

Visible-Light Photocatalysis of Aerobic Oxidation Reactions Using Carbazolic Conjugated Microporous Polymers

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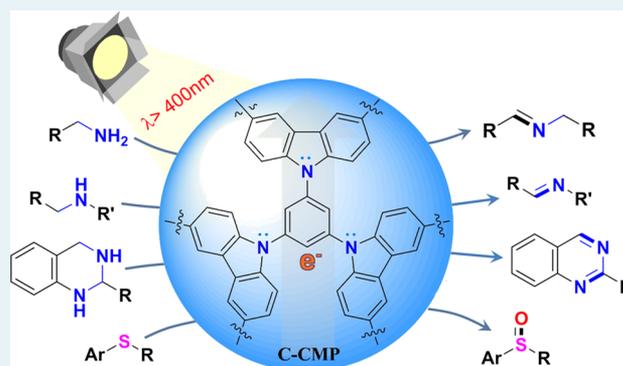
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Supporting Information

ABSTRACT: Carbazolic conjugated microporous polymer (C-CMP) is obtained via straightforward carbazole-based oxidative coupling polymerization. C-CMP exhibits high porosity and a specific surface area of 1137 m² g⁻¹, and it is thermally stable to 600 °C in nitrogen. C-CMP is shown to be a highly effective heterogeneous photocatalyst for a wide range of reactions, including the oxidative coupling of primary amines, aerobic dehydrogenation of nonactive secondary amine substrates such as pharmaceutically relevant nitrogen heterocycles, and selective oxidation of sulfide using molecular oxygen and visible light. This work highlights the potential of developing photoactive N-containing CMPs as a highly stable, molecularly tunable, reusable, and metal-free visible light photocatalysts for a wide variety of organic transformations.

KEYWORDS: visible-light photocatalysis, conjugated microporous polymers, metal-free, selective oxidations, heterogeneous catalysis



INTRODUCTION

The utilization of solar energy as a clean and renewable energy resource for driving synthetic transformations has become an important thrust in green chemistry.¹ During the last decades, transition-metal complexes^{1a} and organic dyes^{1c} which absorb mainly in the visible spectrum had been widely employed as photoredox catalysts to trigger synthetic transformations. However, the poor stability of the organic dye, the inclusion of precious metal in transition-metal complexes, and the difficulty to remove and reuse these homogeneous photocatalysts restrict their practical applications. Metal-free heterogeneous visible-light photocatalysts that are highly stable, easily handled, recoverable, and reusable are needed to address the aforementioned concerns. Carbon nitride polymers^{1d,2} have been explored for a series of metal-free photocatalytic selective oxidations such as oxidation of alcohols,^{2d,e} amines,^{2f} and cross-dehydrogenative-coupling reactions.^{2g} Engineering the morphology of carbon nitride polymers to obtain a higher surface area and porosity, and incorporating organic moieties in the CN frameworks to enhance functionalities, are effective ways to enhance their catalytic efficiency.²

Conjugated microporous polymer (CMPs),³ a class of π -conjugated organic polymers with photoactive structure, high surface area, permanent nanopores, thermal stability and high

flexibility, provides another type of valuable platform for the design of photoredox catalysts.⁴ The optoelectronic properties of CMPs can be fine-tuned at the molecular level, thus allowing flexible design and structure–property correlation to be investigated.^{4a–c} Nitrogen-containing π -conjugated microporous polymers (N-CMPs) derived from oxidative polymerization of triaryl amines and their derivatives such as carbazoles have recently emerged as an important class of photoactive N-CMPs.^{5,6} The nitrogen-containing conjugated structure allow the electron-rich N-CMPs to be applied as redox-active materials in a wide variety of optoelectronic applications such as electric energy storage,^{5b,c} light harvesting,^{5a,6f} and optical sensing.^{6d,e} Despite these remarkable advantages, there are scant reports on the use of these N-CMPs as a visible-light photocatalyst for synthetic transformations;^{4c} in particular, there are no reports of selective aerobic oxidations. In this work, we synthesized carbazolic conjugated microporous polymer (C-CMP)⁶ and applied it as catalysts for three classes or representation reactions, namely: visible-light driven oxidative coupling of primary amines, aerobic dehydrogenation

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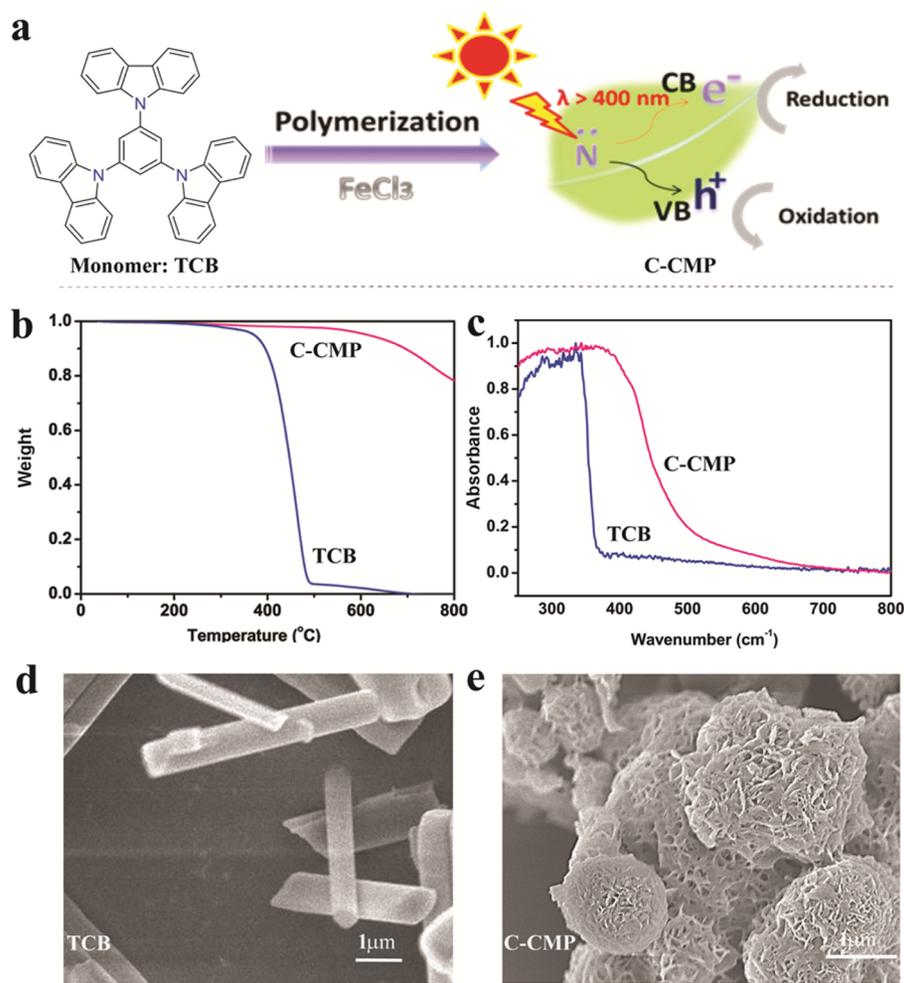


Figure 1. (a) Oxidative polymerization of TCB monomer catalyzed by FeCl_3 to produce C-CMP, which could serve as a photoredox catalyst. (b) Thermal gravimetry of C-CMP and its monomer TCB. (c) UV–visible absorption spectra of C-CMP and its monomer TCB. (d) SEM image of TCB monomer, scale bar $1\ \mu\text{m}$. (e) SEM image of C-CMP, scale bar $1\ \mu\text{m}$.

of nonactive secondary amine substrates, and selective oxidation of sulfides under mild condition. Because C-CMP is a metal-free heterogeneous photocatalyst that shows good recyclability and can be reused efficiently in multiruns, it can be considered as a green catalyst.

EXPERIMENTAL SECTION

Preparation of C-CMP:^{6b} A preheated 250 mL flask (with a stir bar) was charged with FeCl_3 inside the glovebox and sealed with rubber stopper before taking out of the glovebox. Two hundred milligrams (0.37 mmol) of 1,3,5-tri(9-carbazolyl)-benzene (TCB) was dissolved in 60 mL of anhydrous chloroform and then injected into the flask. The solution was stirred at room temperature for 3 days under argon protection. After that, 100 mL of methanol was added into the reaction mixture, and the solution was stirred for another hour. The precipitate was collected using filtration and washed with 250 mL of methanol. The collected solids were added into a 250 mL flask with 150 mL of 37% HCl, and the suspension was stirred for 2 h. The suspension was then filtered and washed with deionized water and methanol. All solids were further purified through Soxhlet extraction with boiling methanol for 24 h and then tetrahydrofuran for 48 h. The collected polymer was dried and kept in vacuum desiccators.

RESULTS AND DISCUSSION

Carbazole derivatives with excellent electron-donating capabilities are good candidates for the production of photoactive N-CMPs as these monomers have been used as photocatalysts

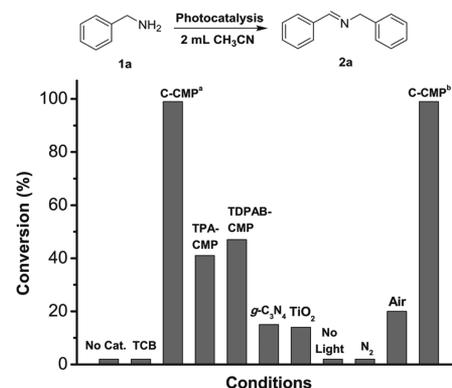
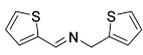


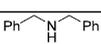
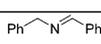
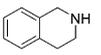
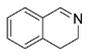
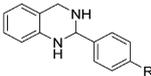
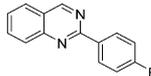
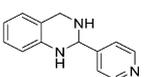
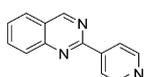
Figure 2. Optimization the conditions of photocatalytic oxidative conversion of benzyl amine into imine: The reaction was carried out by using 1.0 mmol of primary amine, oxygen (1 atm), 20 mg of catalyst, and 2 mL of CH_3CN at specified conditions. ^aConditions: as made C-CMP, 300 W, 2 h; ^bannealed C-CMP, 150 W, 4 h.

Table 1. Photocatalytic Oxidative Conversion of Primary Amines into Imines^a

Entry	Product	t (h)	Conv. (%) ^b	Yield (%) ^c
1	X = H (2a)	4	>99	94
2	X = <i>p</i> -Cl (2b)	4	>99	98
3	X = <i>p</i> -Me (2c)	4	>99	95
4	X = <i>o</i> -Me (2d)	4	>99	98
5	X = <i>m</i> -M (2e)	3	>99	97
6	X = <i>p</i> -CF ₃ (2f)	5.5	>99	97
7	X = <i>p</i> -OMe (2g)	3	>99	95
8	 (2h)	4.5	>99	95

^aUnless specified, the reaction was carried out by using 1.0 mmol of primary amines, 20 mg of C-CMP, and 2 mL of CH₃CN at RT under visible light (150 W Xe lamp). ^bDetermined by GC-MS. ^cIsolated yields.

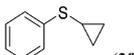
Table 2. Photocatalytic Aerobic Dehydrogenation of Non-Active Secondary Amine Substrates^a

Entry	Substrate	Product	t (h)	Yield (%) ^b
1 ^c			4	76
2 ^d			10	72 ^e
3			18	66
	R = H	R = H		
4	R = Ph- <i>p</i> -F	R = Ph- <i>p</i> -F	14	74
5	R = Ph- <i>p</i> -NO ₂	R = Ph- <i>p</i> -NO ₂	14	58
6			14	61

^aUnless specified, the reaction was carried out by using 0.5 mmol of secondary amines, 20 mg of C-CMP, and 2 mL of CH₃CN at RT under visible light (150 W Xe lamp). ^bIsolated yields. ^cThe reaction was carried out by using 1.0 mmol of diphenyl amine, 20 mg of C-CMP, and 2 mL of CH₃CN at 10 °C. ^dThe reaction was carried out by using 1.0 mmol of 1,2,3,4-tetrahydro isoquinoline, 30 mg of C-CMP, and 2 mL of CH₃CN at 10 °C. ^eGC-Yield with anisole as the internal standard.

in several UV light-promoted organic reactions.⁷ It is well-known that polymerization of these carbazole derivatives to produce C-CMPs⁶ could result in enhanced visible light absorption cross-section because of the extended π -conjugation, which probably allows the C-CMPs to be efficient visible light photocatalysts. A commercially available 1,3,5-tri(9-carbazolyl)-benzene (TCB)^{6b} is selected as the candidate monomer to demonstrate our hypothesis. Oxidative coupling polymerization

Table 3. Photocatalytic Selective Oxidation of Sulfides^a

Entry	Substrate	Visible Light (W)	T (h)	Conv. (%) ^b	Select. (%) ^c	Yield (%) ^d
1	R ₁ = Ph R ₂ = CH ₃ (3a)	250	8	>99	93:7	92
2	R ₁ = <i>p</i> -Br-Ph R ₂ = CH ₃ (3b)	300	10.5	>99	93:7	95
3	R ₁ = <i>p</i> -OMe-Ph R ₂ = CH ₃ (3c)	300	4.5	>99	95:5	90
4	R ₁ = <i>p</i> -Me-Ph R ₂ = CH ₃ (3d)	300	7	>99	93:7	96
5	R ₁ = Ph R ₂ = CH ₂ CH ₃ (3e)	300	8	>99	93:7	98
6	 (3f)	300	12	>99	93:7	99

^aUnless specified the reaction was carried out by using 1.0 mmol of sulfides, 20 mg of C-CMP, and 2 mL of CH₃CN at RT under 1 atm of oxygen. ^bDetermined by GC-MS. ^cDetermined by ¹H NMR. ^dTotal isolated yield of 4 and 5.

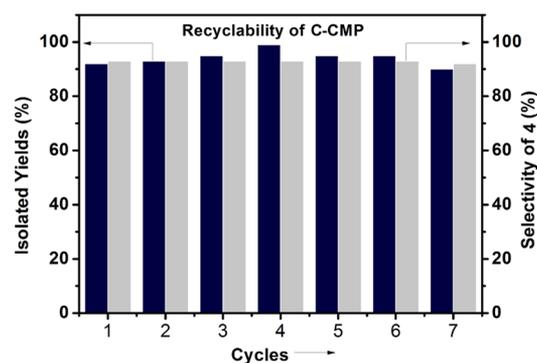


Figure 3. Recyclability of C-CMP in sulfide oxidation reaction. Conditions: room temperature, oxygen (1 atm), 1.0 mmol of PhSMe, 20 mg of catalyst, 8 h, 250 W Xe lamp.

of TCB was readily performed by using anhydrous FeCl₃ in chloroform under nitrogen protection at room temperature (Figure 1a).^{6a,b} To demonstrate the successful formation of C-CMP, extensive characterizations using TGA, UV, FTIR, and SEM are performed. After polymerization, the thermal stability of C-CMP is greatly improved, as shown in Figure 1b. The bandgap of the C-CMP, as compared to its monomer, is smaller due to the significant increase in conjugation length. This is supported by the red-shift of the absorption spectrum (Figure 1c) to the visible region. From the FTIR spectrum, most of the fingerprint peaks of the monomer are retained in its polymer (Figure S1). The Brunauer–Emmett–Teller (BET) surface areas of TCB and C-CMP are measured to be 2.28 m² g⁻¹, and 1137 m² g⁻¹, with pore volumes of 0.00058 cm³ g⁻¹, and 0.68 cm³ g⁻¹, respectively (Table S3). The scanning electron microscopy (SEM) images of C-CMP and its monomer are shown in Figure 1d–e. TCB forms a rod-like crystal with lengths of several micrometers. The SEM image of C-CMP indicates agglomerated micrometer particles with highly curved surface. The superior surface area and high pore volumes can be

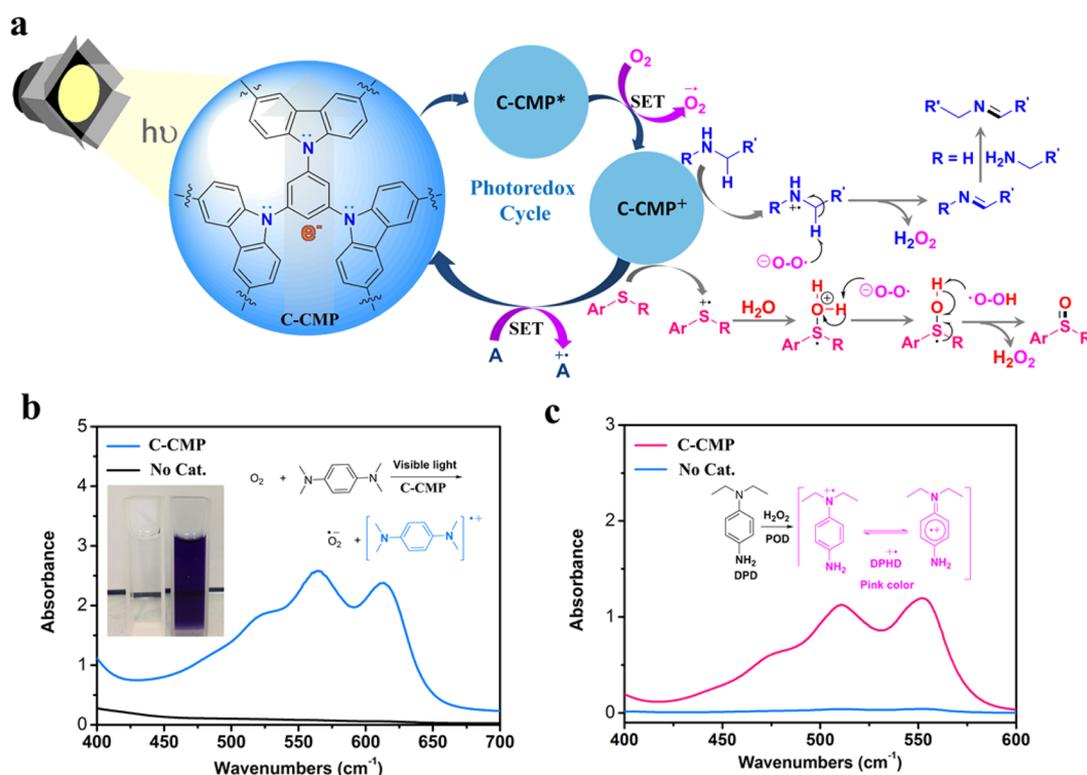


Figure 4. (a) Mechanism of C-CMP catalyzed photoredox oxidations; (b) UV-vis absorption spectra and photograph of the cationic radical species of 1,4-bis(dimethylamino)benzene generated by C-CMP in the presence of visible light and oxygen; (c) UV-vis absorption spectra of reaction system (benzylamine oxidation) with or without catalyst after adding DPD and POD.

assigned to the rigid structure of carbazole units, the inherent permanent porosity and the interparticle porosity between the agglomerated particles.

We first performed the oxidative coupling of benzylamine to investigate the photocatalytic effectiveness of C-CMP.⁸ As evident in Figure 2, the conversion rate is negligible in the absence of the catalyst. Because the monomer TCB only absorbs UV light and the lamp has a UV filter, it shows no photocatalytic reactivity. In contrast, C-CMP shows remarkably enhanced visible light absorption (>400 nm), better stability, higher porosity, and higher surface area than the monomer and allows >99% conversion with 95% selectivity (determined by ¹H NMR). It is clear from Figure 2 that C-CMP provides the best performance among all the tested heterogeneous photocatalysts including the well-explored *g*-C₃N₄, TiO₂ as well as other *N*-CMPs (TPA-CMP and TDPAB-CMP)^{5c,6a} prepared from the monomers like triphenylamine (TPA), 1,3,5-tris-(diphenylamino)benzene (TDPAB) (Table S1–3). The photoactive-carbazole units in C-CMP form a rigid conjugated network. CMP also has an open 3D network with much higher porosity (Table S1–3) than the other classes of *N*-CMPs. All these factors may contribute to its superior performance. To avoid the formation of the overoxidized product benzaldehyde (4–5% as determined by ¹H NMR) which occurred when a high intensity lamp was used, a 150 W lamp was used for the photochemical reaction, in which a selectivity >98% can be attained with a slightly prolonged reaction time (Table S1).

In this section, substrate scope and synthetic applications are systematically studied. First, a series of primary amines **1** could be readily oxidized to produce imines **2** in excellent yields (Table 1). Electron-withdrawing groups such as $-CF_3$ require a longer time to achieve complete conversion, whereas electron-

donating groups like $-OMe$ reduce the reaction time. Ortho- and para-methyl substituents have little impact on the coupling process, but the meta-substituted methyl benzylamine increases the rate of reaction and shortens the reaction time. 2-*t*-Thiophenemethylamine, a representative of the heterocyclic amines, is well-tolerated.

Next we examine the efficiency of the photocatalytic aerobic dehydrogenation of nonactive secondary amine substrates. Dibenzyl amine, a representative of the secondary amines, is converted to the corresponding imine in 76% yield (Table 2, entry 1). Selective oxidation of 1, 2, 3, 4-tetrahydroisoquinone furnishes the 3, 4-dihydroisoquinoline in good yield (Table 2, entry 2). Utilizing this protocol, we successfully demonstrate the efficient transformation of substituted tetrahydroquinazolines to the corresponding quinazolines, which are important pharmaceuticals compounds (Table 2, entries 3–6).

Metal-free photocatalysis using C-CMP has also been applied to the synthesis of substituted sulfoxides from sulfides. As summarized in Table 3, C-CMP catalyzed conversions furnish the corresponding sulfoxides with high levels of efficiency and selectivity. Having electron-donating substituent on thioanisole (*p*-methoxythioanisole, entry 3) reduces the reaction time significantly and furnishes the oxidized products in 90% with good selectivity (95:5). In contrast, having the electron-withdrawing substituent (*p*-bromothioanisole, entry 2) on the substrate takes a much longer time to reach completion. One advantage of our approach is the mild reaction conditions, which allows the cyclopropane moiety to be intact, as these can be easily destroyed by harsh catalysis conditions. We have recycled and reused the C-CMP catalyst by simple filtration and rinsing in acetonitrile. The catalyst maintains its high

photocatalytic activity up to the seventh cycle when applied in the selective oxidation of thioanisole, as shown in Figure 3.

A probable reaction mechanism is proposed in Figure 4. First, excited C-CMP (CB, -1.42 V vs SCE, see Table S4 and Figure S7–8) reduces molecular oxygen to give C-CMP⁺ and a superoxide radical ($E_{\text{red}} = -0.86$ V vs SCE). Amines and sulfides are oxidized by C-CMP⁺ to form radical cations and regenerate neutral C-CMP in a photoredox cycle. The superoxide radical then abstracts protons from the activated amine substrate, from which an imine product/intermediate and hydrogen peroxide are produced. When using primary amines as the substrates ($R = H$), imine intermediates or hydrolyzed benzaldehydes can further react with the free amines to furnish the coupling products.⁸ In the case of the oxidation of sulfides, the activated substrates are probably nucleophilic attacked by water from the solvent and further oxidized by superoxide radical to give corresponding sulfoxides (Figure 4a). The ability of C-CMP to mediate electron transfer from electron-donating substrates (amines or sulfides) to oxygen to generate superoxide radical is confirmed by employing 1,4-bis(dimethylamino)benzene as the indicator (Figure 4b). The generation of H₂O₂ in the photoredox aerobic oxidation reactions is also captured by using by Horseradish peroxidase (POD) catalyzed oxidation of *N,N*-diethyl-1,4-phenylenediammonium sulfate (DPD) (Figure 4c).

CONCLUSIONS

We have demonstrated that carbazole-based conjugated microporous polymer (C-CMP) shows superior photocatalytic efficiency compared to many classes of *N*-CMPs, as well as *g*-C₃N₄ and TiO₂. C-CMP can be used for the visible light photocatalyzed oxidation of primary and secondary amines, aerobic dehydrogenation of nitrogen heterocycles, and oxidation of sulfides, all attained with high efficiency. Furthermore, C-CMP photocatalyst can be recycled and reused for multiruns without obvious decrease in catalytic efficiency. The strategy disclosed here will be helpful for the development of the function of C-CMPs. Since the catalytic efficiency of C-CMPs, as well as its applicability to other catalytic reactions, can be tuned at a molecular level by altering the substituents or the backbone structure, it is envisaged that C-CMPs will emerge as powerful photocatalysts for mediating synthetic transformations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00443.

General procedures, synthesis, FTIR spectra, UV–vis spectra, and NMR spectra (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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