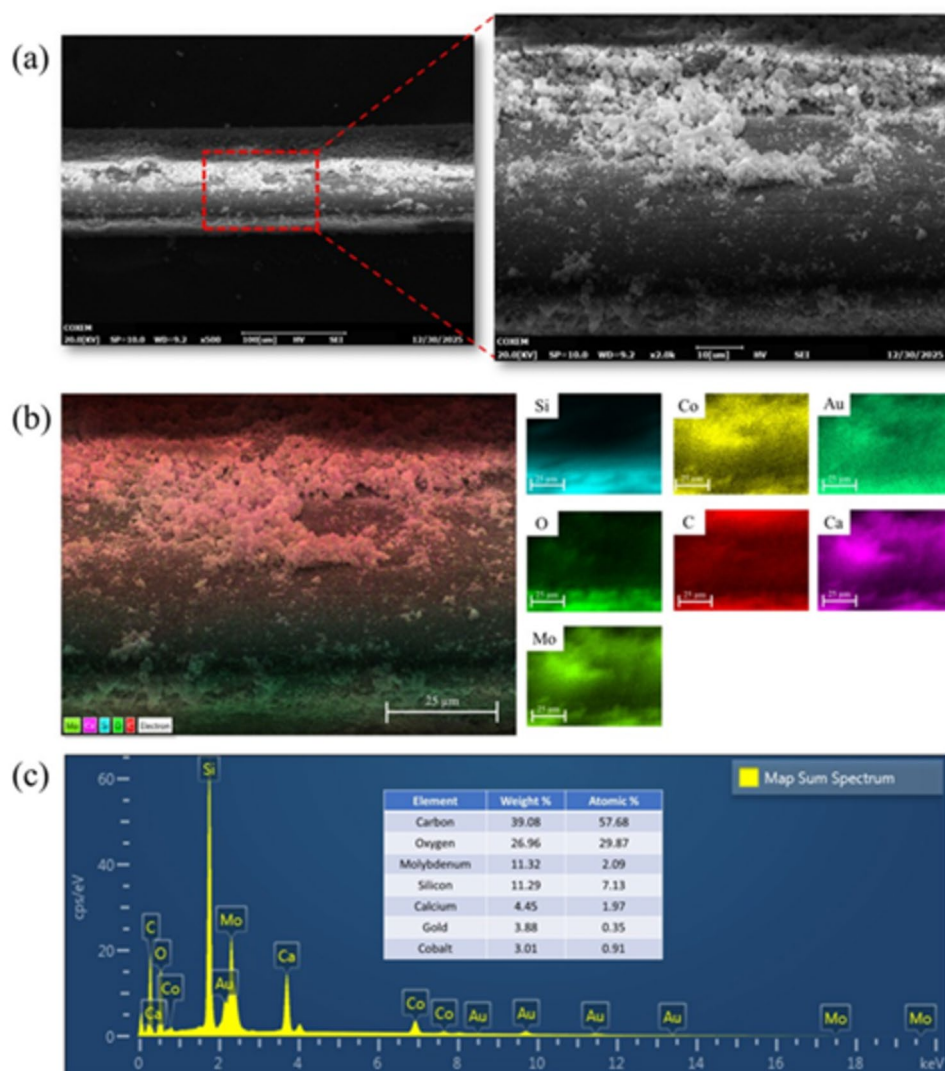


Fig. 2. (a) FESEM morphology, (b) elemental mapping, and (c) EDX spectra of CaMoCo-MIM.

interactions between the pyrrole moiety and the pyridine nitrogen⁴². The lack of these peaks in the CaMoCo-MIM-TMOF spectrum suggests that the metal nodes are coordinated to the secondary amine groups of MIM⁴³. Furthermore, the N—H stretching vibration, which is a noticeable characteristic peak of MIM at 1840 cm^{-1} , is missing from CaMoCo-MIM-TMOF. It means that the deprotonation of the MIM ligand was complete during MOF formation⁴². These two observations confirmed that the metal-organic bonding exists at two different points. Subsequently, the characteristic peaks of MIM within CaMoCo-MIM-TMOF were identified at 1655 cm^{-1} , corresponding to the C=N stretching vibration in the imidazole ring, and within the range of 1400–1500 cm^{-1} , indicative of the stretching and bending modes associated with the imidazole ring^{44,45}. Additionally, the observed peak at 773 cm^{-1} may be attributed to the stretching vibration of the metal-oxygen-hydrogen bond^{46,47}. A hydroxyl group from physically adsorbed water was identified as the source of the signal at 3430 cm^{-1} ⁴⁸.

The linear absorption characteristics of the MIM SA were analyzed to assess its appropriateness for operation within the 2 μm mid-infrared wavelength range. The sample was examined using an amplified spontaneous emission (ASE) source, with the THDFL employed as the gain medium. Figure 4(a) shows a linear absorption of about 24.3% at 1895.21 nm in the linear absorption spectra of the CaMoCo-MIM SA. It is worth noting that the linear absorption is measured at a CaMoCo-MIM solution concentration of 10 mg/mL. This considerable absorption is attributed to the combined effects of the intrinsic electronic transitions within the CaMoCo-MIM framework and the baseline absorption of the deionized water solvent, which generally exhibits a strong absorption band near 1900 nm.

The nonlinear absorption characteristics of the SA were further examined using a twin-detector measurement technique, employing an independent mode-locked fiber laser as the excitation source. The mode-locked laser generated pulses with a pulse duration of 1.02 ps, a repetition rate of 15.8 MHz, and a central wavelength of 1970 nm. An optical attenuator was placed before the SA to control and vary the incident optical intensity, and the corresponding transmitted power was measured with an optical power meter. The detailed configuration

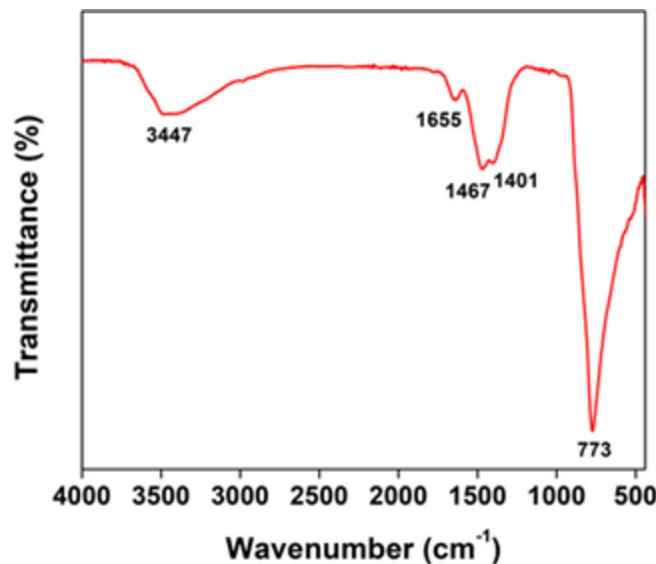


Fig. 3. FTIR spectroscopy of CaMoCo-MIM.

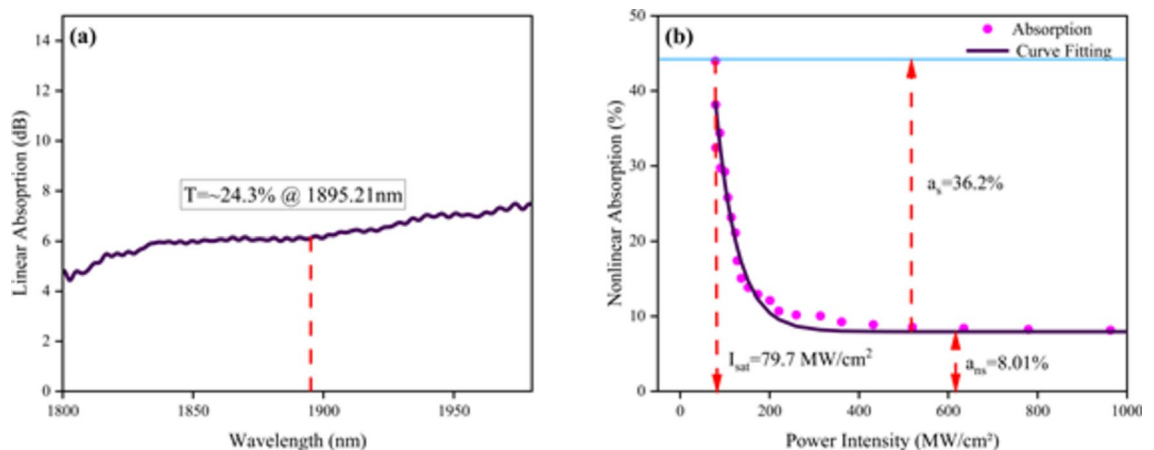


Fig. 4. (a) Linear absorption spectrum, and (b) nonlinear absorption spectrum of CaMoCo-MIM SA.

and procedure for this measurement setup have been previously reported in our earlier studies⁴⁹. A key characteristic of SA is the reduction in optical absorption with increasing incident laser intensity. This intensity-dependent absorption behaviour is clearly observed in the experimental result shown in Fig. 4(b). The nonlinear transmission data were fitted using the conventional SA model, expressed as in reference^{10,17}:

$$A(I) = \alpha_o \times \exp\left(-\frac{I}{I_{sat}}\right) + \alpha_{ns} \quad (1)$$

According to Eq. (1), α_o stands for the depth of modulation, I_{sat} describes the intensity of saturation, and α_{ns} represents the non-saturable loss.

The data were analyzed for the SA's individual parameters. By numerical fitting, the CaMoCo-MIM SA exhibited a high modulation depth (a_s) of 36.2%. This value is beneficial because it enables a self-starting mode-locked mechanism and ensures the generation of high-contrast, ultra-short pulses with considerable peak power. Additionally, the saturation intensity I_{sat} was measured at 79.7 MW/cm², demonstrating that the TMOF material exhibits strong power-handling capabilities and can withstand high-energy pulses before reaching its saturation limit. The non-saturable loss, denoted by the symbol a_{ns} , was measured at 8.01%.

For comparison, the nonlinear absorption characteristics of a bare arc-shaped fiber with the same insertion loss of 2.5 dB were previously investigated in earlier work, where a modulation depth of only 0.66% was obtained⁴⁰. In contrast, after drop-casting the SA onto the arc-shaped fiber, the measured modulation depth increased significantly to 36.2%. This substantial enhancement indicates that the nonlinear response is predominantly contributed by the SA material rather than the arc-shaped fiber structure itself. Therefore, the

arc-shaped fiber primarily functions as a deposition platform for the SA, facilitating light–matter interaction while contributing minimally to the overall nonlinear absorption. By combining these nonlinear features with a high modulation depth, it is demonstrated that the TMOF-based suspension functions as an efficient, high-performance SA suitable for applications involving steady mid-infrared lasers.

Fabrication of arc-shaped fiber and THDFL cavity setup

The polishing depth was controlled by monitoring transmitted optical power during fabrication. Initially, the optical power was measured by transmitting light from a 1550 nm light source into the fiber and recording the output using an optical power meter before polishing. During polishing, the transmitted power was continuously monitored, and polishing was gradually continued until the desired insertion loss was achieved. The SA performance is sensitive to the loss of the arc-shaped fiber, which depends on the arc length and residual fiber diameter. If the fiber loss is high, it implies that the cladding cut is very close to the core by a few micrometers, which increases light–matter interaction by orders of magnitude. However, if the loss is too low, insufficient evanescent field interaction occurs between the optical mode and the SA material. It will affect the formation of the mode-locked pulses. On the other hand, unlike diameter, the effect of arc length is generally linear: a longer arc length increases total absorption. Through systematic testing of losses from 0.5 dB to 3 dB, an insertion loss of 2.5 dB was found to provide the optimal balance, ensuring effective SA interaction while maintaining sufficient cavity power for stable mode-locked pulses. During the fabrication of the arc-shaped fiber, a certain amount of the cladding will be cut off, and light will escape, resulting in a loss. In this measurement, only the loss at the arc-shaped fiber was measured, without accounting for the connectors' loss, which is typically less than 0.3 dB. Furthermore, a 5-centimeter length of SMF-28 fiber was cleaned and securely fastened to a fiber holder before shaping. The exposed fiber region was initially rough-polished with 1000P silicon carbide (SiC) abrasive paper until an insertion loss of 2.4 dB was achieved. To smooth the rough surface, the fiber was subsequently fine-polished with a 3 μm grit Thorlabs diamond polishing sheet, which increases the loss by 0.1 dB, giving a total loss of 2.5 dB. Following the drop-casting deposition of the CaMoCo-MIM SA, the total insertion loss increased to 7.8 dB. Therefore, the additional loss introduced by the CaMoCo-MIM layer is approximately 5.3 dB, which can be attributed to the optical absorption and scattering from the deposited SA material. Dimensional parameters of the fabricated fiber, including its length and curvature, were examined using an optical microscope interfaced with ToupView imaging software, in accordance with the method outlined in ⁽⁵⁰⁾. The resulting microscopy image of the arc-shaped fiber, along with an inset schematic diagram, is shown in Fig. 5(a). The fabricated arc-shaped fiber exhibits a longitudinal length of 2.01 mm and a polishing depth of 36.5 μm . Based on these dimensions, the remaining cladding thickness between the polished arc surface and the fiber core edge is approximately 21.5 μm .

The arc-shaped fiber was then covered with the TMOF layer using a drop-casting method, as previously described⁵¹. In principle, the deposition method can slightly influence the measured nonlinear saturable absorption characteristics by affecting the uniformity of the material distribution on the fiber surface. During drop-casting, a phenomenon commonly known as the “coffee-ring effect” may occur⁵². This effect arises from capillary flow during solvent evaporation, in which the liquid evaporates faster at the edges of the droplet than at its center. As a result, suspended particles migrate outward and accumulate along the droplet perimeter, producing a non-uniform film thickness with higher material concentration at the edges and lower density at the center. Such non-uniform deposition may lead to localized variations in optical interaction, particularly on evanescent-field platforms such as arc-shaped fibers, where the interaction between the guided light and the deposited material occurs only along the fiber's exposed region. Consequently, regions with greater material

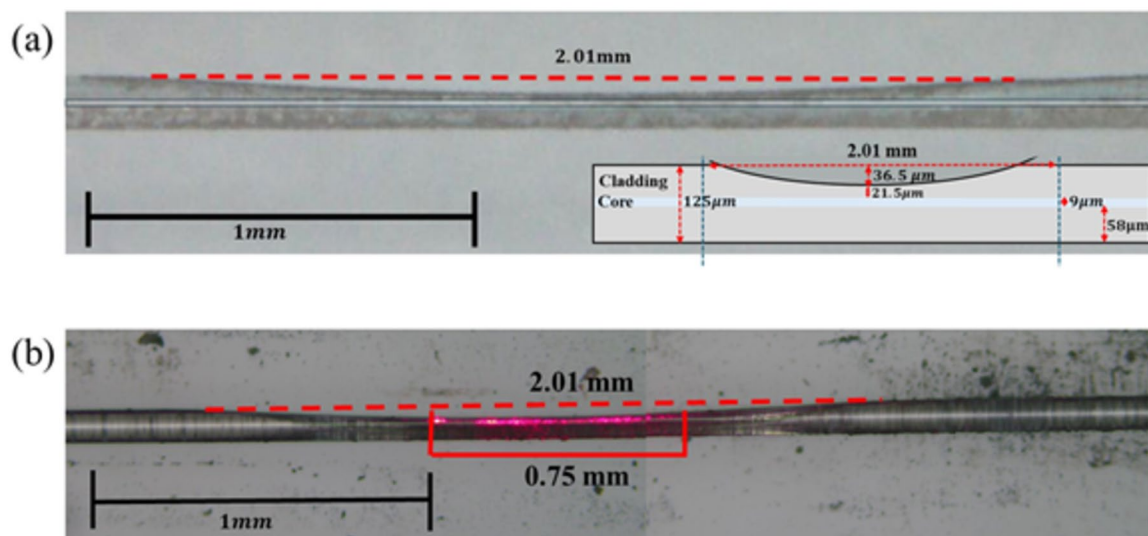


Fig. 5. (a) Bare arc-shaped fiber and (b) arc-shaped fiber coated with CaMoCo-MIM SA, illuminated using a red-light source to visualize the interaction region.

accumulation may exhibit slightly stronger nonlinear absorption than thinner regions. However, despite this potential non-uniformity, drop-casting remains a widely used and practical technique for SA fabrication due to its simplicity, low cost, and minimal equipment requirements. In this work, the deposited CaMoCo-MIM film still provided sufficient interaction with the evanescent field of the arc-shaped fiber to enable effective pulse modulation. As shown in Fig. 5(b), a red-light source was transmitted through the arc-shaped fiber to visualize the interaction region. The illuminated section clearly indicates that the effective interaction length between the evanescent field and the deposited layer is approximately 0.75 mm.

It is worth noting that in this arc-shaped configuration, evanescent field interaction occurs primarily in the thinned region above the core, where the cladding thickness is reduced to $\sim 21.5 \mu\text{m}$ from the core edge to the cladding edge. Although this value appears larger than the typical mode field diameter (MFD) at $\sim 1.8 \mu\text{m}$, several factors contribute to effective light-matter interaction. The $21.5 \mu\text{m}$ thickness is an approximate value obtained from optical microscopy under white-light illumination, which can be very difficult to measure accurately. Due to fiber glare and scattering effects during imaging, the remaining cladding thickness may be overestimated, suggesting that the actual residual thickness could be smaller. The presence of the evanescent field is indicated by the measurement of the loss in the arc-shaped fiber drop-casted with the SA material, which has been discussed earlier. Moreover, the relatively long interaction length ($\sim 2.01 \text{ mm}$) enables cumulative overlap between the evanescent field and the deposited CaMoCo-MIM SA, allowing sufficient evanescent interaction. Finally, as shown in Fig. 5(b), the observed red-light leakage along the arc region further confirms that the optical field is not fully confined to the core, providing direct experimental evidence of evanescent-field interaction with the deposited material.

Fig. 6 illustrates the THDFL cavity configuration, in which the arc-shaped fiber integrated with a SA is incorporated into the laser setup. The gain medium used is a thulium-holmium doped fiber (THDF) obtained from CorActive/INO (fiber model TH512). This fiber has a core diameter of $8 \mu\text{m}$, a cladding diameter of $124.7 \mu\text{m}$, and a coating diameter of $250 \mu\text{m}$. The absorption coefficients of the THDF are $\geq 120 \text{ dB/m}$ at $\sim 790 \text{ nm}$ and $\geq 100 \text{ dB/m}$ at $\sim 1212 \text{ nm}$. In this work, a 1.5 m length of THDF was employed as the gain medium to facilitate laser generation in the THDFL cavity. The THDF was optically stimulated by two pump laser diodes, LD_1 and LD_2 , to gain enough amplification inside the cavity. Before being launched into the THDF, the light from both LDs was first routed via optical isolators (ISOs) to avoid back reflections. It was then coupled into the common ports of wavelength-division multiplexers (WDMs). WDM_1 was subsequently connected to ISO_3 via a 90:10 optical coupler. The optical coupler divides the circulating signal, diverting 10% for real-time monitoring and characterization, while maintaining the remaining 90% within the laser loop. The cavity was closed by recirculating the remaining optical signal through the SA, the polarization controller (PC) for state-of-polarization tuning, and WDM_2 , thereby enabling stable laser operation.

The overall cavity length was 14.67 m , consisting of 1.5 m of THDF, serving as the gain medium, and 13.17 m of standard single-mode fiber (SMF-28). Within the THDF, the group velocity dispersion (GVD) was $-0.05568 \text{ ps}^2/\text{m}$ and $-0.06403 \text{ ps}^2/\text{m}$ for SMF-28, giving a net cavity dispersion -0.9 ps^2 , taking into consideration the various lengths. According to the computed net dispersion, the cavity was operating in negative dispersion.

Results and Discussion

By integrating a CaMoCo-MIM SA and adjusting the PC within the THDFL cavity, stable mode-locked pulses were successfully generated at a consistent pump power of 307 mW . Notably, PC adjustment is required to achieve the appropriate polarization state in the cavity to initiate mode-locking. Once the optimal polarization

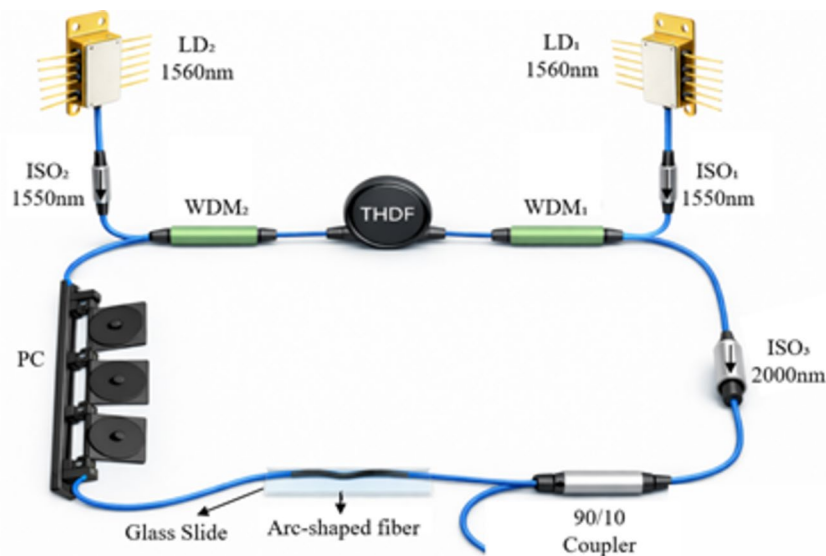


Fig. 6. THDFL cavity setup with arc-shaped fiber.

condition is established, the PC position is fixed. Subsequently, when the pump laser is turned off and then back on, the mode-locked pulses self-start without further adjustment of the PC. This behaviour indicates that the laser operates in a self-starting regime after the appropriate polarization state has been established in the cavity. Fig. 7(a) depicts the optical spectrum acquired through the optical spectrum analyzer (OSA), characterised by a 3-dB bandwidth of 3.03 nm and a central wavelength (λ_0) of 1895.21 nm. Hence, the demonstrated laser operates at $\sim 1.89 \mu\text{m}$, which lies near the $2 \mu\text{m}$ spectral region commonly defined as approximately 1.8 to $2.1 \mu\text{m}$, as described in the literature⁵³. Therefore, the demonstrated laser can appropriately be categorized as a $2 \mu\text{m}$ -band laser. Notably, operation at $1.89 \mu\text{m}$ offers several practical advantages. This wavelength falls within an atmospheric transmission window and overlaps with a strong water absorption band. This characteristic is reflected by the dips observed in the measured spectrum, which correspond well with the water absorption peaks reported in the high-resolution transmission molecular absorption database (HITRAN). Consequently, lasers operating at this wavelength are particularly suitable for biomedical applications, such as tissue ablation, due to their strong interaction with water-rich biological tissues⁵⁴. Beyond medical applications, the $2 \mu\text{m}$ wavelength region is also highly valuable for environmental monitoring and gas spectroscopy. Many molecules exhibit characteristic absorption features in this region, enabling sensitive detection for sensing applications and Light Detection and Ranging (LIDAR) systems⁵⁵. Moreover, the laser cavity operates in a soliton-pulse regime when Kelly's sidebands are clearly defined^{56,57}. The temporal profile of a single pulse, shown by the purple curve in Fig. 7(b), is well-fitted by a sech^2 function. A weak pedestal is visible in the autocorrelation trace and is mainly due to the measurement system's noise floor⁵⁸. The pulse duration extracted from the fitting is 1.25 ps. An estimated time bandwidth product (TBP) of about 0.316 was obtained by integrating the pulse duration with the measured central wavelength and optical bandwidth. It indicates a negligible amount of chirp in the output pulses⁵⁹. The oscilloscope trace in Fig. 7(c) shows a set of pulses with a 68.4 ns time interval, giving a calculated repetition rate of 14.6 MHz. Fig. 7(d) displays the radio-frequency (RF) spectrum with a signal-to-noise ratio (SNR) of 38 dB, further demonstrating that the THDFL is stable when mode-locked with the CaMoCo-MIM SA. The inset in Fig. 7(d) presents the RF spectrum over a wide frequency range from 0 MHz to 1 GHz. Across this broad span, regularly spaced frequency peaks corresponding to the cavity repetition rate can be observed. Spectral gaps are also present, indicating that certain harmonic components are absent within specific frequency regions. These gaps in the long-range RF spectrum arise from the harmonic structure of the periodic pulse train generated in the mode-locked cavity. However, the harmonic components are not always uniformly or continuously distributed across the frequency span, leading to non-equally spaced and partially missing peaks. This behaviour can be attributed to intracavity pulse-shaping effects, including gain competition, dispersion management, and nonlinear propagation within the laser cavity^{40,60}. The absence of sidebands

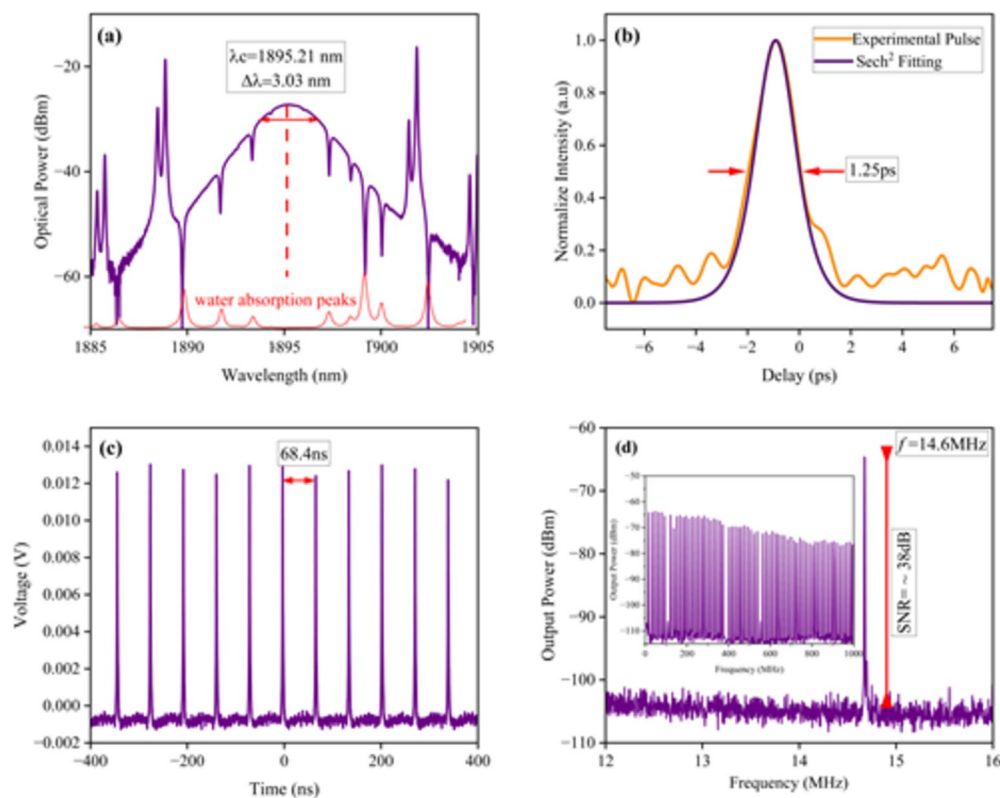


Fig. 7. (a) Mode-locked optical spectrum (blue) and water absorption (red) from HITRAN database, (b) autocorrelation trace, (c) mode-locked pulse train, and (d) RF spectrum of CaMoCo-MIM SA deposited onto the arc-shaped fiber, with an inset showing the spectrum over a wider frequency range.

indicates that the laser operates in a stable fundamental mode-locked regime. This clean RF spectral distribution across the wide frequency range further confirms the stability of the generated pulse train. It is worth noting that in the absence of the CaMoCo-MIM SA, the laser cavity operated only in continuous-wave (CW) mode. No Q-switching or mode-locking behavior was observed, even after extensive adjustment of the PC. It confirms that the CaMoCo-MIM SA plays a crucial role in initiating and stabilizing the mode-locking process in the laser cavity. Moreover, in this cavity, the CaMoCo-MIM SA initiates the mode-locked pulses, not through the non-linear polarization rotation (NPR) effect. For NPR-induced mode-locking, a polarization-dependent isolator is normally required in the cavity, but in this work, a polarization-independent isolator was used. Therefore, it can be inferred that mode-locking is induced solely by the SA.

To test the stability of mode-locked operation over time, it was continuously monitored for 4 h. Fig. 8(a) illustrates the evolution of the autocorrelation traces, while Fig. 8(b) depicts the pulse duration as a function of time. The pulse profile remains consistently uniform throughout the observation period. The pulse duration was maintained between 1.18 ps and 1.25 ps, indicating that the laser's temporal characteristics remain robust against environmental fluctuations. Notably, the autocorrelation traces presented correspond to the fitted autocorrelation profiles obtained by applying the sech^2 fitting function to the measured data. This fitting process suppresses background noise and fluctuations typically present in the raw autocorrelation signal, allowing the pulse characteristics to be extracted more clearly. As a result, the traces shown represent the smoothed fitted curves rather than the raw autocorrelation data, which explains the absence of the noise-level fluctuations observed in the initial measurement. Applying RF spectroscopy to the mode-locked laser allowed for a more thorough evaluation of its frequency stability. Fig. 8(c) shows that the fundamental frequency peak remained sharp and clearly distinguishable throughout the four-hour measurement period. According to the data shown in Fig. 8(d), the fundamental frequency remained constant at 14.6 MHz, and the SNR fluctuated by ~ 6.1 dB. While the SNR fluctuated by approximately 6.1 dB, the mode-locking state remained self-starting and stable. No degradation in pulse quality or pulse breakdown was observed, and no sidebands appeared in the optical spectrum throughout the measurement. It indicates that the laser performance remains robust despite fluctuations in the measured SNR. However, in terms of the pulse shape, there will be slight changes, but they were not detectable. These findings confirm that the CaMoCo-MIM SA enables mode-locking with excellent stability and repeatability, supporting its suitability for real-world ultrafast applications.

Fig. 9 illustrates the connection between the mode-locked laser's average output and incident pump power. As the pump is raised, the CaMoCo-MIM SA shows a consistent, linear rise in output power from 290 mW

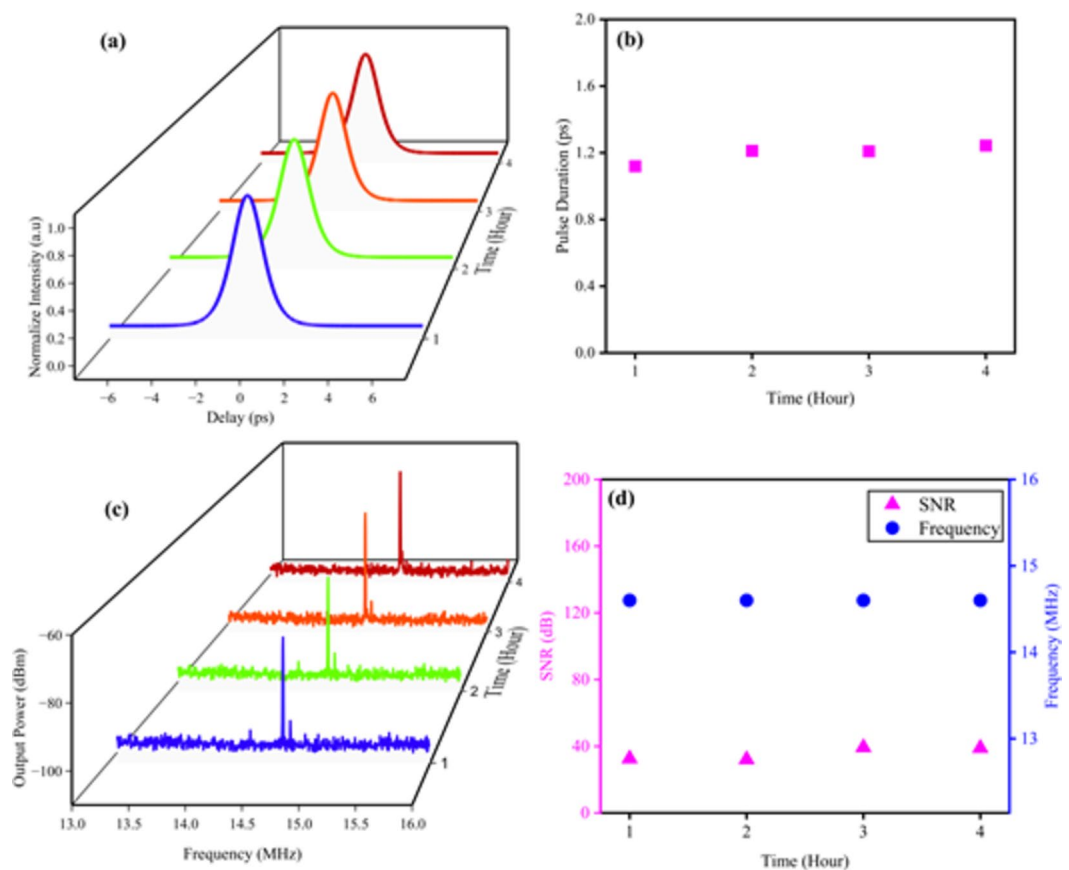


Fig. 8. Stability analysis of the fundamental mode-locked fiber laser using CaMoCo-MIM SA over a four-hour duration. (a) Fitted autocorrelation traces, (b) pulse duration as a function of time, (c) RF spectrum evolution, and (d) SNR and fundamental frequency stability.

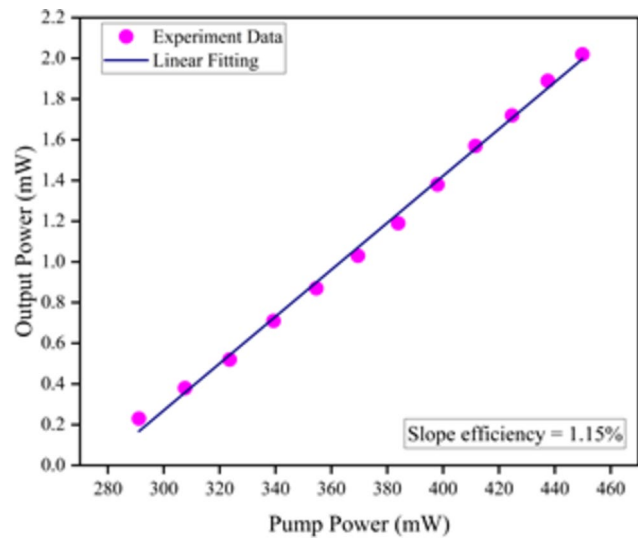


Fig. 9. Output power versus pump power relation for CaMoCo-MIM SA.

Materials	Modulation Depth (%)	Time Bandwidth Product (TBP)	Pulse width (ps)	Operation Wavelength (nm)	SNR (dB)	Maximum stability duration (Hour)	Laser efficiency (%)	Ref.
Ni-MOF	14.25	0.318	1.3	1882	64	-	-	29
Cu-MOF	5.7	0.324	1.08	1949	60	4	5.03	61
Zn-MOF	9.98	0.316	1.772	1906.75	51	1.67	1.33	62
NiO-MOF	18.98	0.321	0.766	1555	62.8	-	-	63
Co-MOF	10.41	0.323	0.793	1558.9	60.5	-	2.36	64
nickel-trimesic acid MOF	4.1	0.303	1.41	1951.6	51	1	-	65
CaMoCo-MIM	36.2	0.316	1.25	1895.21	38	4	1.15	This work

Table 1. Comparison of recent works on MOF or MOF-derived materials for mode-locked fiber lasers.

to 450 mW. At full pump power, the laser has a slope efficiency of 1.15%. The relatively low slope efficiency reported in this work is mainly attributed to the output power measurement configuration. The laser output was characterized via the 10% port of a 90:10 optical coupler, meaning that only 10% of the intracavity laser power was extracted and measured, while the remaining 90% recirculated within the cavity. As a result, the measured output power and corresponding slope efficiency appear significantly lower than the actual intracavity laser efficiency. To improve the apparent slope efficiency, a coupler with a higher output coupling ratio, such as 80:20 or 70:30, could be employed to extract a larger portion of the laser power for measurement. Nevertheless, the linear trend validates a predictable power response. It confirms that the CaMoCo-MIM SA maintains its functional integrity without reaching a thermal-damage threshold or exhibiting power saturation over the investigated range.

Table 1 compares the current work on MOF-derived materials. The SAs enumerated in the table encompass nickel-p-phenylenedicarboxylic acid metal-organic frameworks (Ni-MOF)²⁹, copper-derived metal-organic frameworks (Cu-MOF)⁶¹, zinc-based metal-organic frameworks (Zn-MOF)⁶², nickel oxide micron polyhedral metal-organic frameworks (NiO-MOF)⁶³, cobalt-oriented metal-organic frameworks (Co-MOF)⁶⁴, and nickel-trimesic acid MOF⁶⁵. Among the materials compared, the proposed CaMoCo-MIM exhibits the highest modulation depth, reaching 36.2%, which is significantly greater than those reported for Ni-MOF (14.25%), Zn-MOF (9.98%), Co-MOF (10.41%), Cu-MOF (5.7%), and nickel-trimesic acid MOF (4.1%). The nonlinear absorption measurement in this study was performed using the twin-detector technique, in which the SA was deposited onto an arc-shaped fiber to facilitate effective interaction with the optical field. Similarly, all the studies included for comparison in Table 1 employed a similar twin-detector measurement approach, in which the SA materials were integrated onto fiber hosts prior to characterization. The fiber platforms used in those studies include arc-shaped and tapered fibers, which enable evanescent-field interaction with the deposited materials. The only exception is the NiO-MOF case, in which nonlinear absorption was measured by placing the SA between the fiber ferrules. A high modulation depth indicates strong nonlinear optical absorption, which plays a crucial role in practical pulse shaping and self-starting mode-locking⁶⁶. In the 2-μm spectral area, the CaMoCo-MIM operates at a central wavelength of 1895.21 nm and is especially compatible with THDFL devices. The improved nonlinear optical performance, enabled by its higher modulation depth, enables more effective pulse shaping

and more reliable self-starting in mode-locked operation⁶⁶. Regarding pulse characteristics, the CaMoCo-MIM-based laser generates near-transform-limited pulses with a TBP of 0.316, which closely approaches the theoretical value for sech^2 -shaped pulses, indicating minimal chirp and efficient intracavity dispersion control. The measured TBP is lower than the values reported for Ni-MOF of 0.318, NiO-MOF of 0.321, Co-MOF of 0.323, and Cu-MOF of 0.324, indicating that the CaMoCo-MIM SA supports the generation of high-quality, near-transform-limited ultrashort pulses. The resulting pulse width of 1.25 ps confirms ultrafast operation and aligns closely with the performance reported for other MOF-derived SA. Notably, despite exhibiting a significantly higher modulation depth, the CaMoCo-MIM SA does not induce excessive intracavity loss or pulse broadening, suggesting an efficient balance between nonlinear absorption and cavity dispersion. This favorable balance enables stable, high-quality ultrashort-pulse generation without compromising pulse duration. In terms of operational stability, the CaMoCo-MIM SA achieves an SNR of 38 dB, which is relatively high and corresponds to a linear value of 6309 times. The CaMoCo-MIM SA also delivered superior operational stability of 4 h, outperforming Zn-MOF at 1.67 h and the nickel-trimesic acid MOF at 1 h, and matching the leading stability of Cu-MOF-based devices. While other SA reports higher SNR values, the 38 dB SNR in this work is maintained consistently over several days, demonstrating long-term stability. This combination of high SNR and prolonged, stable operation supports the claim of superior stability compared with systems that exhibit higher SNR but only short-term performance. Moreover, although most of the referenced studies did not report long-term measurements, evaluating stability over extended periods is important. In this work, long-term stability was assessed over 4 h of continuous operation to evaluate stability for long-term use. Unfortunately, this cannot be compared with other works because there were no reports on long-term measurements. Reporting long-term stability in this work provides a benchmark for assessing the practical applicability of mode-locked lasers. The result highlights the suitability of CaMoCo-MIM for sustained mode-locked operation and underscores its potential for practical deployment in ultrafast fiber laser systems. In addition, a laser efficiency of 1.15% is achieved in this study. The reported laser efficiencies were determined based on the laser cavity configurations used in each study. In the present work, a 90/10 output coupler was used, meaning that only 10% of the intracavity power was extracted and measured as output, while the remaining 90% was retained within the cavity to sustain the feedback required for stable pulse formation. In contrast, other studies used different output coupling ratios. For example, the Co-MOF-based laser employed a configuration that samples 30% of the output power, resulting in a slightly higher reported slope efficiency of 2.36%. Therefore, higher output efficiency could potentially be achieved in the present system by using a different output coupler, such as a 70/30 coupler. However, the 90/10 coupler was intentionally retained in this cavity design to ensure sufficient intracavity feedback and support stable pulse generation. Overall, the CaMoCo-MIM SA offers a well-balanced combination of high modulation depth, good pulse quality, and stable operation, highlighting its potential for ultrafast fiber laser applications.

Conclusion

This study demonstrates that a CaMoCo-MIM functions as an efficient saturable absorber (SA), enabling stable, self-starting mode-locking in thulium-holmium doped fiber laser (THDFL) operating around 2 μm . The CaMoCo-MIM demonstrated exceptional nonlinear optical characteristics, specifically a modulation depth of 36.2%, exceeding that of other reported metal-organic framework (MOF)-based SAs. At 307 mW of pump power, the laser generated a steady soliton pulse with a centre wavelength of 1895.21 nm, a 3 dB spectral bandwidth of 3.03 nm, and a pulse duration of 1.25 ps. A measured signal-to-noise ratio (SNR) of 38 dB and a calculated time bandwidth product (TBP) of 0.316 both indicate the generation of stable, high-quality pulse trains, which closely align with the sech^2 -transform-limited value of 0.316. Extended stability assessments conducted over 4 h confirmed dependable performance under environmental variations, maintaining a consistent repetition frequency of 14.6 MHz. The laser demonstrated a linear relationship between input and output power, with a slope efficiency of 1.15% and a maximum pump power of 450 mW. These results demonstrate that CaMoCo-MIM is a reliable and effective SA, with strong potential for integration into mid-infrared ultrafast fiber lasers and paving the way for advanced photonic applications.

Data availability

The datasets analysed during this study are available from the corresponding author on reasonable request.

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Author contributions

H. Ahmad – Supervision, Idea, N. Mokhtar – Running the experiment, drafting of the manuscript, N. A. M. Rusni – Sample preparation, drafting of the manuscript, M. S. M Sa’ad – Checking of manuscript, I. S. Imaduddin – Sample preparation and characterization, S. R. Majid – Sample preparation and characterization, M. Z. H. Mayzan – Sample characterization, M. A. M. Lutfi – Running the experiment and data collection, Mousa Hussein – Review, editing and final draft, S. Sun – Review, editing and final draft, K. Thambiratnam – Review, editing and final draft.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

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