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Editorial

Donor–acceptor covalent organic frameworks: Enhanced photocatalytic activity through synergistic utilization of singlet and triplet excitation energies

In general, the performance of a photocatalytic system hinges on the modulation of its singlet (S_1) and triplet (T_1) excited states, which may lead to distinct reaction pathways [1,2]. The S_1 excited states, generated *via* direct photon absorption, are widely utilized in photo-redox catalysis owing to their high efficiency in various electron transfer reactions, in which energy transfer processes are often overlooked. In contrast, the T_1 excited states, accessed *via* intersystem crossing from the S_1 states, play a critical role as intermediates in energy transfer processes. Owing to their extended lifetimes, the T_1 excited states circumvent limitations associated with redox potentials, improve photocatalyst stability, and enable energy migration over longer distances compared to electron transfer process. However, current approaches predominantly rely on optimizing each energy state, either enhancing singlet–state charge separation or extending triplet–state lifetime, which often fails to cope with complex reaction systems and improve overall catalytic efficiency.

Accordingly, the development of dual-modal functional materials capable of synergistically harnessing energies from S_1 and T_1 states represents a novel strategy to access highly efficient photocatalysis. Covalent organic frameworks (COFs), a class of porous polymeric materials fabricated by organic building blocks *via* covalent linkages, represent a highly promising platform for this purpose [3]. Therefore, the rational design of COFs by incorporating strong electron-donating and electron-accepting units may offer a viable approach to access parallel electron and energy transfer pathways. Donor–acceptor (D–A) COFs constructed from electron-donating and electron-accepting units have emerged as promising candidates in photochemistry [4]. This design strategy is crucial for breaking the intrinsic limitation of overlapping electronic/energy transfer pathways in traditional COFs, thereby holding great potential for enhancing photocatalytic efficiency and expanding functional versatility. In conventional photocatalytic systems employing a single chromophore (C) as the catalyst (Fig. 1a), the S_1 state generated from S_0 photoexcitation primarily mediates electron transfer. However, this pathway suffers from significant charge recombination, leading to energy dissipation as heat and limiting overall efficiency. The T_1 state, formed *via* inefficient intersystem crossing (ISC) from S_1, can participate in energy transfer but remains underutilized due to low ISC efficiency, resulting in a predominantly single-pathway catalytic mode that inefficiently exploits excitation energy. In contrast, the D-A framework photocatalyst enables the synergistic coupling of S_1 and T_1 pathways (Fig. 1b). Upon photoexcitation, the S_1 efficiently drives electron transfer, facilitating oxidation and reduction processes. Notably, efficient ISC mediates energy transfer to activate target reactions, thereby overcoming the bottleneck of insufficient energy-transfer activation in conventional systems. This dual-pathway strategy breaks the limitations of single-pathway photocatalysis, offering a new approach to maximize the utilization of excitation energy for enhanced catalytic performance.

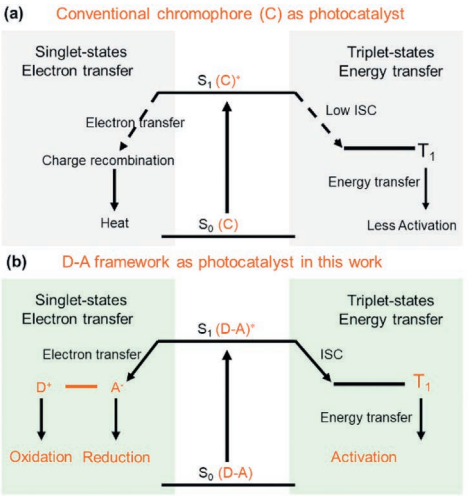


Fig. 1. (a) Photoexcited states and catalytic pathways for conventional chromophore-based photocatalysts. (b) Photoexcited states and dual-channel catalysis from both S_1 and T_1 in the D–A COFs photocatalyst.

Jiang and co-workers proposed a dual-state activation strategy that concurrently promoted both electron transfer and energy transfer within D–A COFs (H_2P-BT$(OMe)_2$-COF), which were constructed by electron-donating porphyrin and electron-accepting benzothiadiazole units (Fig. 2a) [5]. And the mechanism of both energy transfer *via* T_1 and electron transfer through S_1 in H_2P-BT$(OMe)_2$_COF was clarified in Fig. 2b. Through the synergistic integration of strong donor–acceptor pairing, short D–A distances, and hydrogen–bond interactions, resulting COFs enable concurrent harnessing of both S_1 and T_1 excitation energies to drive various

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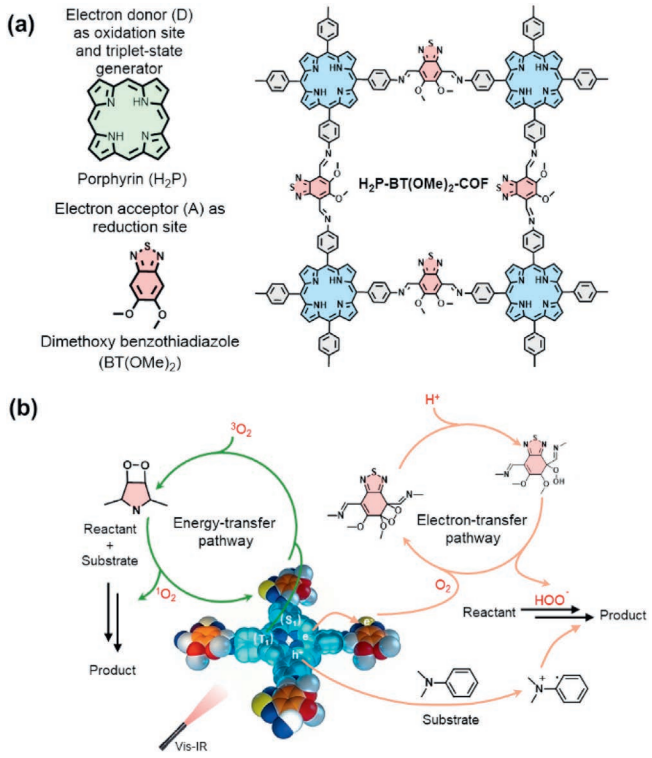


Fig. 2. (a) Structures of porphyrin, dimethoxy benzothiadiazole and H_2P-$BT(OMe)_2$-COF. (b) Dual-pathway activation mechanism of H_2P-$BT(OMe)_2$-COF.

organic transformations with exceptional efficiencies. Additionally, the porous framework further promotes efficient substrate transport, while intralayer and interlayer hydrogen bonds stabilize excited states, enhancing both photostability and reactivity. This is attributed to the fact that hydrogen bonds restrict vibrational motions, facilitating the generation of the S_1 state, while electron-donating methoxy units elevate the frontier orbital energy levels, thus increasing the thermodynamic driving force for electron transfer. H_2P-$BT(OMe)_2$–COF could efficiently catalyze the oxidative coupling of amines under ambient conditions in oxygenated acetonitrile, exhibiting broad functional group tolerance. The substrate scope encompassed electron-donating groups (*e.g.*, methyl, methoxy, *tert*–butyl, isopropyl), electron-withdrawing halogens (F, Cl, Br), as well as heteroaromatic moieties such as thiophene. Furthermore, these COFs also enabled benzimidazole synthesis from *o*-phenylenediamine and aldehydes in O_2-saturated methanol at room temperature, and facilitated cross-dehydrogenative C(sp^3)–H coupling of 2-aryl-1,2,3,4-tetrahydroisoquinolines with diverse nucleophiles under red light irradiation (620–1000 nm), which better highlights the advanced light-harvesting capability of D-A COFs. Through systematic mechanistic investigations, the authors quantitatively deconvoluted the respective contributions of the S_1 and T_1 pathways, revealing distinct activity ratios that vary with the specific reaction mechanism, such as the oxidative coupling reaction is driven by a 38 % contribution from the S1 pathway and a 62 % contribution from the T_1 pathway. These results demonstrate a general design strategy for integrated photocatalysts that achieve synergistic utilization of both singlet and triplet excitation energies.

In contrast to conventional D–A COFs, which are often constrained by single-pathway excitation energy utilization, inefficient charge separation, poor mass transfer–catalysis matching, and thus exhibit limited photocatalytic efficiency [6,7], the H_2P-$BT(OMe)_2$–COF introduces a synergistic dual-state excitation strategy that fundamentally overcomes the limitations inherent in single-pathway photocatalysis. Specifically, the framework incorporates a multi-point hydrogen-bonding network that stabilizes the excited state by suppressing vibrational relaxation, while the incorporation of polar one-dimensional microporous channels significantly enhances substrate mass transport and active-site accessibility. Notably, this rational design endows the COFs with broad-spectrum light-harvesting capability spanning the visible to near-infrared (NIR) region (up to 1000 nm). Together with the highly ordered layered stacking, this feature creates an ideal microenvironment that offers both spatial confinement effects and kinetic advantages for photocatalytic reactions. Furthermore, the D–A COFs demonstrate markedly expanded substrate generality under mild, auxiliary-reagent-free conditions, far exceeding that of traditional photocatalytic systems. These attributes underscore its potential for green synthetic applications and highlight a substantial step forward in the practical translation of D–A COF-based photocatalysts.

In summary, Jiang's work demonstrated the rational construction of D-A COFs that serve as an efficient dual–pathway photocatalyst by concurrently harvesting both singlet and triplet excitation energies. By leveraging spatially distinct electron– and energy–transfer channels within the well–defined porous architecture, the COF material drives diverse condensation and coupling reactions with high efficiency and selectivity. Furthermore, this study establishes a general strategy for integrated photocatalysts, opening avenues for designing versatile and efficient photocatalytic systems with potential impacts across renewable energy, environmental remediation, and synthetic chemistry.

CRediT authorship contribution statement

Yifan Fan: Writing – original draft. **Tao Tu:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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