

RESEARCH ARTICLE Hot Paper

Single-Site Nickel-Anchored Photosensitive Covalent Organic Framework for Metallaphotocatalytic C–S/C–N Cross-Coupling Reactions

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ABSTRACT

The development of multifunctionally heterogeneous catalysts, simultaneously bearing photosensitizer and nonnoble metal catalyst in close spatial proximity, represents a promising solution for promoting metallaphotoredox-mediated catalysis, albeit it remains challenging. Herein, a single-site Ni-functionalized photosensitive covalent organic framework (COF), TTA-BPyDA(Ni)-COF, has been constructed by implementing a postsynthetic metallization strategy in a triazine-based COF scaffold. The precise integration of photosensitizer and Ni-catalytic active centers within TTA-BPyDA(Ni)-COF not only dramatically improves the metallaphotocatalytic (MPC) performance in C–S/C–N cross-coupling reaction between diverse thiols/amines and aryl iodides with electron-rich/neutral/deficient groups but also confers TTA-BPyDA(Ni)-COF with outstanding recyclability and durability compared with its homogeneous counterpart. Importantly, the MPC C–S/C–N reaction mechanisms have been well established by comprehensive experimental and theoretical simulations. This work offers valuable insights for developing single-site nonnoble metal-functionalized COF catalytic platforms that integrate photoredox centers with catalytic transition-metal cores.

1 | Introduction

Artificial solar-to-chemical conversion has been recognized as one of the most promising technologies to address the increasing concerns in energy and environmental issues due to its green, clean, and environmentally benign features [1–5]. In modern industrial production, utilizing solar energy to drive organic catalytic reactions for constructing C–X (C, S, O, N, P, etc.) bonds has emerged as an alternative research avenue for the

sustainable, energy-efficient, and green synthesis of high-value pharmaceuticals and chemical commodities [6–10]. Thereinto, the merging of photoredox catalysis with transition-metal catalysis, denoted metallaphotocatalysis (MPC), as a complement to transition-metal catalysis, offers a unique opportunity in organic synthetic methodologies. This can be primarily attributed to its unparalleled reaction mode, which is an integration of transition-metal mediated substrate activation and bond formation driven by the excited-state chemistry of photoactive centers, involving

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single-electron transfer (SET) or energy transfer (ET) processes [11–17]. Despite its considerable advancement over the past decade, it remains a challenge to simultaneously achieve highly efficient and recyclable photocatalysis, as a consequence of the homogeneous nature of conventional MPC catalysts. Generally, the highly tunable homogeneous catalysts are deactivated through interactions of the catalytic transition-metal centers, forming nanoparticles or clusters as a result of sluggish electron transfer kinetics as substrate concentrations become limited, thereby increasing the difficulty of catalyst recovery and separation. Moreover, in MPC systems, the most efficient photoredox catalysts are often composed of noble metal-based polypyridyl complexes, for example $\text{Ru}(\text{bpy})_3\text{Cl}_2$, $\text{Ir}(\text{dF}(\text{CF}_3))_2(\text{ppy})_2(\text{bpy})\text{PF}_6$, or organic dye molecules, 4CzIPN, MesAcr, Eosin Y, etc. [11, 18], wherein the former is scarce and expensive, the latter suffers from decomposition during the photocatalysis process. Therefore, it is indispensable to delicately design and establish novel nonnoble metal-functionalized MPC platforms, featuring clear and fast electron transfer pathways, easy recovery and separation, and high stability, to address these challenges.

Covalent organic frameworks (COFs), serving as a class of porous crystalline solid materials constructed with organic monomers via covalent bonds, have attracted extensive attention in heterogeneous photosynthesis owing to their customizable features, including designable structures, tunable functionality, confined pore environments, and large surface area [19–27]. The extended conjugated nature imbues the frameworks with inherent semiconductor properties, making them promising candidates for artificial photosynthesis applications, including hydrogen production [28–30], conversion of CO_2 to high-value products [31–33], hydrogen peroxide synthesis [34–36], and organic small molecule transformations [37–39]. Importantly, the structural designability and functional adjustability provide COFs with the impressive ability to precisely merge photosensitive organic motifs and transition-metal sites to construct cooperative dual catalytic relationships at the molecular level via *de novo* or post-synthetic modification, thus providing an ideal heterogeneous platform for constructing MPC-based COF photocatalysts [40–44]. The inherent reticular chemistry of COF synthesis allows fine-tuning of the photoredox activity by incorporating organic dye monomers into COFs, assisting and/or regulating the metal-catalysis process. Therefore, we envision that the integration of organic photosensitizers with metal-catalysts in COFs may represent a promising strategy to construct dual-functionalized metallaphotoredox catalysts, which may present superior reaction efficiency compared with their homogeneous counterparts due to the accelerated electron transfer rate arising from the shortened spatial distance between multiple photoredox/metal-catalytic centers in the confined nanospaces of the crystalline COFs. Moreover, the confinement effect and site-isolation effect may enhance the stability of catalytic sites involving photosensitizers and/or metal ions, preventing decomposition of organic photosensitive centers and/or deactivation of transition-metal centers during the photocatalysis process. So far, considerable progress in merging photosensitive centers and metal centers into COFs has been made, of which most of them have been used in photocatalytic C–S, C–P, C–O, and C–N coupling reactions [40, 42, 43, 45]. Nevertheless, the elaborate design and synthesis of single-site nonnoble metal-functionalized photosensitive COFs with the precise location of photoredox and metal-catalytic sites

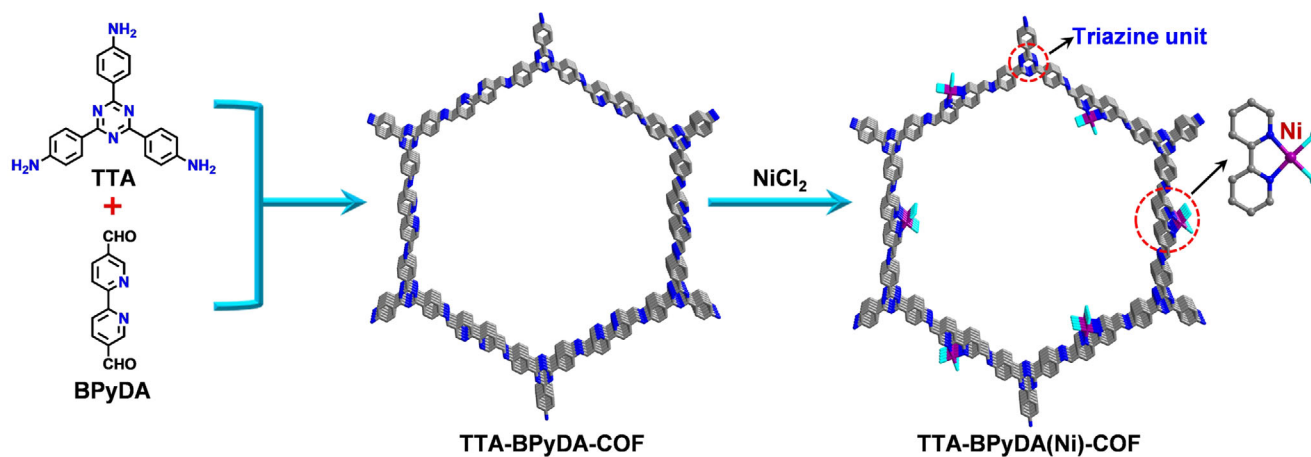
in proximity for simultaneously achieving efficient C–S/C–N coupling reactions is still in its infancy [46, 47], albeit it is of great importance for facilitating catalytic reactions via a synergistic dual-catalytic mode and deciphering the underlying reaction mechanism at the molecular level.

Herein, a single-site nickel-anchored photosensitive triazine-COF, termed TTA-BPyDA(Ni)-COF, featuring photosensitive triazine units and catalytically active Ni sites, has been constructed for metallaphotocatalytic (MPC) C–S/C–N cross-coupling reactions. The immobilization of single-atom Ni sites into TTA-BPyDA-COF promotes electron transfer from the photosensitive organic linkers to the isolated catalytic Ni centers due to the close spatial proximity between the photosensitive COF and Ni sites, thus achieving an excellent MPC C–S/C–N coupling reaction between various thiols/amines and electron-poor/rich/neutral aryl iodides under mild conditions. Recycling experiments reveal the outstanding durability and reusability of TTA-BPyDA(Ni)-COF due to the site isolation and confinement effect, preventing both the deactivation of Ni catalytic sites and decomposition of photosensitizers. Additionally, the photocatalytic mechanism associated with C–S/C–N coupling reactions has been well established by comprehensive experiments, including ultraviolet-visible diffuse reflectance spectra (UV-vis DRS), Mott-Schottky plots (M-S), femtosecond time-resolved transient absorption spectra (fs-TA), steady-state photoluminescence spectra (PL), time-resolved photoluminescence spectra (TR-PL), photoluminescence (PL) quenching, radical trapping experiments, electron paramagnetic resonance spectrum (EPR), and theoretical calculations.

2 | Results and Discussion

2.1 | Synthesis and Structural Characterization

The photosensitive TTA-BPyDA-COF was synthesized through the condensation reaction of 4,4',4''-(1,3,5-triazine-2,4,6-triyl)triphenylamine (TTA) and 2,2'-bipyridine-5,5'-dicarboxaldehyde (BPyDA) under solvothermal conditions in a sealed ampoule according to the documented method with slight modification (Scheme 1) [48]. Fourier-transform infrared (FT-IR) spectroscopy was utilized to reveal the absence of peaks corresponding to aldehyde or amine groups characteristic of the two monomers, consistent with complete conversion thereof (Figure 1b). The characteristic vibrational band observed at 1626 cm^{-1} indicates the successful formation of the imine bond ($-\text{C}=\text{N}$) in TTA-BPyDA-COF (Figure 1b) [49–51]. Solid-state ^{13}C NMR was employed to further characterize the chemical structure of TTA-BPyDA-COF (Figure S2). The characteristic peak at 169.9 ppm corresponds to the carbon atoms in the triazine, while a signal located at 155.8 ppm indicates the presence of the imine carbon [49, 51]. Powder X-ray diffraction (PXRD) was performed to confirm the structure and phase purity of TTA-BPyDA-COF. As shown in Figures 1a and S3, TTA-BPyDA-COF exhibited a prominent diffraction peak at $2\theta = 2.39^\circ$, corresponding to the (100) crystal plane on the simulated AA stacking structure, which indicated the highly ordered long-range structure. Pawley refinement of the AA stacking structure model based on the experimental PXRD profile was performed to further demonstrate the 2D AA stacking structure of the synthesized



SCHEME 1 | Schematic synthesis of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF.

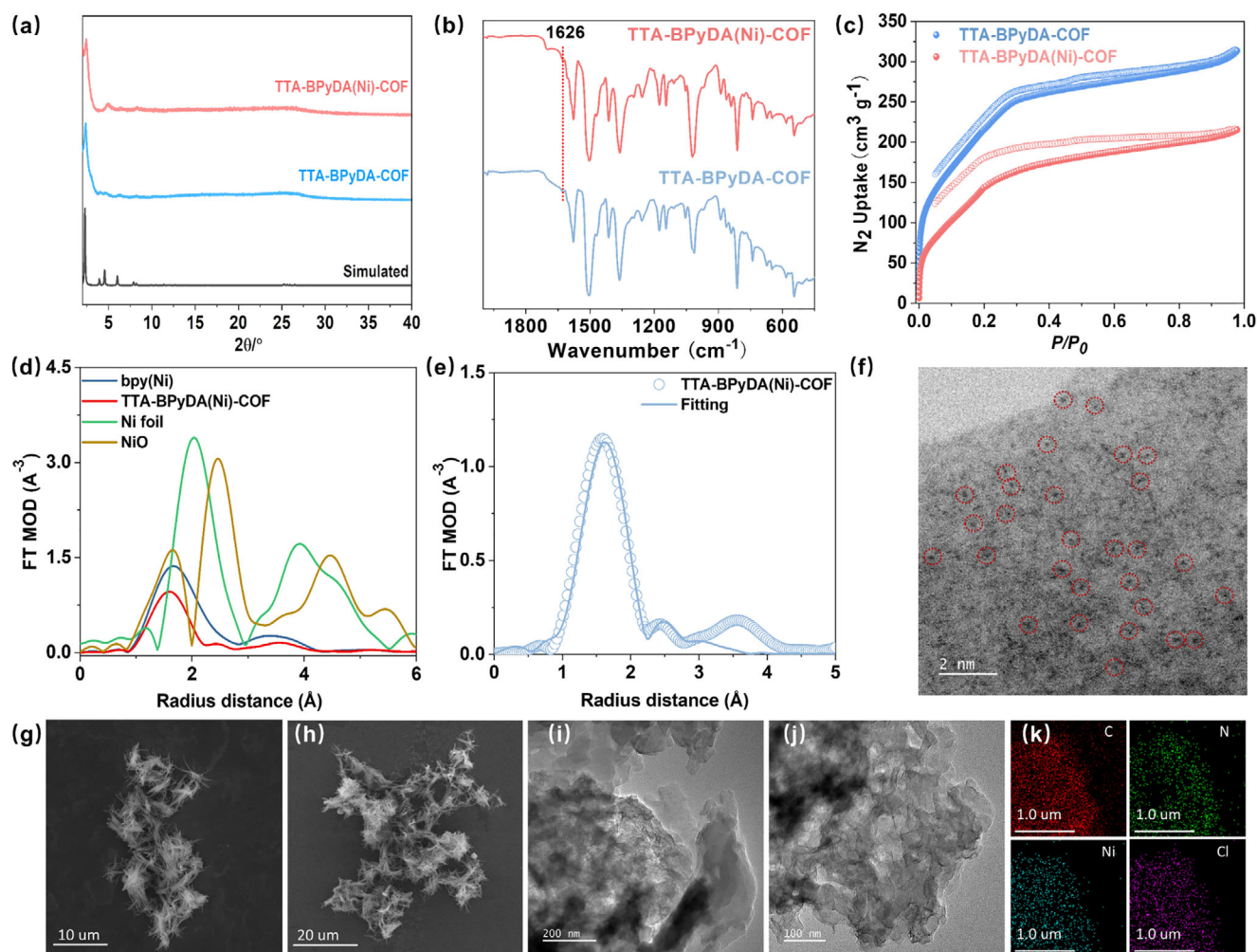


FIGURE 1 | (a-c) The PXRD patterns, FT-IR spectrum, and N₂ (77 K) adsorption isotherms of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF. (d) Ni K-edge XAFS spectra of the BpyNiCl₂, TTA-BPyDA(Ni)-COF, Ni foil, and NiO. (e) Radial distribution function (RDF) curve fitting of the TTA-BpyDA(Ni)-COF spectrum. (f) HAADF-STEM image of TTA-BPyDA(Ni)-COF. (g,h) The SEM images of TTA-BPyDA(Ni)-COF. (i,j) The TEM images of TTA-BPyDA(Ni)-COF. (k) The EDX mapping images of TTA-BPyDA(Ni)-COF.

TTA-BPyDA-COF with small R_{wp} and R_p values ($R_{wp} = 5.62\%$ and $R_p = 4.24\%$) (Figure S4). In addition, the other diffraction peaks were also in good agreement with the simulated structure, further confirming the phase purity of TTA-BPyDA-COF. Subsequently, TTA-BPyDA(Ni)-COF was synthesized by implementing a post-synthetic metallization strategy (Scheme 1). PXRD was conducted to demonstrate that the structural integrity of TTA-BPyDA-COF was conserved after anchoring Ni into the COF structure (Figure 1a). To analyze the electronic state of Ni in the COF material, X-ray photoelectron spectroscopy (XPS) of TTA-BPyDA(Ni)-COF was conducted (Figure S5). As shown in Figure S5, the peaks at 855.5 eV and 873.1 eV correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, binding energies consistent with the expectation that the Ni ions primarily exist in the divalent state within TTA-BPyDA(Ni)-COF. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis revealed that the mass content of Ni in TTA-BPyDA(Ni)-COF sample was $\sim 3.17\%$, corresponding to 0.54 mmol Ni per gram of TTA-BPyDA(Ni)-COF (Table S1). To further investigate the coordination environment of Ni^{II}, extended X-ray absorption fine structure (EXAFS) spectroscopy was performed on TTA-BPyDA(Ni)-COF. As shown in Figure 1d, the radial distribution function (RDF) curve of TTA-BPyDA(Ni)-COF was significantly different from those of the Ni foil and NiO curves but showed great similarity with BpyNiCl₂. TTA-BPyDA(Ni)-COF displayed only one major peak corresponding to the first coordination shell between 1.60 Å and 1.70 Å, while the peak of the second coordination shell with low intensity was located at 3.58 Å. For Ni foil and NiO, the peaks located at 2.02 Å and 2.47 Å, respectively, have been assigned to Ni–Ni bonds [52], which were not observed in TTA-BPyDA(Ni)-COF, suggesting the atomic dispersion of Ni species in TTA-BPyDA(Ni)-COF, as corroborated by aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging results (Figure 1f). The quantitative XAFS fitting revealed that Ni was ligated by two N atoms with Ni–N distance of 2.10 Å and two chlorine atoms with Ni–Cl distance of 2.27 Å, which was consistent with the model compound BpyNiCl₂ (Figures 1e and S7 and Table S2). Based on the above results, it could be concluded that a single-site Ni-anchored COF was successfully constructed.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging were performed to reveal the stick morphology of TTA-BPyDA(Ni)-COF (Figures 1g–j and S8, S9). The energy dispersive X-ray (EDX) spectrum indicated that C, N, Cl, and Ni elements were uniformly distributed throughout the entire framework of TTA-BPyDA(Ni)-COF (Figure 1k). Thermogravimetric analysis (TGA) was conducted to assess the thermal stability of TTA-BPyDA(Ni)-COF, revealing that it is stable up to 400 °C (Figure S15). N₂ adsorption isotherms were performed at 77 K to evaluate the porosity of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF, demonstrating the BET surface areas of 840 and 600 m² g^{−1}, corresponding to pore volumes of 0.48 and 0.33 cm³ g^{−1}, respectively (Figures 1c and S16, S17 and Table S3). The pore size distributions were calculated to be 2.80 and 2.52 nm for TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF (Figure S19 and Table S3), matching well with the simulated structure. Notably, the reserved mesoporous trait in TTA-BPyDA(Ni)-COF ensured the effective accessibility of substrates to the catalytically active Ni sites during the MPC process as well as facile product release.

To assess the feasibility of TTA-BPyDA(Ni)-COF for MPC organic transformation reactions, a series of photo/electrochemical measurements was carried out. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) showed that TTA-BPyDA-COF displays a broad optical absorption range from 260–550 nm (Figure 2a). Incorporation of Ni ions effectively broadened the optical absorption of the system, with the absorption band ranging from 260 to 600 nm, suggesting enhanced visible-light response performance for TTA-BPyDA(Ni)-COF (Figure 2a). The band gaps of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF were calculated to be 2.38 eV and 2.15 eV, respectively, according to the Kubelka-Munk theory (Figure 2b). Notably, the introduction of Ni narrowed the band gap of TTA-BPyDA-COF. Given that the band gap is negatively correlated with electron excitation transition efficiency, it can be deduced that the incorporation of Ni into COF improved the electron transition efficiency. To determine the band structure, Mott-Schottky (M-S) measurements were carried out. As shown in Figure 2c,d, the positive slope for both samples indicated their *n*-type semiconductor properties. The flat band potentials of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF were estimated to be −1.10 and −0.97 eV, respectively (vs. Ag/AgCl). Since the conduction band (CB) position for *n*-type semiconductors is equal to their flat band potential, the CB of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF were −1.10 and −0.97 eV (vs. Ag/AgCl), respectively, corresponding to the valence band (VB) positions of 1.28 and 1.18 eV (vs. Ag/AgCl). Overall, these optoelectronic properties demonstrated good photocatalytic potential for organic synthesis.

2.2 | Metallaphotoredox Catalysis Studies

C–S and C–N bonds represent fundamental structural motifs in numerous active pharmaceutical ingredients, underpinning key pharmacokinetic and pharmacodynamic properties, including enhanced metabolic stability, improved oral bioavailability, and increased target binding affinity. Representative examples include C–N bonds in amide linkages and nitrogen-containing heterocycles, and C–S bonds in sulfonamide pharmacophores and thioether functionalities. Considering their prevalence of organosulfur/nitrogen compounds in artificial synthetic pharmaceuticals and organic chemicals, the photocatalytic C–S and C–N cross-coupling reactions were chosen to evaluate the MPC potentials of TTA-BPyDA(Ni)-COF [53–57]. Initially, the C–S cross-coupling reaction between 4-iodotrifluorotoluene (1a) and 4-methoxythiophenol (2a) in the presence of TTA-BPyDA(Ni)-COF (1.1 mol% based on Ni centers) with pyridine (Py) as an organic base under blue LED light irradiation (455 nm) at room temperature was evaluated, which demonstrated that TTA-BPyDA(Ni)-COF could efficiently drive the coupling reaction, producing the corresponding thioether product (3a) with an excellent yield of 99% (Table S4, entry 1), corresponding to a TON of 91.7 (Table S6). Solvent optimization experiments revealed that acetonitrile (ACN) was the best reaction solvent (Table S4, entries 1–5). The yield of 3a slightly decreased to 90% when 2,6-lutidine was used as the organic base (Table S4, entry 6). Next, the optimization of the catalyst amount was performed, which demonstrated that reducing the amount of TTA-BPyDA(Ni)-COF from 1.1 to 0.55 mol% resulted in a slightly decreased 3a yield from 99% to 95% (Table S4, entry 7), corresponding to a TON of 175.9 (Table S6). Additionally, shortening the reaction time from

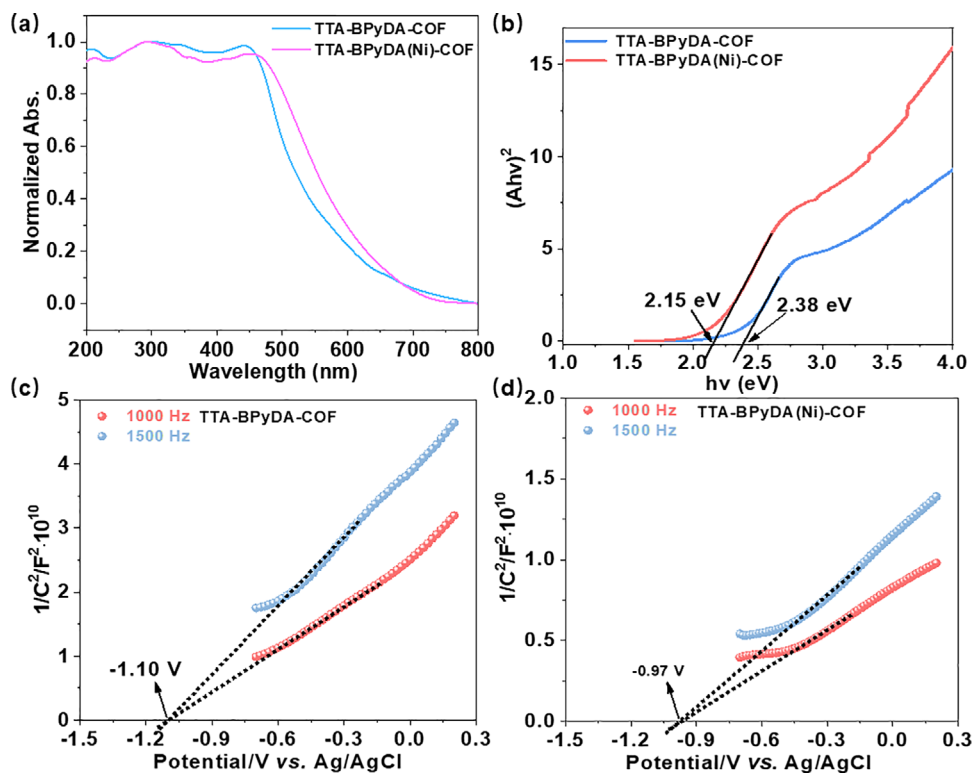


FIGURE 2 | (a) The ultraviolet-visible diffuse reflectance spectra of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF. (b) The Tauc plots of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF. (c-d) The M-S plots of TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF.

24 to 12 h led to a significantly reduced yield to 64% (Table S4, entry 8). Further optimization revealed the pivotal role of Ni, light, Py, and TTA-BPyDA(Ni)-COF in the MPC C–S coupling reaction (Table S4, entries 9–13). Note that TTA-BPyDA(Ni)-COF presents good C–S cross-coupling catalytic efficiency, which is comparable with many reported COF-based MPC catalysts (Table S6). [40, 42] Under the optimized reaction conditions, homogeneous control experiments were conducted by using TTA + Ph-N=C-BPy(Ni), and TTA+BpyNiCl₂, as catalysts, affording the product 3a with a yield of 7 and 1.4% (Table S4, entries 14–15). The physical mixture sample of TTA-BPyDA-COF and BpyNiCl₂ was also used as a catalyst to drive the C–S coupling reaction, revealing a poor yield of 0.5% (Table S4, entry 16). Time-dependent C–S coupling product, 3a, by TTA-BPyDA(Ni)-COF, was implemented to reveal that TTA-BPyDA(Ni)-COF presented good reaction kinetics (Figures S24). These results fully corroborated the superiority of TTA-BPyDA(Ni)-COF over its homogeneous constituents due to the close spatial proximity of the photosensitive COF with the isolated catalytically active Ni sites, synergistically promoting the MPC process.

The versatility of TTA-BPyDA(Ni)-COF as an MPC catalyst in catalyzing C–S cross-coupling reactions was evaluated under the optimized reaction conditions. As shown in Table 1, various aryl iodides bearing either electron-withdrawing groups (trifluoromethyl, cyano, acetyl, and methyl ester) or electron-donating groups (methoxy, hydrogen, or methyl) could undergo the C–S cross-coupling reaction in good to excellent yields (60%–99%). When comparing 3a (99%), 3d (94%), 3g (90%), 3m (71%), and 3p (79%), it was found that electron-poor aryl iodides participate in the cross-coupling reaction more smoothly than electron-rich

TABLE 1 | Substrate scope of TTA-BPyDA(Ni)-COF catalyzed C–S cross-coupling between aryl iodides and thiols.

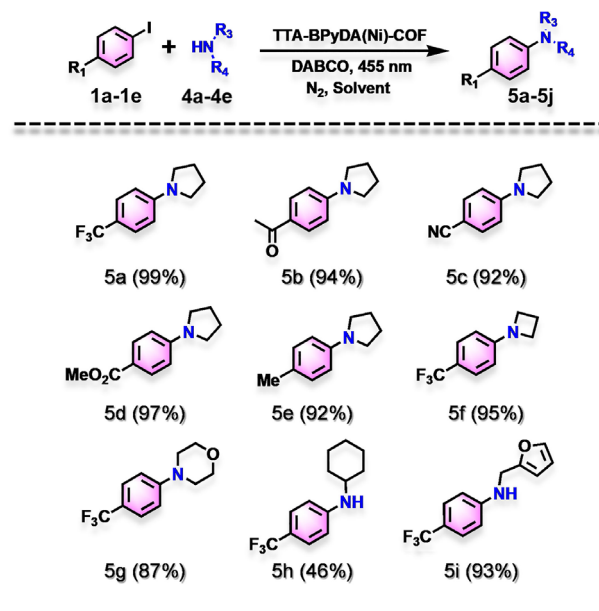
$\text{R}_1\text{-I} + \text{HS-R}_2 \xrightarrow[\text{Py, 455 nm, N}_2, \text{Solvent}]{\text{TTA-BPyDA(Ni)-COF}}$		
1a-1g	2a-2c	3a-3r
		3a (99 %)
		3b (92 %)
		3c (94 %)
		3d (94 %)
		3e (95 %)
		3f (88 %)
		3g (90 %)
		3h (72 %)
		3i (60 %)
		3j (91 %)
		3k (92 %)
		3l (89 %)
		3m (71 %)
		3n (76 %)
		3o (64 %)
		3p (79 %)
		3q (92 %)
		3r (84 %)

^a The reactions were performed in a vial (10 ml) with 1a-1g (0.5 mmol), 2a-2c (0.75 mmol), pyridine (1.0 mmol), and TTA-BPyDA(Ni)-COF (1.1 mol %, based on Ni centers) in ACN (5.0 mL) under N₂ atmosphere. Isolated yield.

aryl iodides, likely due to the electron-withdrawing groups being more conducive to the oxidative addition process. Conversely, aryl thiols bearing electron-donating groups underwent the C–S cross-coupling reactions more effectively than electron-poor aryl iodides still presented good reactivity with aryl thiols bearing electron-withdrawing/neutral/donating groups, delivering the desired thioether products with yields of 64–92% (3m–3r), suggesting that the electronic effect exerted a limited impact on the C–S cross-coupling reaction performance. Overall, it can be concluded that TTA-BPyDA(Ni)-COF can serve as a dual photoredox and Ni catalyst to effectively catalyze the C–S cross-coupling reaction between diverse aryl iodides and thiols with no significant influence of electron effect on the reaction efficiency.

Promoted by the achievement of C–S cross-coupling reactions using TTA-BPyDA(Ni)-COF as an MPC catalyst, the catalytic potential of TTA-BPyDA(Ni)-COF in photoredox/Ni dual-catalyzed C–N cross-coupling reactions was investigated. Initially, the optimized experiments were similarly implemented to identify the optimal reaction condition (Table S5). Note that TTA-BPyDA(Ni)-COF can drive the C–N cross-coupling reactions highly efficiently, which is comparable with many reported COF-based MPC catalysts (Table S6) [43, 45, 58, 59]. Under the optimized reaction condition, TTA + Ph–N=C–BPyDA(Ni), and TTA+BpyNiCl₂, were used as homogeneous catalysts to catalyze the C–N coupling reaction, affording the desired product (5a) in a poor yield of 6% and 0.02% (Table S5, entries 15–16), thus further demonstrating the superior MPC performance over its homogeneous counterparts. Additionally, the physical mixture sample of TTA-BPyDA-COF and BpyNiCl₂ was also used as a catalyst to drive the C–N coupling reaction, revealing a poor yield of 2.9% (Table S5, entry 17), corroborating the superiority of TTA-BPyDA(Ni)-COF. Time-dependent C–N coupling product, 5a, by TTA-BPyDA(Ni)-COF, was carried out to demonstrate good catalytic C–N coupling reaction kinetics (Figures S25), underscoring the good catalytic performance for the C–N cross-coupling reaction. Subsequently, the substrate scope of TTA-BPyDA(Ni)-COF in C–N cross-coupling reactions was explored under the optimized reaction conditions. As shown in Table 2, a variety of aryl iodides bearing electron-withdrawing groups, including trifluoromethyl, acetyl, cyano, and carbomethoxy, displayed excellent reaction compatibility with pyrrolidine, furnishing the desired products in high yields (up to 99%, 5a–5d). The electron-rich aryl iodides could also participate in the C–N cross-coupling reaction with pyrrolidine smoothly, delivering the product in a yield of 92% (5e). In addition to this, several alkyl amines, including cyclobutylamine, morpholine, cyclohexylamine, and furfurylamine, also presented high compatibility with this C–N cross-coupling reaction, delivering the desired products in moderate-to-excellent yields of 46–95% (5f–5i). Note that recyclability and durability are also important metrics for evaluating the practical applications of TTA-BPyDA(Ni)-COF; therefore, the recycling experiments of both C–S and C–N cross-coupling reactions were conducted under the optimized conditions. As depicted in Figures S26, S27, TTA-BPyDA(Ni)-COF could be reused at least five times without significant loss of catalytic activity. XPS spectra, TGA, PXRD patterns, FT-IR, N₂ (77 K) adsorption, ICP, SEM, HAADF-STEM, and EDX mapping images demonstrated that the structure of TTA-BPyDA(Ni)-COF remained intact after the recycling experiments, corroborating its

TABLE 2 | Substrate scope of TTA-BPyDA(Ni)-COF catalyzed C–N cross-coupling between aryl iodides and amines.



^a The reactions were performed in a vial (10 ml) with **1a–1e** (0.5 mmol), **4a–4e** (1.0 mmol), DABCO (1.0 mmol), and TTA-BPyDA(Ni)-COF (1.1 % mmol, based on Ni centers) in DMAC (5.0 mL) under N₂ atmosphere. Isolated yield.

excellent recyclability and durability (Figures S6, S10–S15, S18, S20–S23 and Tables S1, S3).

To get insight into the electron transfer mechanism between TTA-BPyDA-COF and Ni sites, a series of photophysical measurements was carried out. As shown in Figure S28, TTA-BPyDA(Ni)-COF exhibited significantly decreased PL intensity compared with TTA-BPyDA-COF, implying improved charge transfer ability due to the introduction of Ni sites, which facilitates the electron transfer process from the COF to Ni sites [60]. The steady-state PL quenching experiment of TTA-BPyDA-COF by NiCl₂ was conducted, revealing an obvious PL quenching behavior along with the gradually increasing NiCl₂ concentration (Figure S29). The quenching efficiency for NiCl₂ was quantified by the Stern-Volmer equation, which demonstrated a quenching constant *K*_{sv} of 0.156 ± 0.012, indicating the occurrence of electron transfer from TTA-BPyDA-COF to Ni centers (Figure S30). Additionally, the time-resolved PL (TR-PL) for TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF was implemented, manifesting that TTA-BPyDA(Ni)-COF exhibited a shorter lifetime than TTA-BPyDA-COF, further confirming the electron transfer process from TTA-BPyDA-COF to Ni centers (Figures S33, S34). To further elucidate the electron transfer dynamics, femtosecond time-resolved transient absorption spectroscopy (fs-TA) was employed using a pump wavelength of 370 nm. As shown in Figure 3, TTA-BPyDA-COF and TTA-BPyDA(Ni)-COF were excited to the excited state via absorbing pump light with a wavelength of 370 nm, resulting in an increasing number of excited-state molecules. Both samples presented broad excited-state absorption (ESA) around 682 nm, accompanied by gradually decreasing ESA intensity along with the increase of decay

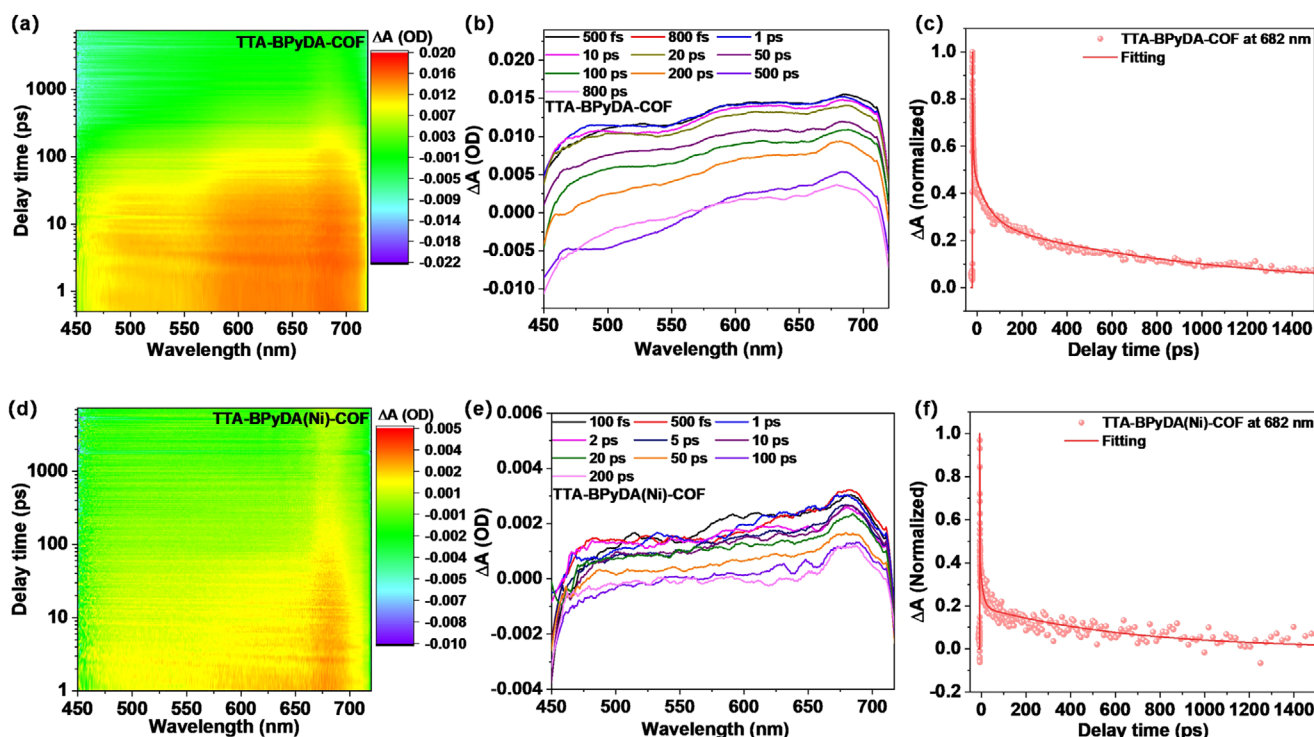


FIGURE 3 | (a) The femtosecond time-resolved transient absorption spectra (fs-TA) of TTA-BPyDA-COF excited at 370 nm. (b) The fs-TA spectra of TTA-BPyDA-COF at various pump-probe delay times. (c) The fs-TA kinetics of TTA-BPyDA-COF at 682 nm. (d) The fs-TA spectra of TTA-BPyDA(Ni)-COF excited at 370 nm. (e) The fs-TA spectra of TTA-BPyDA(Ni)-COF at various pump-probe delay times. (f) The fs-TA kinetics of TTA-BPyDA(Ni)-COF at 682 nm.

time (Figure 3a,b,d,e). Note that TTA-BPyDA(Ni)-COF displayed significantly reduced ESA intensity compared with TTA-BPyDA-COF at the same pump-probe delay time. Given that TTA-BPyDA(Ni)-COF exhibited much lower PL intensity than TTA-BPyDA-COF, it could be rationally deduced that the reduced ESA signal for TTA-BPyDA(Ni)-COF might result from the occurrence of electron migration from COF to Ni sites. The recovery at 682 nm was characterized by three-time constants, which were $\tau_1 = 65.1$ ps (23.8%), $\tau_2 = 994$ ps (27.1%), and $\tau_3 = 2.87$ ps (49.1%), for TTA-BPyDA-COF ($\tau_{\text{ave.}} = 286.28$ ps), and $\tau_1 = 12.6$ ps (8.32%), $\tau_2 = 652$ ps (6.77%), and $\tau_3 = 0.0893$ ps (84.9%), for TTA-BPyDA(Ni)-COF ($\tau_{\text{ave.}} = 45.26$ ps), respectively (Figure 3c,f). Compared with the parent TTA-BPyDA-COF, the significantly shortened decay time for TTA-BPyDA(Ni)-COF signified accelerated charge transfer kinetics from COF to Ni sites. Based on these results, it could be concluded that the excited COF might have the ability to mediate the oxidation state of Ni sites via an SET process, thus facilitating the Ni-catalytic cross-coupling cycle.

To probe the underlying C–S/C–N catalytic mechanism, the steady-state PL spectrum of TTA-BPyDA(Ni)-COF with varying 4-iodobenzotrifluoride (1a), 4-methoxythiol (2a), and pyrrolidine (4a) concentrations was performed (Figure 4a–c). The results revealed that the gradually increasing concentration of 2a or 4a gave rise to the dramatically decreased PL intensity, whereas 1a led to a slight change in PL intensity. The quenching efficiencies for 2a and 4a were quantified by the Stern-Volmer equation, demonstrating the quenching constants K_{sv} for 2a and 4a of 0.123 ± 0.009 and 0.129 ± 0.006 , respectively, which implied the much more efficient quenching efficiency of 2a and 4a on

TTA-BPyDA(Ni)-COF* than 1a, thus indicating the occurrence of effective SET from TTA-BPyDA(Ni)-COF* to 2a or 4a (Figures S31, S32). To investigate whether the C–S/C–N coupling reactions involve a radical-mediated pathway, radical trapping experiments were conducted, wherein 1a, 2a, or 4a, base, TTA-BPyDA(Ni)-COF, and 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO) were added in ACN or DMAC solution and stirred under 455 nm LED light irradiation at room temperature (Figures S35, S36, S38). For the C–S coupling reaction, ^{19}F NMR spectra revealed that the characteristic peak for product 3a was hardly observed, indicating that the C–S cross-coupling reaction was completely suppressed (Figure S35). Instead, gas chromatography-mass spectrometry (GC-MS) revealed the formation of a stable TEMPO-thiol adduct, consistent with the formation of thiol radicals under the reaction conditions (Figure S36). Similarly, for the C–N coupling reaction, only a trace amount of product 5a (5%) was detected, and a significant amount of starting material remained in the reaction system, indicating that the C–N cross-coupling reaction was also fully suppressed by the addition of TEMPO (Figure S38). To further identify the types of radicals involved in the MPC process, electron paramagnetic resonance (EPR) measurements were carried out, in which 1a, 2a, or 4a, TTA-BPyDA(Ni)-COF, and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a radical trapping agent were added to toluene solution under N_2 atmosphere at room temperature (Figures 4d–f and S37, S39). The results showed that insignificant or very weak EPR signals were observed in the C–S cross-coupling reaction in the absence of pyridine, light irradiation, or TTA-BPyDA(Ni)-COF (Figure 4d). In contrast, a strong EPR signal with $g \approx 2.006$ ($\text{AN} = 1.325$, $\text{AH} = 1.455$) was observed under standard conditions, indicating the generation of

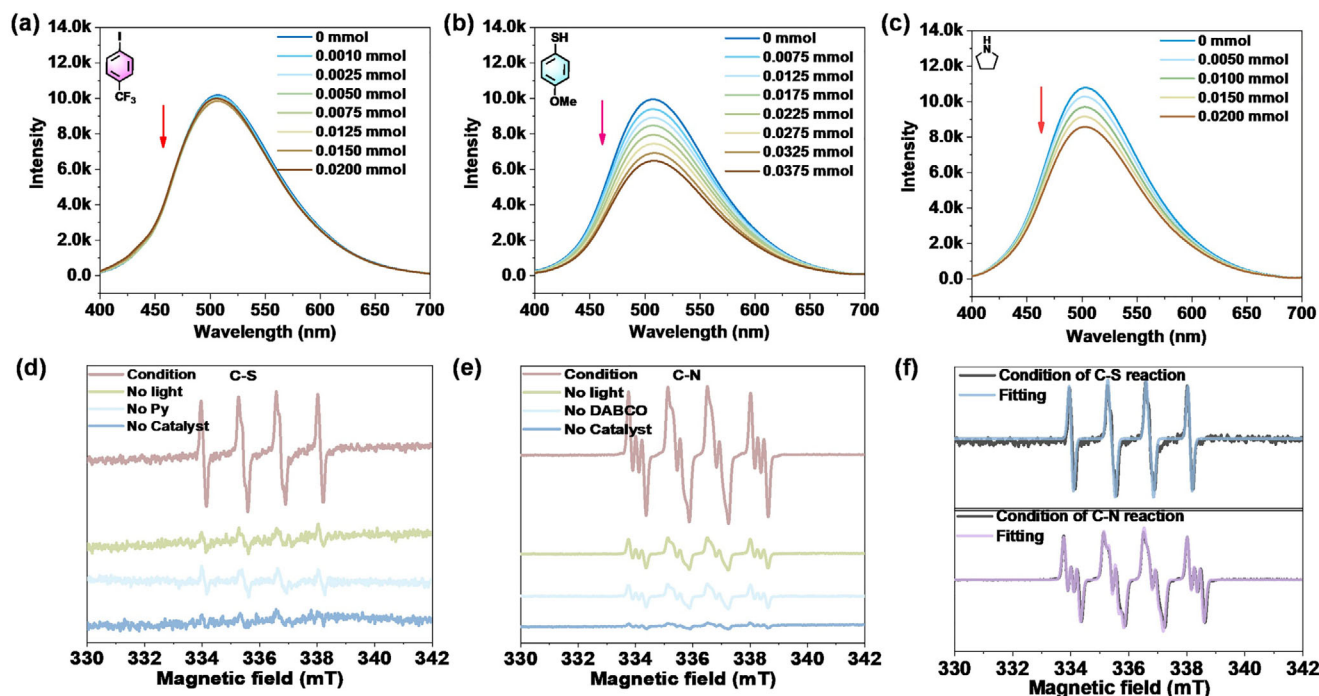


FIGURE 4 | (a–c) Steady-state PL emission quenching of TTA-BPyDA(Ni)-COF* with 1a, 2a, and 4a excited at 365 nm. (d,e) EPR spectroscopy for C–S and C–N cross-coupling reactions under various conditions. (f) The simulated EPR spectrum under different conditions (the DMPO as a spin-trapping agent for EPR detection results).

a thiol radical (Figure 4d,f). Similarly, for the C–N cross-coupling reaction, very weak EPR signals were observed in the absence of DABCO, light irradiation, or TTA-BPyDA(Ni)-COF (Figure 4e). Conversely, under standard conditions, a strong EPR signal with $g \approx 2.006$ ($AN[1] = 1.375$, $AH = 1.515$, $AN^2 = 0.205$) was detected, unambiguously indicating the formation of a pyrrolidine radical (Figure 4e,f).

Based on the above analysis results, a photoredox/Ni-mediated dual-catalyzed C–S/C–N cross-coupling mechanism, involving TTA-BPyDA(Ni)-COF photoredox cycle and Ni catalytic cycle, was proposed (Figure 5a). Specifically, TTA-BPyDA(Ni)-COF was excited under light irradiation, generating holes and electrons. A SET oxidation process from the photoexcited TTA-BPyDA(Ni)-COF* to aryl thiols or amines occurred to generate the corresponding thiol or amino radicals and TTA-BPyDA(Ni)-COF^{•−}. Meanwhile, the single-electron reduction occurred between Ni^{II} (A) and TTA-BPyDA(Ni)-COF^{•−} to deliver the Ni^I (B) species and regenerate TTA-BPyDA(Ni)-COF. In the Ni catalytic cycle, a radical trapping process happened between B and thiol or amino radicals, forming the Ni^{II}-sulfide/amine intermediates C or F, which underwent a SET process to deliver Ni^I-complex D or G. Subsequently, an oxidative addition process occurred to produce the Ni^{III}-complex E or H, which underwent a reductive elimination to form the C–S or C–N cross-coupling product through metathesis of the respective bond, respectively, meanwhile, regenerating TTA-BPyDA(Ni)-COF. To further gain the investigation into the C–S or C–N cross-coupling reaction, the Ni catalytic cycle was examined by theoretical simulation, which demonstrated the feasibility of C–S or C–N coupling reaction using TTA-BPyDA(Ni)-COF as an MPC catalyst via comparing the changes of Gibbs free energy during the catalytic reaction process (Figure 5b,c). To simplify the simulation process, some

fragments of TTA-BPyDA(Ni)-COF were chosen to implement the catalysis calculations (Figures S40, S41). As depicted in Figure 5b, for the C–S coupling reaction, the SET, radical capture, and reductive elimination steps were exothermic and spontaneous, while oxidative addition was found to be endothermic. The reaction energy barrier TS1 (10.54 kcal mol^{−1}) of the oxidative addition process is significantly higher than that of TS2 (4.78 kcal mol^{−1}) of reductive elimination, indicating that the oxidative addition process is the rate-determining step of the C–S cross-coupling reaction. Moreover, the mechanistic C–N coupling studies were also calculated, revealing a similar Ni-catalyzed cycle mechanism to that of the C–S cross-coupling reaction (Figure 5c). These results support the proposition that TTA-BPyDA(Ni)-COF serves as a photoredox-mediated Ni-catalyzed bifunctional catalyst effectively driving the C–S/C–N cross-coupling reaction under mild conditions through synergistic catalysis.

3 | Conclusion

In summary, we have developed a single-site Ni-functionalized photosensitive COF, TTA-BPyDA(Ni)-COF, bearing photosensitive triazine units and catalytic Ni sites via post-synthetic metallization of Ni into the parent TTA-BPyDA-COF for dual photoredox/Ni-catalyzed C–S/C–N cross-coupling reactions. Remarkably, TTA-BPyDA(Ni)-COF showcases outstanding MPC performance, broad substrate applicability, excellent recyclability, and durability for C–S/C–N coupling reactions between various thiols/amines and electron-poor/neutral/rich aryl iodides. This performance can be attributed to the precise integration and close proximity of photosensitizers and isolated catalytic Ni centers, along with site-isolation and confinement effects.

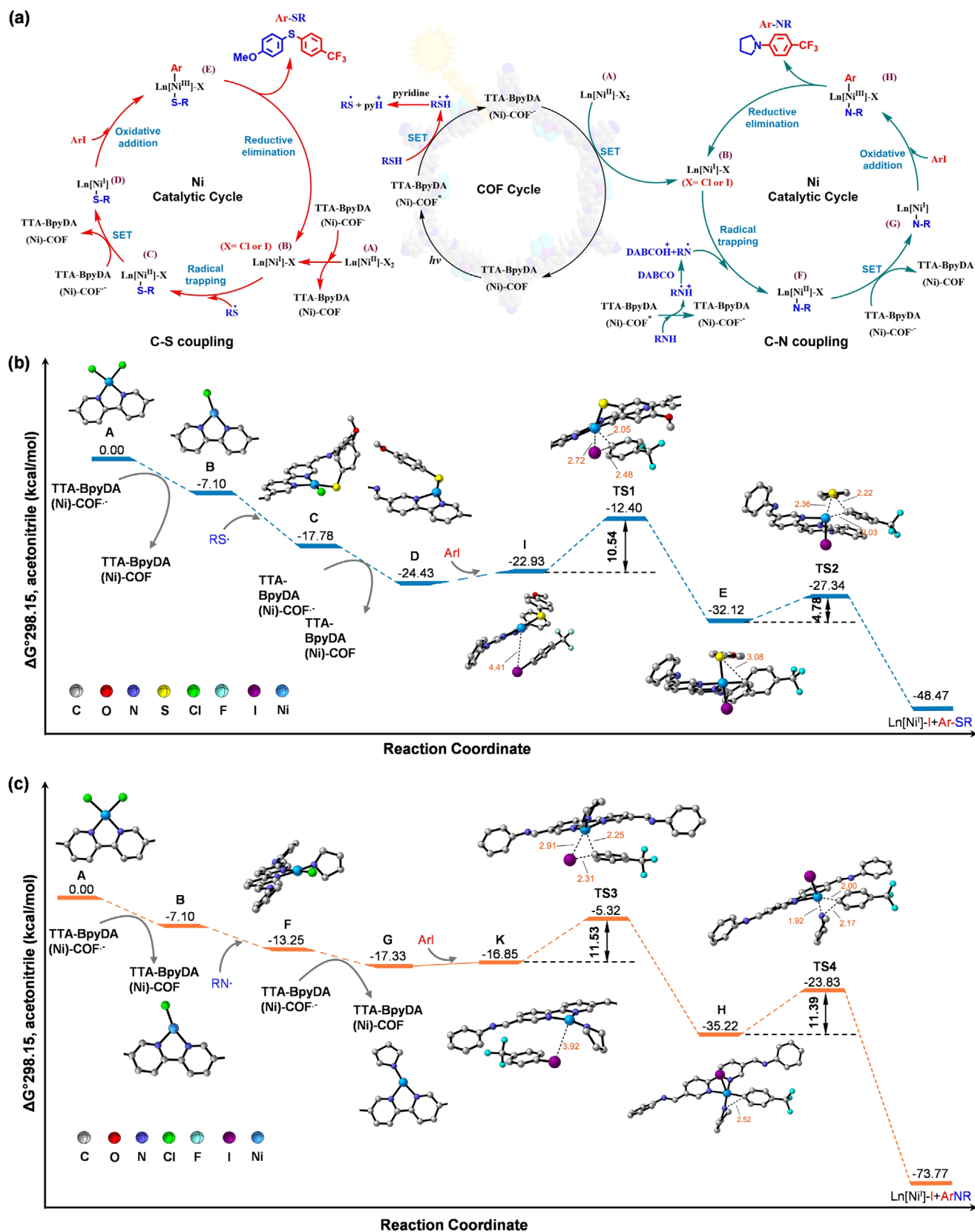


FIGURE 5 | (a) The proposed catalytic mechanism of C–S and C–N coupling reactions. The calculated Gibbs free energy profile of TTA-BpyDA(Ni)-COF catalyzed (b) C–S and (c) C–N cross-coupling reactions.

Moreover, the underlying reaction mechanisms have been well elucidated by comprehensive experiments and detailed theoretical calculations. This work provides a promising protocol for rational design and construction of multifunctional COFs for metallaphotoredox-mediated catalysis applications.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: anie72175-sup-0001-SuppMat.pdf.