

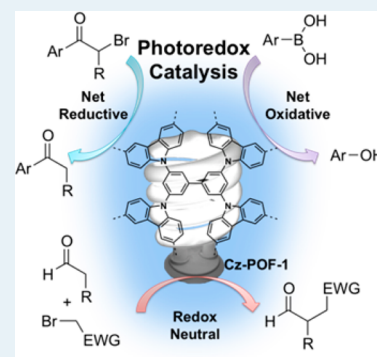
Carbazolic Porous Organic Framework as an Efficient, Metal-Free Visible-Light Photocatalyst for Organic Synthesis

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Supporting Information

ABSTRACT: We report the visible-light-promoted photocatalytic activity of a highly porous carbazolic organic framework, Cz-POF-1, toward three prototypic organic transformations: net reductive dehalogenation of phenacyl bromide and its derivatives, net oxidative hydroxylation of arylboronic acids, and redox-neutral α -alkylation of aldehydes. We show that the extended π -conjugation in Cz-POF-1 enhances its visible light absorption, and the large porosity accelerates the reaction rate. For α -alkylation of aldehydes, Cz-POF-1 requires less strict reaction conditions and can be easily recovered and reused for up to 10 times. This work reveals a bright future for Cz-POFs as a new generation of metal-free photocatalysts for organic synthesis.



KEYWORDS: photocatalysis, carbazole, porous organic framework, metal-free, heterogeneous catalysis

Visible-light-promoted organic transformation has recently witnessed a dramatic resurgence of interest from synthetic chemists due to its high selectivity, simple setup, and mild reaction conditions.¹ Because most organic substrates do not absorb photons in the visible region, photocatalysts such as $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (ppy = 2-phenyl-pyridine) are often used due to their rich redox chemistry at the MLCT (metal-to-ligand charge-transfer) excited states. Indeed, recent studies have shown that photoactive transition metal complexes can drive many important organic reactions.² However, the scarcity, high price, and low recyclability of Ru and Ir impose a significant limit on scale-up synthesis. From a standpoint of sustainability, an ideal photocatalyst should be both recyclable and free of precious metals. Recent work on heterogenization of transition metal complexes onto synthetic porous materials such as mesoporous silica and metal–organic frameworks only partially addresses the issue of recyclability.³ It is thus highly desirable to develop efficient heterogeneous photocatalysts that are inexpensive, recyclable, and free of precious metals to decrease the processing costs in large-scale synthesis.

To this end, π -conjugated porous organic frameworks (POFs, also known as conjugated microporous polymers⁴) provide an ideal photocatalysis platform. POFs have large surface areas, permanent nano/mesopores, and superior chemical and thermal stabilities that are well suited for catalysis.⁵ More importantly, one can easily tailor the optoelectronic properties⁶ of π -conjugated POFs for applications in light emission,⁷ light harvesting,⁸ optical sensing,⁹ and photocatalysis.¹⁰ Finally, in the long-term, the excellent recyclability of POFs can compensate their initial preparation

cost. Despite such great advantages, the use of π -conjugated POFs as photocatalysts for organic synthesis has been rare.¹¹

Carbazole and its derivatives are photoactive molecules with excellent electron-donating capabilities,¹² and they have been used as catalysts in several light-promoted organic reactions such as deoxygenation of secondary alcohols.¹³ Unfortunately, the requirement of using UV irradiation limits their wider use. We envision that incorporating carbazole into a three-dimensional π -conjugated framework could provide a heterogeneous photocatalytic system with an enhanced visible light absorption cross-section because the extended conjugation can, to some extent, decrease the HOMO–LUMO energy gap (E_g). Here, we report a carbazolic porous organic framework, Cz-POF-1, as a highly efficient, visible-light-driven photocatalyst toward three prototypic organic reactions: dehalogenation of phenacyl bromide and its derivatives, hydroxylation of arylboronic acids, and α -alkylation of aldehydes. Our results reveal the great potential of Cz-POFs as a new generation of efficient, metal-free solid photocatalysts for visible light promoted organic transformations.

Cz-POF-1 was prepared using FeCl_3 -induced, oxidative polymerization¹⁴ of carbazole-based monomer Cz-1, 3,3',5,5'-tetra(9*H*-carbazol-9yl)-1,1'-biphenyl (Figure 1a).^{14b} Cz-POF-1 exhibits a high BET (Brunauer–Emmett–Teller) surface area ($2065 \text{ m}^2 \text{ g}^{-1}$) and a large pore volume (1.57 mL g^{-1}).^{14b} In addition, 72% of the pore volume is contributed by mesopores (pore width $> 2 \text{ nm}$),^{14b} an ideal structural feature for organic reactions involving large-sized substrates or products. As shown

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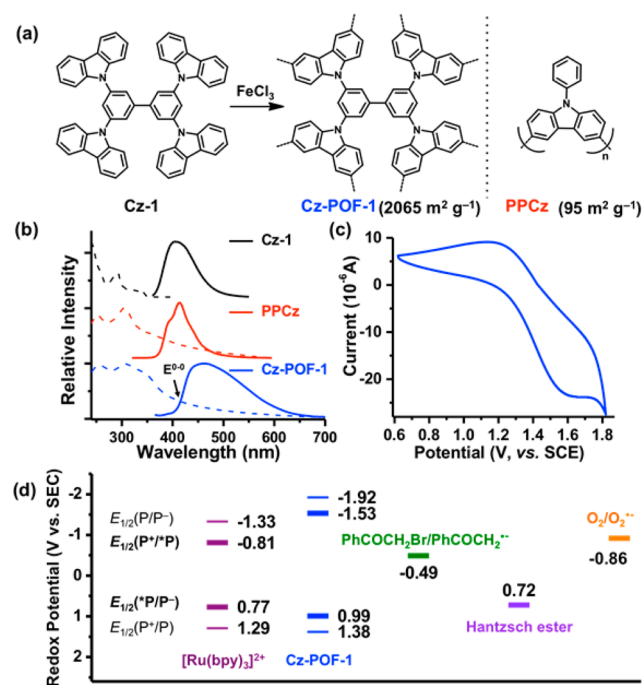


Figure 1. (a) Synthesis of Cz-POF-1 (left) and structure of PPCz. (b) Normalized UV-vis absorption (dashed) and emission (solid) spectra of Cz-1 ($\lambda_{\text{ex}} = 338$ nm, in CH_2Cl_2), PPCz ($\lambda_{\text{ex}} = 304$ nm, at solid state), and Cz-POF-1 ($\lambda_{\text{ex}} = 350$ nm, at solid state). (c) Cyclic voltammetry of Cz-POF-1 with a scan rate of 100 mV s^{-1} . (d) Redox potentials of Cz-POF-1 and $[\text{Ru}(\text{bpy})_3]^{2+}$ as well as several substrates used in this study. P = photocatalyst, * = excited state. $E_{1/2}(\text{P}^+/\text{*P})$, $E_{1/2}(\text{*P}/\text{P}^-)$, $E_{1/2}(\text{P}^+/\text{P})$, $E_{1/2}(\text{P}/\text{P}^-)$ describe half-reactions $\text{P}^+ + \text{e}^- \rightarrow \text{*P}$, $\text{*P} + \text{e}^- \rightarrow \text{P}^-$, $\text{P}^+ + \text{e}^- \rightarrow \text{P}$, and $\text{P} + \text{e}^- \rightarrow \text{P}^-$, respectively.

in Figure 1b, monomer Cz-1 has minimal visible light absorption; however, upon polymerization, the resulting Cz-POF-1 exhibits a broad absorption band that extends to the visible region ($\lambda > 390$ nm). Cz-POF-1 shows an intense, long-lived luminescence band at 464 nm (Figure 1b and Figure S4). As a comparison, a linear polycarbazole, PPCz (poly-9-phenyl-9H-carbazole) (Figure 1a, see Supporting Information for synthetic details), also exhibits a broad absorption extending to the visible region (Figure 1b), indicating that the extended π -conjugation indeed enhances visible light absorption. However, linear PPCz is essentially nonporous, as shown by the negligible BET surface area of $95 \text{ m}^2 \text{ g}^{-1}$ (Figure S6).

Cyclic voltammetric (CV) characterization of Cz-POF-1 reveals a half wave potential ($E_{1/2}$) at +1.38 V (Figure 1c), which can be assigned to the Cz-POF-1⁺/Cz-POF-1 couple. On the basis of a free energy change (E^{0-0}) between the ground state and the vibrationally related excited state of 2.91 eV (426 nm, Figure 1b), the $E_{1/2}$ of Cz-POF-1⁺/*Cz-POF-1 couple was calculated as -1.53 V, more negative than that of $[\text{Ru}(\text{bpy})_3]^{2+}$ (-0.81 V) (Figure 1d, also see Supporting Information Table S3 for detailed redox potentials and photophysical parameters). Because the reduction potential of Cz-POF-1 was not detectable using CV, we estimated E_g to be 3.30 eV based on the reported value of a linear polycarbazole^{12b} and calculated the $E_{1/2}$ of $\text{*Cz-POF-1}/\text{Cz-POF-1}^-$ couple to be likely close to +0.99 V. Nevertheless, it is clear that Cz-POF-1⁺ (+1.38 V) is a good oxidant, which is comparable to $[\text{Ru}(\text{bpy})_3]^{3+}$ (+1.29 V).

On the basis of the promising photoredox properties of Cz-POF-1, we set out to determine its photocatalytic activity for

three prototypic organic transformations. We first chose the dehalogenation of phenacyl bromide and its derivatives¹⁵ to test the potential utility of Cz-POF-1 in net reductive reactions, where an electron donor serves as the stoichiometric reductant to reduce C-Br to C-H. Here, diethyl-1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch ester) was used as the stoichiometric reductant for the reduction of phenacyl bromide (1a). Irradiation with a household fluorescent lamp (14 W) for 24 h generated acetophenone (2a) with a high yield of 98% (Table 1, entry 1) and the pyridinium byproduct. The

Table 1. Photocatalytic Reductive Dehalogenation of Phenacyl Bromide and Its Derivatives^a

entry	1	2	% conversion ^b	% yield ^b
1	1a	2a	>99	98
2 ^c			26	18
3 ^d			<5	trace
4 ^e			44	41
5 ^f			65	64
6	1b	2b	>99	92
7	1c	2c	>99	90
8	1d	2d	>99	93
9	1e	2e	>99	79

^aReaction condition: Cz-POF-1 (5.0 μmol , 2.5 mol % based on monomer), bromide (0.20 mmol), Hantzsch ester (0.22 mmol), CH_3CN (2.5 mL), 14 W compact fluorescent lamp (distance ≈ 10 cm). ^bConversions and yields determined by ¹H NMR using diethyl 2-bromomalonate as an internal standard. ^cNo Hantzsch ester. ^dNo light irradiation. ^eReaction performed in the absence of Cz-POF-1. ^fPPCz was used as the catalyst.

reducing reagent, light, and photocatalyst are all essential for this reaction (entries 2–4). When nonporous PPCz was used as the catalyst, the reaction proceeded with a slower reaction rate (Figure S14a) and lower yield at 24 h (entry 5), indicating the important effect of the porosity on reaction rate. Similar reactions with derivatives of phenacyl bromide (entries 6–9) proceeded with high selectivity and excellent yields (79–93%). The reaction is proposed to be initiated by a single electron transfer (SET) from *Cz-POF-1 ($E_{1/2}^{\text{red}} = -1.53$ V) to phenacyl bromide (1a, $E_{1/2}^{\text{red}} = -0.49$ V),¹⁶ which gives the α -carbonyl radical and a bromide anion (Scheme S1). The Cz-POF-1⁺ intermediate ($E_{1/2}^{\text{red}} = +1.38$ V) may then oxidize the Hantzsch ester ($E_{1/2}^{\text{red}} = +0.72$ V).¹⁷ The α -carbonyl radical then can accept an electron and a proton from the Hantzsch ester-derived radical cation to furnish the acetophenone product 2a. The proposed catalytic cycle is supported by a Stern–Volmer study: phenacyl bromide (1) quenches the fluorescence of Cz-POF-1 (Figure S7), which strongly indicates that the reaction proceeds via the oxidative quenching of *Cz-POF-1 to give a Cz-POF-1⁺ as the oxidative intermediate.

We next tested the capability of Cz-POF-1 in the photomediated oxidative hydroxylation of arylboronic acids¹⁸ using a sacrificial reductant (Et_3N) and molecular oxygen in air as the green oxidant.¹⁹ The reaction of phenylboronic acid (3a) with O_2 in air in the presence of Cz-POF-1 and Et_3N under irradiation with a household fluorescent lamp (14 W) yielded the desired phenol 4a in 94% yield after 24 h (Table 2, entry 1).

Table 2. Photocatalytic Oxidative Hydroxylation of Arylboronic Acids^a

3a: R = C₆H₅
 3b: R = 3,5-Me₂-C₆H₃
 3c: R = 3-C(O)OMe-C₆H₄
 3d: R = 4-CN-C₆H₄
 3e: R = 4-C₆H₅-C₆H₄

3f: (HO)₂B-C₆H₄-B(OH)₂
 4f: HO-C₆H₄-OH

entry	3	4	t (h)	% yield ^b
1			24	94
2 ^c	3a	4a	24	28
3 ^c			96	83
4	3b	4b	48	86
5	3c	4c	24	92
6	3d	4d	36	71
7	3e	4e	36	97
8	3f	4f	48	65

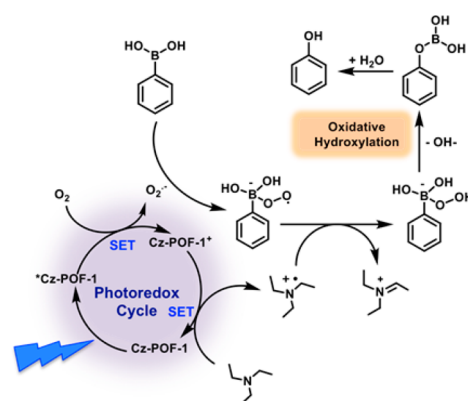
^aReaction condition: Cz-POF-1 (20.0 μmol, 2.0 mol % based on monomer), boronic acid (1.0 mmol), Et₃N (3.0 mmol), DMF (5.0 mL), 14 W compact fluorescent lamp (distance ≈ 10 cm). ^bIsolated yield after purification by flash column chromatography. ^cPPCz was used as the catalyst.

Light, air, photocatalyst, and Et₃N are all essential for this reaction (Table S1). Cz-POF-1 can also effectively promote the hydroxylation of several other arylboronic acids bearing electron-neutral, -donating, and -withdrawing substituents (entries 4–7) with high selectivity and excellent yields (71–97%). Remarkably, Cz-POF-1 exhibits a good efficiency toward the conversion of 1,4-phenylenediboronic acid (3f) into hydroquinone (4f) with a 65% yield after 48 h (entry 8). Again, nonporous PPCz can catalyze this reaction but requires a much longer time (Table 2, entries 2 and 3, and Figure S14b).

Fluorescence-quenching experiments showed that O₂ can effectively quench the emission of Cz-POF-1 (Figure S8). Moreover, insignificant quenching was observed in the presence of Et₃N and the aryl boronic acid (Figure S9). Therefore, the hydroxylation of arylboronic acids likely undergoes the oxidative quenching process, which is reasonable because *Cz-POF-1 ($E_{1/2}^{\text{red}} = -1.53$ V) is capable of reducing O₂ ($E_{1/2}^{\text{red}} = -0.86$ V in DMF)²⁰ to the key reactive species superoxide anion (O₂^{•-}), which is believed to add to the vacant *p*-orbital of the Lewis acidic boron.^{18a} The subsequent abstraction of a hydrogen atom and 1,2-aryl shift proceed to give the final phenolic product. The proposed mechanism (Scheme 1) is in contrast to previous reports where the reductive quenching was found to be operative due to the relatively positive $E_{1/2}^{\text{red}}$ of [Ru(bpy)₃]²⁺^{18a} and methylene blue.^{18b} Our proposed mechanism was further supported by electron paramagnetic resonance (EPR) spectroscopy: strong EPR signals were observed when DMPO (5,5-dimethyl-1-pyrroline *N*-oxide), a radical trapping agent of O₂^{•-}, was present in an aerated DMF solution of Cz-POF-1 upon light irradiation (Figure S11), consistent with the photoredox-mediated generation of O₂^{•-}. Notably, in the presence of the boronic acid, the signal significantly decreased due to the fast consumption of O₂^{•-}.

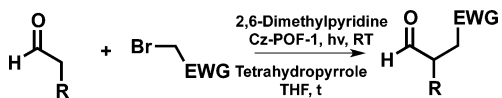
The third reaction tested was the α-alkylation of aldehydes through a merged photoredox and enamine organocatalysis.^{1a} This redox-neutral reaction includes a single-electron oxidation

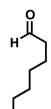
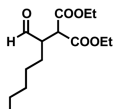


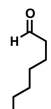

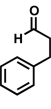


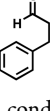


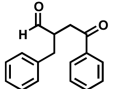
Scheme 1. Proposed Mechanism of Hydroxylation of Arylboronic Acids



and a single-electron reduction at different points in the reaction process, and thus, no external reductant or oxidant is required to complete the photocatalytic cycle. The earlier work employed a chiral secondary amine to achieve enantioselectivity;^{1a} we instead used an achiral amine, tetrahydropyrrole, to demonstrate this proof of concept. To our delight, Cz-POF-1 exhibited good to excellent yields (68%–92%) for reactions involving different combinations of aldehydes and bromides (Table 3, entries 1, 11–13). No alkylation product was observed in the absence of light exposure, photocatalyst, tetrahydropyrrole, and 2,6-dimethylpyridine (Table S2). In particular, Cz-POF-1 led to a slightly higher yield toward α-alkylation of heptaldehyde than [Ru(bpy)₃]²⁺ (entries 1 and 4). The slightly lower yield and selectivity (entries 11 and 13) can be attributed to the presence of proton donors (e.g., trace amount of water, for instance), which led to the formation of dehalogenation byproduct. The proposed mechanism is illustrated in Scheme 2. Under blue LED irradiation, the reaction is initiated by the oxidative quenching of *Cz-POF-1 with the electron-deficient alkyl bromide 5 to provide the strongly oxidizing Cz-POF-1⁺ and radical 6, which reacts with the enamine 7 and provides the α-amino radical 8, which is oxidized by the intermediate Cz-POF-1⁺ ($E_{1/2}^{\text{red}} = +1.38$ V). Hydrolysis of the resulting iminium 9 generates the α-alkyl aldehyde 10. Fluorescence-quenching experiments support the proposed reaction mechanism, where the electron-deficient alkyl bromide quenches the fluorescence of Cz-POF-1 but the alkyl aldehyde does not (Figure S10).

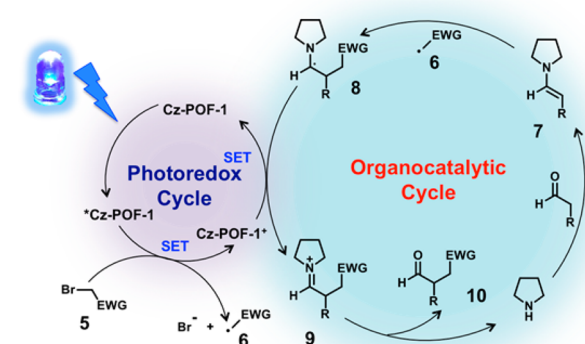
Besides the excellent photocatalytic activity and wide substrate scope, several other attributes of Cz-POF-1 were noteworthy. First, it can be easily recovered and reused via centrifugation. No sign of significantly decreasing reactivity was observed after reusing Cz-POF-1 for 5 times for debromination of phenacyl bromide and oxidative hydroxylation of phenylboronic acid (Figure S12) and 10 times for the reaction between heptaldehyde and diethyl bromomalonate (Figure S13). Meanwhile, FT-IR spectra of recovered Cz-POF-1 indicate no apparent structural change, suggesting a satisfactory stability (Figure S15). Second, reactions catalyzed by Cz-POF-1 require less strict conditions. Oxygen and moisture residue in the solvent significantly decreased the yield and selectivity when [Ru(bpy)₃]²⁺ was used as the catalyst (Table 3, entries 5 and 6), and diethyl malonate (46%) was determined to be the side product when wet solvent was used (entry 6). However, such detrimental effect was insignificant for reactions catalyzed by Cz-POF-1 (entries 2 and 3), possibly due to the

Table 3. Photocatalytic α -Alkylation of Aldehydes^a


entry	aldehyde	bromide	product	t (h)	% yield ^b
1					92
2 ^c					89
3 ^f					77
4 ^e				12	87
5 ^g					41
6 ^{d,f}					38 ⁱ
7 ^d					Trace (<5 ^j)
8 ^g				12	23 (36 ^k)
9 ^g				48	66 ^l
10 ^h				36	87 ^k
11				36	72 ^j
12				24	85
13				48	68 ^l

^aReaction condition: Cz-POF-1 (5.0 μ mol, 2.0 mol % based on monomer), aldehyde (0.75 mmol), bromide (0.25 mmol), 2,6-dimethylpyridine (0.75 mmol) and tetrahydropyrrole (0.05 mmol), 2.5 mL dry THF, 465 nm LED (0.135 W, distance \approx 1 cm). ^bYields determined by ¹H NMR using 2-phenyl-1,2,3,4-tetrahydroisoquinoline as an internal standard. ^c[Ru(bpy)₃]²⁺ was used as the catalyst. ^dCz-1 was used as the catalyst. ^eReaction performed in an aerated solvent. ^fSolvent containing of 0.5% water. ^gPPCz was used as the catalyst. ^h2.5 mmol scale. ⁱDiethyl malonate formed as the byproduct. ^jConversion yield. ^kIsolated yield. ^lAcetophenone formed as the byproduct.

Scheme 2. Proposed Mechanism of α -Alkylation of Aldehydes



hydrophobic pore environment. Finally, monomer Cz-1 essentially gave no conversion (entry 7) and nonporous PPCz required a much longer reaction time (Figure S14c) and led to poor yield and selectivity (entries 8 and 9), further

confirming the importance of both extended π -conjugation and large porosity of Cz-POF-1 for the enhanced visible light absorption and accelerated reaction rate, respectively. Moreover, a 2.5 mmol scale trial led to a satisfactory isolated yield (0.593 g, 87%, entry 10), indicating the feasibility of using Cz-POF-1 for scale-up synthesis.

In summary, we have used Cz-POF-1 as an example to demonstrate the vast potential of π -conjugated POFs as efficient, metal-free solid photocatalysts for organic synthesis. Due to its strong electron-donating properties, Cz-POF-1 efficiently catalyzes three photoreactions via oxidative-quenching mechanisms. In light of the highly tunable optical properties of Cz-POFs, this work paves the way for future discovery of new POFs with excellent photoredox properties and uses in promoting a wider scope of organic transformations. Such work is currently underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00025.

Materials, general procedures, synthesis, physical measurements, fluorescence spectra, EPR spectra, catalyst recycle study, and proposed mechanisms (PDF)

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Notes

The authors declare no competing financial interest.

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