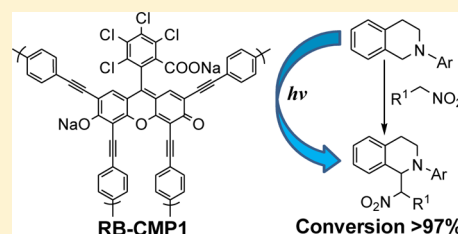


## Conjugated Microporous Polymers with Rose Bengal Dye for Highly Efficient Heterogeneous Organo-Photocatalysis

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## Supporting Information

**ABSTRACT:** Rose Bengal dye has been successfully integrated into the skeleton of a conjugated microporous polymer via palladium-catalyzed Sonogashira–Hagihara cross-coupling polycondensation. These polymers are stable in various solvents, including concentrated hydrochloric acid, and are thermally stable. The resulting polymers show substantial porosity and are highly active for heterogeneous photocatalytic aza-Henry reactions at room temperature for a wide range of substrates. Moreover, this noble-metal-free photocatalyst shows robust recycling capability with good retention of photoactivity over 10 cycles without significant loss of conversion (<10%). These data show that dye-functionalized conjugated microporous polymers are stable, highly active, and reusable noble-metal-free heterogeneous photo-organocatalysts.



## 1. INTRODUCTION

As an emerging class of organic porous materials, conjugated microporous polymers (CMPs)<sup>1,2</sup> that combine  $\pi$ -conjugation structure with high surface area and permanent nanopores have attracted much interest. Various polymerization methods, monomer building blocks and synthetic methods have been exploited to develop a range of CMPs with different structures and physical properties.<sup>3</sup> Unlike other organic porous materials (e.g., polymers of intrinsic microporosity (PIMs),<sup>4</sup> hyper-crosslinked polymers (HCPs)<sup>5,6</sup> and covalent organic frameworks (COFs)<sup>7,8</sup>) that are not  $\pi$ -conjugated, CMPs possess a greater degree of extended  $\pi$ -conjugation along the main chain. This gives CMPs materials potential in the area of energy storage and conversion,<sup>9</sup> and there are reports of CMP supercapacitors,<sup>10</sup> light harvesting CMP,<sup>11</sup> light emitting CMPs,<sup>12</sup> optoelectronic CMPs<sup>13</sup> and CMP photocatalysts.<sup>14</sup> The first CMPs comprised rather simple aromatic building blocks, and those studies focused on their physisorptive for gas storage.<sup>1,15</sup> More recently, specific functionalities were achieved by the introduction of designed active sites into CMPs, particularly for heterogeneous catalysis because these materials are synthetically versatile, have good thermal stability, and excellent chemical robustness to acids, bases, and organic solvent.<sup>16</sup> For example, a CMP produced from Tröger's base was the first example of heterogeneous catalysis on the addition of diethylzinc to an aromatic aldehyde.<sup>17</sup> An iron(III) porphyrin-based CMP was found to be highly active for catalyzing the oxidation of sulfides to the corresponding sulfoxides,<sup>18</sup> and an Ir-loaded CMP showed good catalytic activity for reductive aminations.<sup>19</sup> Ir/Ru-incorporated CMPs have also been demonstrated as efficient photocatalysts for aza-

Henry reactions.<sup>20</sup> To achieve an economically and environmentally acceptable chemical process, it is desirable to develop recyclable, reusable, and noble metal-free heterogeneous photocatalysts. The ability to recover and reuse such heterogeneous photocatalysts can both eliminate the contamination of organic products by trace amounts of heavy metals, and also reduce processing and waste disposal costs in large-scale reactions.

Organic dyes have been studied widely in the areas such as dye-sensitized solar cells<sup>21,22</sup> and homogeneous catalysis.<sup>23–25</sup> The incorporation of a dye molecule into a CMP skeleton might open up second-generation porous materials with useful combined chemical and physical properties such as photocatalytic activity, or light-absorption/emission. For example, dye-based CMP materials might be of interest in heterogeneous catalysis or photocatalysis, where high surface areas would be beneficial. Kiskan et al.<sup>26</sup> reported the CMP with phenolphthalein motif in the main chain, whereby the colored, alkaline salt form of the phenolphthalein CMP showed effective heterogeneous photosensitization for methyl methacrylate photopolymerization. Kang et al.<sup>14</sup> synthesized benzodifuran-functionalized CMPs by post modification, and the resulting polymer showed high photocatalytic activity for the coupling of primary amines.

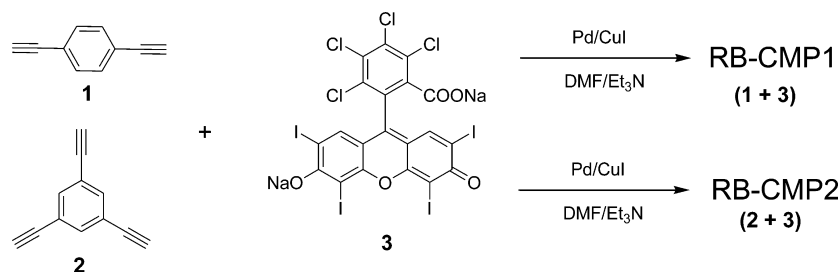
Rose Bengal is an effective noble metal-free photo-organocatalyst, and has been studied in the area of homogeneous photocatalysis because of its low cost and low toxicity.<sup>27</sup>

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## Scheme 1. Sonogashira–Hagihara Coupling Route to the RB-CMP Networks



However, there are no reports on the synthesis of Rose Bengal-based CMPs for heterogeneous photocatalytic organic reactions. We report here a novel bottom-up strategy for preparing organic dye-functionalized CMPs by introducing Rose Bengal into the main chain. The resulting polymers show highly porosity (surface area >830 m<sup>2</sup>/g) and are highly active for heterogeneous photocatalytic aza-Henry reactions at room temperature for a range of substrates. Moreover, the photocatalyst shows robust recycling capability with well-retained photoactivity over recycling ten times. These data show that dye-functionalized CMPs are stable, highly active, and reusable noble metal-free heterogeneous photo-organocatalysts.

## 2. EXPERIMENTAL SECTION

**Chemicals.** 1,3,5-Triethynylbenzene was purchased from ABCR; 1,4-diethynylbenzene, Rose Bengal, tetrakis(triphenylphosphine)palladium, copper(I) iodide and other chemicals were all purchased from Aldrich and used as received.

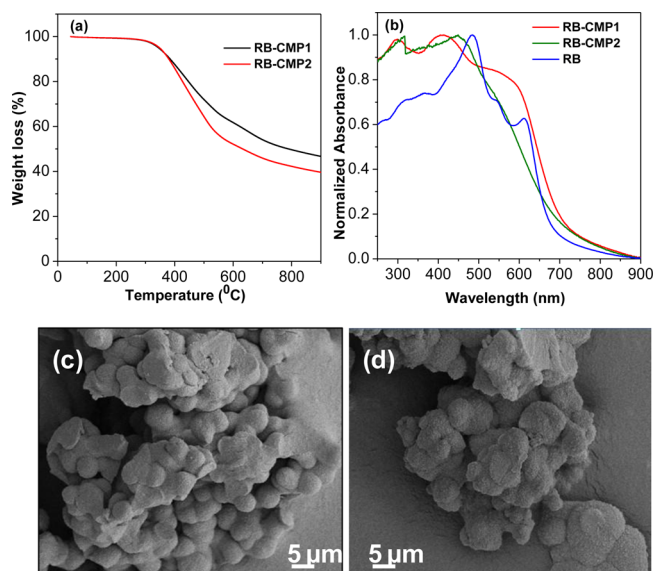
**Synthesis of RB-CMP1.** 1,4-Diethynylbenzene (126 mg, 1.0 mmol), Rose Bengal (508.5 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg), and copper(I) iodide (10 mg) were dissolved in a mixture of DMF (5.0 mL) and Et<sub>3</sub>N (5.0 mL). The reaction mixture was heated to 100 °C and stirred for 24 h under a nitrogen atmosphere in order to rigorously exclude oxygen and to prevent homocoupling of the alkyne monomers. The mixture was cooled to room temperature and the precipitated network polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any unreacted monomer or catalyst residues. Further purification of the polymers was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C. (Yield: 75.6%). IR (KBr cm<sup>-1</sup>): 3297.8 (–C≡C–H), 2201.5 (–C≡C–). Anal. Calcd for C<sub>40</sub>H<sub>10</sub>Cl<sub>4</sub>Na<sub>2</sub>O<sub>5</sub>: C, 63.36; H, 1.33; Cl, 18.70. Found: C, 59.47; H, 1.21; Cl, 13.80.

**Synthesis of RB-CMP2.** 1,3,5-Triethynylbenzene (150 mg, 1.0 mmol), Rose Bengal (762.75 mg, 0.75 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg), and copper(I) iodide (10 mg) were used in the polymerization. Yield: 73.4%. Anal. Calcd for C<sub>108</sub>H<sub>18</sub>Cl<sub>12</sub>Na<sub>6</sub>O<sub>15</sub>: C, 61.23; H, 0.86; Cl, 20.08; Found: C, 57.35; H, 1.04; Cl, 14.90.

**Standard Procedure for Dehydrogenative Aza-Henry Reaction with 5 mol % RB-CMP1 under Visible Light.** An oven-dried reaction tube with stirring bar was cooled down to room temperature, RB-CMP1 (19 mg, 0.025 mmol), *N*-phenyl tetrahydroisoquinoline (104.5 mg, 0.5 mmol), and nitromethane (1.0 mL) were charged into the tube. The tube was sealed with a rubber stopper and the reaction mixture was connected to the air through a needle in the stopper. The tube was subsequently stirred at room temperature under the irradiation of a 60 W bulb light for 15 h. The reaction mixture was then extracted with ethyl acetate (3 × 5 mL), and the combined organic layer was then concentrated and purified by a silica column using elution with hexane/ethyl acetate (95/5) to give the pure product.

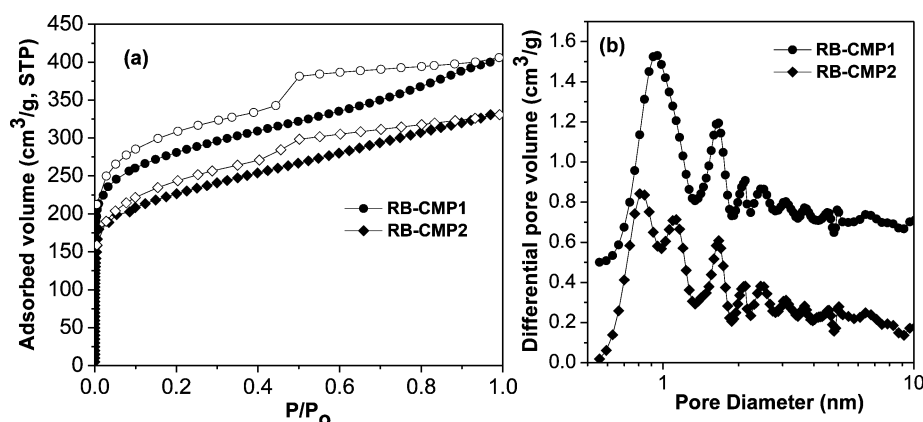
## 3. RESULTS AND DISCUSSION

The polymer networks were synthesized by palladium-catalyzed Sonogashira–Hagihara cross-coupling polycondensation of 1,4-diethynylbenzene (1) or 1,3,5-triethynylbenzene (2) with Rose Bengal (RB, 3), which has four iodine functionalities that are suitable for this reaction without any further synthetic elaboration. The general synthetic routes for the RB-CMP networks are shown in Scheme 1. Reaction of 1,4-diethynylbenzene with Rose Bengal gave the polymer RB-CMP1, as a deep purple powder. The equivalent reaction of 1,3,5-triethynylbenzene with Rose Bengal gave the copolymer RB-CMP2 as a dark brown powder. Both of these polymers are insoluble in conventional organic solvents because of their highly cross-linked structures and they are also chemically stable, for example, with respect to aqueous solutions of acids and bases, such as HCl and NaOH. The RB-CMP networks are thermally stable in nitrogen up to 300 °C, as revealed by TGA (Figure 1a). No palladium residue could be detected in the



**Figure 1.** (a) Thermogravimetric analysis (TGA) curves for the RB-CMP networks under a nitrogen atmosphere with a heating rate of 10 °C/min. (b) UV–visible absorption spectra for the monomer of RB and the RB-CMP networks as solid state powders. (c and d) SEM images for the RB-CMP1 (c) and RB-CMP2 (d) network.

networks by energy dispersive X-ray spectroscopy (EDX) after exhaustive purification. Powder X-ray diffraction measurements indicate that the RB-CMP networks are amorphous in nature, as for most other reported CMP networks.<sup>28–32</sup> The UV–visible absorption spectra of the RB-CMP networks recorded for solid state powders demonstrates that both polymers show



**Figure 2.** (a) N<sub>2</sub> adsorption–desorption isotherms measured at 77.3 K (adsorption branch is labeled with filled symbols) for the RB-CMP networks. For clarity, the isotherms of RB-CMP1 were shifted vertically by 50 cm<sup>3</sup> g<sup>−1</sup>. (b) NL-DFT pore size distribution curves the RB-CMP networks.

broad absorption in the range from 350 to 700 nm (Figure 1b), which is similar to that of the Rose Bengal monomer, indicating that the RB-CMP networks can absorb light across a wide range of the visible spectrum. Electron microscopy images showed that the RB-CMP networks comprise aggregates of small beads (Figure 1, parts c and d).

The porous properties of the RB-CMP networks were investigated by nitrogen adsorption analyses at 77.3 K. As shown in Figure 2a, both of the RB-CMP networks showed similar adsorption and desorption isotherms, and gave rise to type I nitrogen gas sorption isotherms. The adsorption isotherm displays a steep nitrogen gas uptake at low relative pressure ( $P/P_0 < 0.001$ ) reflecting the presence of micropores, with a slight hysteresis loop implying some mesoporosity in both polymers.<sup>33</sup> The apparent BET surface areas were found to be 833 and 801 m<sup>2</sup> g<sup>−1</sup> for RB-CMP1 and RB-CMP2, respectively. As calculated by nonlocal density functional theory (NL-DFT), both of the RB-CMP networks show relatively wide pore size distributions, with the pore widths centering around 0.9, 1.1, and 1.7 nm (Figure 2b). This demonstrates a significant proportion of micropores in the RB-CMP networks.

Dehydrogenative coupling reactions, performed under oxidative conditions, are important as C–C bond formation methods. The industrial use of homogeneous organic dyes<sup>27,34</sup> or heterogeneous noble-metal catalysts (Ir/Ru-based CMP)<sup>20</sup> might be limited either because of separation problems or the high-costs, respectively. Heterogenization of organocatalysts offer an attractive opportunity to resolve these problems, providing that mass transport, activity, selectivity, and recyclability are good. We investigated the aza-Henry reaction as a model reaction to estimate the photocatalytic activities of the RB-CMP networks. A test reaction was carried out using *N*-substituted tetrahydroisoquinoline and CH<sub>3</sub>NO<sub>2</sub> as the substrates in the presence of air with a common fluorescent lamp (60 W) as the light source at room temperature (Table 1). Both of the RB-CMP polymers (5 mol % polymer catalyst loading over the substrate of *N*-phenyl tetrahydroisoquinoline)<sup>35</sup> showed similar photocatalytic activities for this aza-Henry reaction, with around 48% conversion in 3 h (Table 1, entries 1, 3). The conversion was comparable for the homogeneous Rose Bengal monomer (Table 1, entry 5). The reaction was much faster with a standard 60 W household bulb than it was under natural light, both for the heterogeneous catalysts and the homogeneous Rose Bengal monomer (Table 1, entries 2, 4, 6). We need to point out that it is hard to make a

**Table 1. Screening Conditions for the Aza-Henry Reaction<sup>a</sup>**

entry	catalyst	light source	time (h)	convn (%) <sup>b</sup>
1	RB-CMP1	60 W bulb	3	47.5
2	RB-CMP1	natural light	3	9.8
3	RB-CMP2	60 W bulb	3	45.7
4	RB-CMP2	natural light	3	7.5
5	RB	60 W bulb	3	48.3
6	RB	natural light	3	20.3

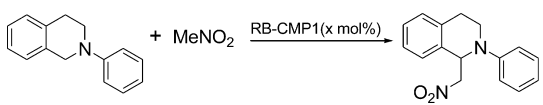
<sup>a</sup>Reaction conditions: tertiary amine (0.5 mmol); MeNO<sub>2</sub> (1.0 mL); catalyst (5 mol %); room temperature. The reaction system was open to the air. <sup>b</sup>Conversion determined by NMR.

linear polymer because the monomer of Rose Bengal employed here itself contains four iodine functions, and also that it is unclear how important the microporosity would be since both of the RB-CMPs have approximately the same BET surface area and show similar catalytic activity (Table 1, entries 1, 3).

The optimization of the reaction conditions was next carried out using RB-CMP1 as the photocatalyst for the same model test reaction (Table 2). The reaction afforded almost full conversion (>97%) with an even lower catalyst loading of 1 or 2 mol % at a prolonged reaction time of 12 h (Table 2, entries 1, 2). When the catalyst loading was 5 mol % or above, full conversion (100%) was obtained in a shorter reaction time of 10 h (Table 2, entries 3–5), which indicates that the higher catalyst loading leads to a faster reaction rate. In addition, the incorporated RB polymer shows much rapid reaction rate compared to its homogeneous counterpart (RB). For example, when the polymer catalyst loading was 2 mol %, the conversion of 99% was obtained in 12 h (Table 2, entry 2), while the conversion was only 73% even in a longer reaction time of 15 h for 2 mol % RB loading alone (Table 2, entry 10), and a higher RB loading of 5 mol % was needed to achieve a 99% conversion (Table 2, entry 11).

A number of control experiments were carried out to demonstrate the heterogeneous and photocatalytic nature of the reactions. Natural light gave low conversion (30%) and there was no reaction in the dark (Table 2, entries 6, 7), indicating that light is necessary to promote the electron transfer.<sup>27,34</sup> Oxygen in air plays a crucial role in the reaction as well: when the reaction was carried out under an argon



**Table 2. Optimization of the Aza-Henry Reaction Conditions with RB-CMP1<sup>a</sup>**


entry	catalyst (x mol %)	light source	air	time (h)	convn (%) <sup>b</sup>
1	RB-CMP1 (1)	60 W bulb	yes	12	97
2	RB-CMP1 (2)	60 W bulb	yes	12	99
3	RB-CMP1 (5)	60 W bulb	yes	12	100
4	RB-CMP1 (10)	60 W bulb	yes	10	100
5	RB-CMP1 (20)	60 W bulb	yes	10	100
6	RB-CMP1 (2)	natural light	yes	15	30
7	RB-CMP1 (2)	dark	yes	15	0
8	RB-CMP1 (2)	60 W bulb	Ar	15	53 <sup>c</sup>
9	RB-CMP2 (2)	60 W bulb	yes	15	90
10	RB (2)	60 W bulb	yes	15	73
11	RB (5)	60 W bulb	yes	15	99
12	CMP-1 (5) <sup>d</sup>	60 W bulb	yes	15	0

<sup>a</sup>Reaction conditions are the same as in Table 1. <sup>b</sup>Conversion determined by NMR. <sup>c</sup>The reaction was carried out under Ar. There was no desired product formed and an unidentified product produced. <sup>d</sup>CMP-1 was synthesized from 1,3,5-triethynylbenzene and 1,4-dibromobenzene.

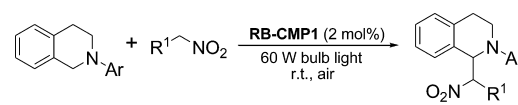
atmosphere excluding oxygen, then the desired product was not observed. Instead, an unidentified product was formed (Table 2, entry 8). There was no reaction occurred when other CMP, CMP-1,<sup>1</sup> was used which does not contain the Rose Bengal unit (Table 2, entry 12), verifying that the Rose Bengal units are critical to the photocatalytic reactions. Absolutely no leaching of dye was observed from the polymers, which would have been obvious given the strongly colored nature of this species.

We subsequently explored the scope of substrates for this organo-photocatalytic reaction by using a variety of tetrahydroisoquinolines with different functional groups, and nitromethane/nitroethane as the other substrate (Table 3). As shown in Table 3, good to excellent isolated yields were obtained for almost all of the aza-Henry reactions catalyzed by the **RB-CMP1** catalyst (90–97% isolated yield), which are comparable to those using the Ir- or Ru-loaded CMP, and the homogeneous Rose Bengal counterpart.<sup>20,34</sup> This demonstrates that the **RB-CMP** networks are versatile organo-photocatalysts for this class of dehydrogenative coupling reaction.

We also examined the recyclability and photocatalytic stability of this heterogeneous organo-photocatalyst (see Supporting Information, Table S1). The recycling experiment was carried out by using a simple filtration method to recover the **RB-CMP1** organo-photocatalyst. The recovered **RB-CMP1** catalyst was then washed with THF and CH<sub>2</sub>Cl<sub>2</sub> to remove any residual products or unreacted substrates, and dried in vacuum overnight before being reused. Owing to the built-in nature of the covalently linked catalytic sites in the main chain, the **RB-CMP1** polymer maintained its structure well, and this allows for recycling with good catalytic photoactivity for at least 10 recycling times (Figure 3). There is a small reduction after 10 cycles, although conversions still exceed 90%. As such, the polymer has promise as a stable, recyclable, and low-cost heterogeneous organo-photocatalyst.

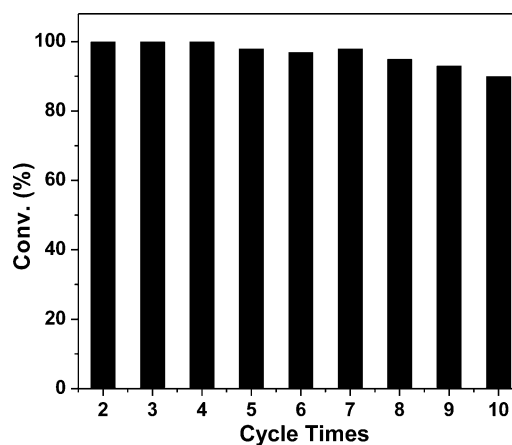
#### 4. CONCLUSION

In conclusion, Rose Bengal dye has been successfully integrated into the skeleton of a conjugated microporous polymer via

**Table 3. Aza-Henry Reaction with RB-CMP1 for a Range of Substrates<sup>a</sup>**


entry	Ar	R1	time (h)	yield (%) <sup>b</sup>
1	Ph	H	15	95
2	4-F-C <sub>6</sub> H <sub>4</sub>	H	15	91
3	4-Br-C <sub>6</sub> H <sub>4</sub>	H	15	90
4	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	H	15	87
5	4-CN-C <sub>6</sub> H <sub>4</sub>	H	15	83
6	4-OMe-C <sub>6</sub> H <sub>4</sub>	H	15	97
7	4-Me-C <sub>6</sub> H <sub>4</sub>	H	15	93
8	4-C(O)C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub>	H	20	91
9	3-CN-C <sub>6</sub> H <sub>4</sub>	H	15	85
10	3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	H	18	89
11	3-MeO-C <sub>6</sub> H <sub>4</sub>	H	18	93
12	3-Me-C <sub>6</sub> H <sub>4</sub>	H	15	95
13	2-Me-C <sub>6</sub> H <sub>4</sub>	H	15	80
14	3,5-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	H	18	96
15	1-naphthyl	H	15	90
16	Ph	Me	18	95
17	Ph	Et	18	93
18	4-Me-C <sub>6</sub> H <sub>4</sub>	Me	18	94
19	4-Me-C <sub>6</sub> H <sub>4</sub>	Et	18	91
20	4-Br-C <sub>6</sub> H <sub>4</sub>	Me	18	93
21	4-Br-C <sub>6</sub> H <sub>4</sub>	Et	18	91
22	4-OMe-C <sub>6</sub> H <sub>4</sub>	Me	18	97
23	4-OMe-C <sub>6</sub> H <sub>4</sub>	Et	18	95

<sup>a</sup>Reaction conditions: 0.5 mmol tertiary amine; 1.0 mL of nitroalkyl; room temperature; 60 W household bulb; in air. <sup>b</sup>Isolated yield.

**Figure 3.** Recycling experiments of **RB-CMP1** for the aza-Henry reaction.

palladium-catalyzed Sonogashira–Hagihara cross-coupling polycondensation. These polymers are stable in various solvents, including concentrated hydrochloric acid, and are thermally stable. The high BET surface area and interconnected pores of **RB-CMP** networks ensured their excellent catalytic activity by increasing the accessibility of catalytic sites and facilitating the mass transport process—indeed, the activity of the heterogeneous photocatalysts is comparable to the homogeneous dye. These **RB-CMP** networks were shown to be highly active, recyclable, and reusable heterogeneous organo-photocatalysts in aza-Henry reactions of a wide variety of substrates at room

temperature, and the catalyst could be reused at least 10 times without significant loss of conversion (<10%). The RB-CMP network might also act as a heterogeneous noble metal-free photocatalyst for other important organic transformations. Moreover, this bottom-up strategy should be readily transferable to other dyes and organocatalysts more generally, perhaps including chiral porous metal-free photocatalysts.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Details of the photocatalytic reactions and characterizations and the  $^1\text{H}$  and  $^{13}\text{C}$  NMR and FT-IR data for the photocatalytic products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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- (35) Note: The estimated loading of RB in the polymer could be calculated from the content of Cl based on the microanalysis (Cl is 14.90 wt.% for RB-CMP1). As for 5 mol% RB-CMP1 (19 mg), it contains 0.021 mmol RB segment (one RB contains four Cl atoms), which results in a 4.2 mol% RB loading over the substrate of N-phenyl tetrahydroisoquinoline (104.5 mg, 0.5 mmol), a slight lower than 5 mol% of RB loading alone.