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Visible-Light-Controlled Ruthenium-Catalyzed Olefin Metathesis

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Supporting Information

ABSTRACT: Olefin metathesis is now one of the most efficient ways to create new carbon−carbon bonds. While most efforts focused on the development of ever-more efficient catalysts, a particular attention has recently been devoted to developing latent metathesis catalysts, inactive species that need an external stimulus to become active. This furnishes an increased control over the reaction which is crucial for applications in materials science. Here, we report our work on the development of a new system to achieve visible-light-controlled metathesis by merging olefin metathesis and photoredox catalysis. The combination of a ruthenium metathesis catalyst bearing two N-heterocyclic carbenes with an oxidizing pyrylium photocatalyst affords excellent temporal and spatial resolution using only visible light as stimulus. Applications of this system in synthesis, as well as in polymer patterning and photolithography with spatially resolved ring-opening metathesis polymerization, are described.

Olefin metathesis is one of the most attractive and powerful tools for the creation of carbon−carbon π bonds, finding numerous applications in synthetic chemistry, fine chemical synthesis and materials science.[1,2] While most synthetic efforts have been devoted to the development of ever-more efficient catalysts, increased attention has been paid to the development of catalysts that can be activated/deactivated on demand.[3] Such latent catalysts are dormant species under ambient conditions and require an external stimulus to become active. Increased control on reactions is crucial not only from an understanding viewpoint but also for applications in materials science for the production of new well-defined materials.[4] Various stimuli have been exploited to achieve such control in metathesis reactions, including heat, light, ultrasound, acid and redox switches.[5] Light is arguably the most convenient and attractive stimulus since it is non-invasive (as in Figure 1), can be easily manipulated and provides the opportunity for high temporal and spatial resolution (Figure 1a).[6] As a consequence, several recent reports have described light-promoted olefin metathesis.[5c,d,7] While these have been important developments, they are dominated by UV light with most reports describing activation rather than gating control of alkene metathesis.

We considered that the merger of olefin metathesis with photoredox catalysis[8] could lead to visible-light control of alkene metathesis. Visible-light photoredox catalysis has already proven successful for metal-free olefin metathesis polymerization via a radical mechanism.[9] In particular, excitation of the appropriate photocatalyst by visible-light

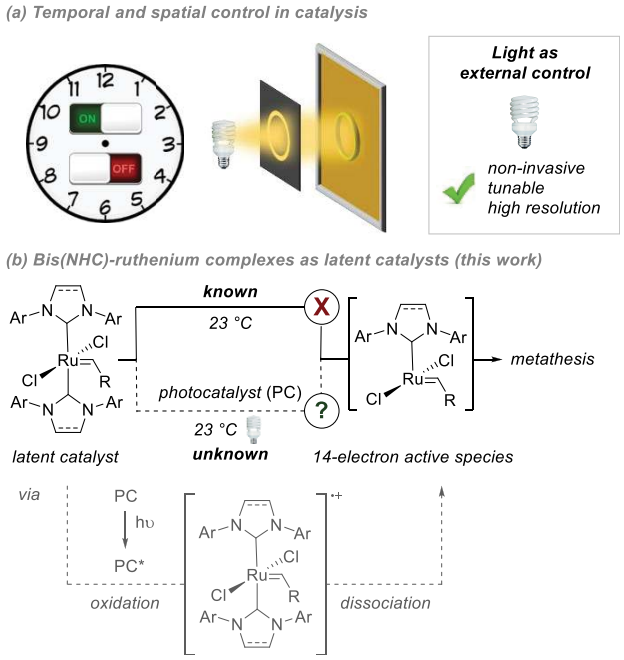

Figure 1. (a) Temporal and spatial control in catalysis. (b) Bis(NHC)-ruthenium complexes as latent catalysts using visible light (this work).

irradiation should permit the activation of a latent metathesis catalyst, most probably by inducing ligand dissociation,[10] and therefore lead to the development of an on-demand metathesis system. Importantly, the use of visible light is more convenient than UV light while still providing high levels of temporal and spatial resolution. Overall, the development of such a system would open new perspectives in photolithography[11,12] and in materials science for the design of new materials,[13] as already illustrated by the impact of recent work reported for photocontrolled, living radical polymerizations.[14]

At the outset of these studies, we needed a ruthenium-based complex that is inactive at ambient temperature, and identified bis-NHC ligated Ru complexes first introduced by Herrmann.[15] When substituted with aromatic groups on the nitrogen atoms, these catalysts lack activity for metathesis at room temperature, most probably because of the difficult dissociation of one NHC ligand to generate the corresponding 14-electron active catalyst.[15,16] At higher temperatures, the activity of these catalysts is restored. In this regard, we surmised that the NHC dissociation event could be promoted

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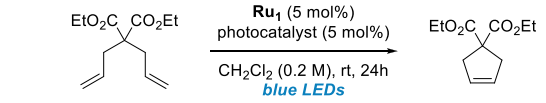
at room temperature by using photoredox catalysis. A carefully chosen photocatalyst should be capable, after excitation upon irradiation with visible light, of activating these catalysts and therefore toggling them into their corresponding active species after dissociation of one NHC (Figure 1b).

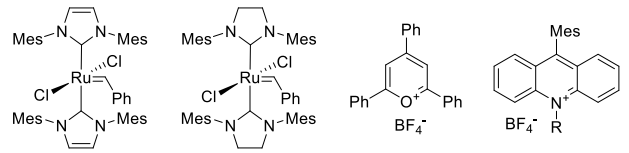
To test our hypothesis, we first evaluated the benchmark ring closing metathesis (RCM) of diethyl diallylmalonate using $RuCl_2(CHPh)(IMes)_2$ and $RuCl_2(CHPh)(SIMes)_2$, previously reported by Fogg[17] and Grubbs,[16] in the presence of different photocatalysts under visible-light irradiation. After screening several photocatalysts and reaction conditions (see Supporting Information for further details), we found that a combination of $RuCl_2(CHPh)(IMes)_2$ (**Ru_1**) and 2,4,6-triphenylpyrylium tetrafluoroborate (TPPT) as photocatalyst gives the desired product in 87% yield after 4 h of irradiation under blue LEDs at room temperature (Table 1, entry 9). While screening photocatalysts, we observed that only highly oxidizing ones such as acridinium and pyrylium derivatives provide some reactivity (entries 6−8), while no product is observed when switching to less oxidizing photocatalysts (entries 1−5). This is consistent with an activation mode involving oxidation of the Ru catalyst followed by dissociation of one NHC to generate the catalytically active species, in the process forming the IMes radical cation.[18] We indeed note that **Ru_1** has two distinct oxidation events as identified by cyclic voltammetry, with the first occurring at +0.44 V, likely corresponding to the generation of the radical cation by a metal-centered oxidation (see SI). While all photoredox catalysts should allow oxidation to the radical cation, the dissociation event might be caused by a second oxidation occurring at one NHC ligand that would only be promoted by highly oxidizing photocatalysts and explain that traditional Ir and Ru photocatalysts are not effective (see Table 1, entries 1−5).[19] Importantly, no reaction is observed in the absence of ruthenium, light or photocatalyst (entries 10−12). The lack of reactivity under light without photocatalyst also rules out a mechanism solely based on photoinduced dissociation of one NHC ligand and highlights the importance of the photoredox system. Finally, the use of $RuCl_2(CHPh)(SIMes)_2$ (**Ru_2**) delivers similar reactivity (entry 13). However, background reactivity is observed in the absence of light and photocatalyst (entry 14), indicating that dissociation of one NHC happens slowly at ambient temperature. $RuCl_2(CHPh)(IMes)_2$ (**Ru_1**) was chosen as it displays optimal latent behavior.

With an efficient system in hand, we first explored its ability to promote different types of metathesis reactions. While standard metathesis reactions can be readily promoted using this photoredox catalytic system, as illustrated with representative examples in Table 1 and SI, we were more interested in interrogating ring-opening metathesis polymerization (ROMP) applications. To this end, several monomers such as norbornene derivatives **1**−**8**, **11**, norbornadiene **9**, 1,5-cyclooctadiene **10** and dicyclopentadiene **12** could be readily polymerized within 1 h under blue LED irradiation in the presence of $RuCl_2(CHPh)(IMes)_2$ and TPPT (Table 2). Molecular weights (M_n) obtained after polymerization of monomers **1**−**4** are significantly higher than the expected values which suggests that polymerization is faster than catalyst initiation. Dispersities were found in the range of 1.63 to 1.88. Monomers **5**−**10** are also smoothly polymerized within an hour of irradiation but lead to insoluble polymers, which precludes GPC analysis. Finally, cross-linking monomers **11** and **12** could also be efficiently polymerized to afford complete

Table 1. Reaction Optimization and Scope of RCM, CM, and ROCM Reactions

(a) Reaction optimization

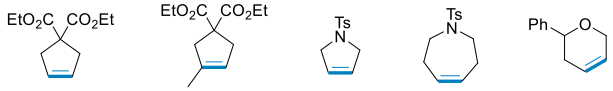




$RuCl_2(CHPh)(IMes)_2$ (**Ru_1**) | $RuCl_2(CHPh)(SIMes)_2$ (**Ru_2**) | TPPT | MesAcrPh (R=Ph) MesAcrMe (R=Me)

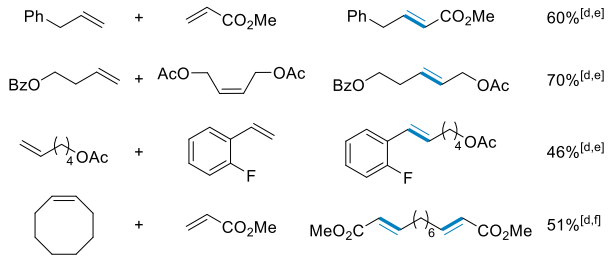
Entry	Conditions	E^*_{ox} (V vs SCE)	Yield[b] (%)
1	$Ir(ppy)_3$	0.31	0
2	$[Ir(ppy)_2(dtbbpy)]PF_6$	0.66	0
3	$Ru(bpy)_3Cl_2$	0.77	0
4	$[Ir(dF\text{-}CF_3ppy)_2(dtbbpy)]PF_6$	1.21	0
5	$Ru(bpz)_3Cl_2$	1.45	0
6	MesAcrPh	2.12	33
7	MesAcrMe	2.18	16
8	TPPT	2.55	84
9	**Ru_1** (2 mol%), TPPT (3 mol%), 4h	-	87
10	no **Ru_1**	-	0
11	no light	-	0
12	no photocatalyst	-	0
13	**Ru_2** instead of **Ru_1**	-	75
14	**Ru_2**, no light, no photocatalyst	-	15

(b) Scope of RCM reactions[c]



86% | 84% | 90% | 89% | 72%

(c) Scope of CM and ROCM reactions[c]



[a]All optimization reactions were conducted on a 0.1 mmol scale. [b]Determined by ^1H NMR spectroscopy using 1,2-dibromoethane as an internal standard. [c]Conditions: substrate (0.2 mmol), $RuCl_2(CHPh)(IMes)_2$ (2 mol %), TPPT (3 mol %), CH_2Cl_2 (0.2M), rt, blue LEDs, 4 h. [d]4 mol % of TPPT. [e]Left substrate (0.2 mmol), right substrate (0.4 mmol). [f]Left substrate (0.2 mmol), right substrate (0.6 mmol). For additional samples, see SI.

gelation within an hour, the latter only requiring 0.01 mol % of **Ru_1**, 0.05 mol % of TPPT and 15 min of irradiation. Importantly, the latency is successfully maintained with dicyclopentadiene **12** since, in the absence of light, less than 5% polymerization is observed after 24 h (5% after 3 days, 9% after a week). When stopped after 90 s under light, 16% polymerization is observed. The rate of polymerization under

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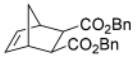
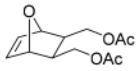
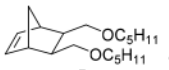
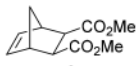
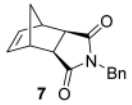
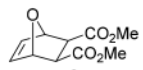
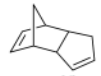
Table 2. Scope of ROMP Reactions

	Monomer	Conversion[b] (%)	Theo. M_n (kDa)	Exp. M_n[c] (kDa)	$Đ$[c]
1		>95	18.8	99.6	1.88
2		>95	66.9	215.2	1.66
3		>95	48.0	327.4	1.63
4		>95	47.7	424.8	1.83
5					
6					
7					
8					
9					
10					
11					
12[d]					

[a]Conditions: monomer (0.2 mmol), $RuCl_2(CHPh)(IMes)_2$ (0.5 mol %), TPPT (1 mol %), CD_2Cl_2 (0.2 M), rt, blue LEDs, 1 h. [b]Determined by ^1H NMR spectroscopy using mesitylene as internal standard. [c]Determined by GPC. [d]Using $RuCl_2(CHPh)(IMes)_2$ (0.01 mol %), TPPT (0.05 mol %) for 15 min under blue LEDs.

visible light can therefore be estimated to be 12 000 times faster than in the dark.

Further experiments were conducted to examine the influence of light and to probe our ability to exert temporal and spatial control over the reaction. First, temporal control was evaluated by conducting on/off experiments with alternating periods of irradiation and darkness for the ring closing metathesis of diethyl diallylmalonate. The ability to exert temporal control over a reaction is of great interest for the design of orthogonal multicomponent reactions, as well as for the development of new systems designed to produce new highly functionalized materials. As can be seen in Figure 2, temporal control can be achieved since maximal reactivity was obtained during irradiation whereas darkness only afforded minimal increases in yields (from 0 to 3%).

A series of experiments (described in the SI) lead us to suggest the following mechanism for the on/off behavior enabled by photoredox catalysis and light irradiation.[9a] It is commonly accepted that Ru catalysts mediate olefin metathesis via a coordinatively unsaturated Ru(II) intermediate such as **II** (Figure 2). Given that only highly oxidizing excited state photocatalysts provide appreciable yield (Table 1), we propose that ligand loss occurs at ambient temperature from an oxidized Ru intermediate, potentially at the IMes moiety to give active metathesis catalyst **II** and reduced pyrylium **V** as well as **VI**. The latter two can combine to form **VII**, analogous to adducts reported lacking substitution at the 4 position.[20] Release of the IMes provides a pool of free ligand which can coordinate **IV** and arrest catalysis.[21]

We also interrogated our ability to exert spatial control over metathesis with this system, due to the potential applications in materials science with polymer patterning, 3D printing and photolithography. In this regard, the development of a system controlled by visible light appears especially attractive and

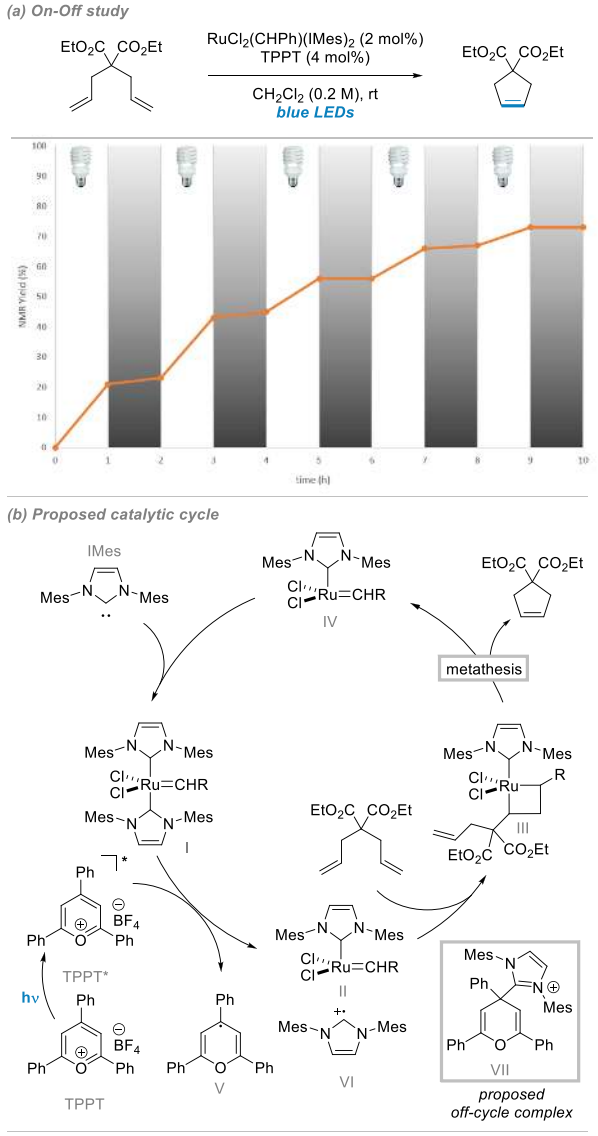


Figure 2. Temporal control over the RCM of diethyl diallylmalonate and corresponding proposed mechanism.

convenient. To this end, dicyclopentadiene **12**, and some other monomers,[22] were first irradiated with visible light (blue Kessil lamp, 40 W) in the presence of $RuCl_2(CHPh)(IMes)_2$ and TPPT through different photomasks in order to produce macroscopic polymers with controlled geometric patterns. Removal of the masks and unreacted monomers nicely affords the corresponding patterned polymers in short irradiation times (15–60 min) and with minimal bleeding in the unexposed areas (Figure 3a–c).[23] Interestingly, the thickness of these patterned polymers can be easily controlled by tuning the irradiation time (see SI). Finally, an important feature of this system is its practicality and user-friendliness. While the excited state TPPT* is modestly sensitive to oxygen, the photomask patterning experiments can be performed with minimal precautions of placing the monomer/catalyst mixture under a blanket of inert gas.

Higher resolutions are required in order to extend this visible-light-controlled system for applications in photolithographic olefin metathesis polymerization (PLOMP). While most photolithographic techniques are based on the use of

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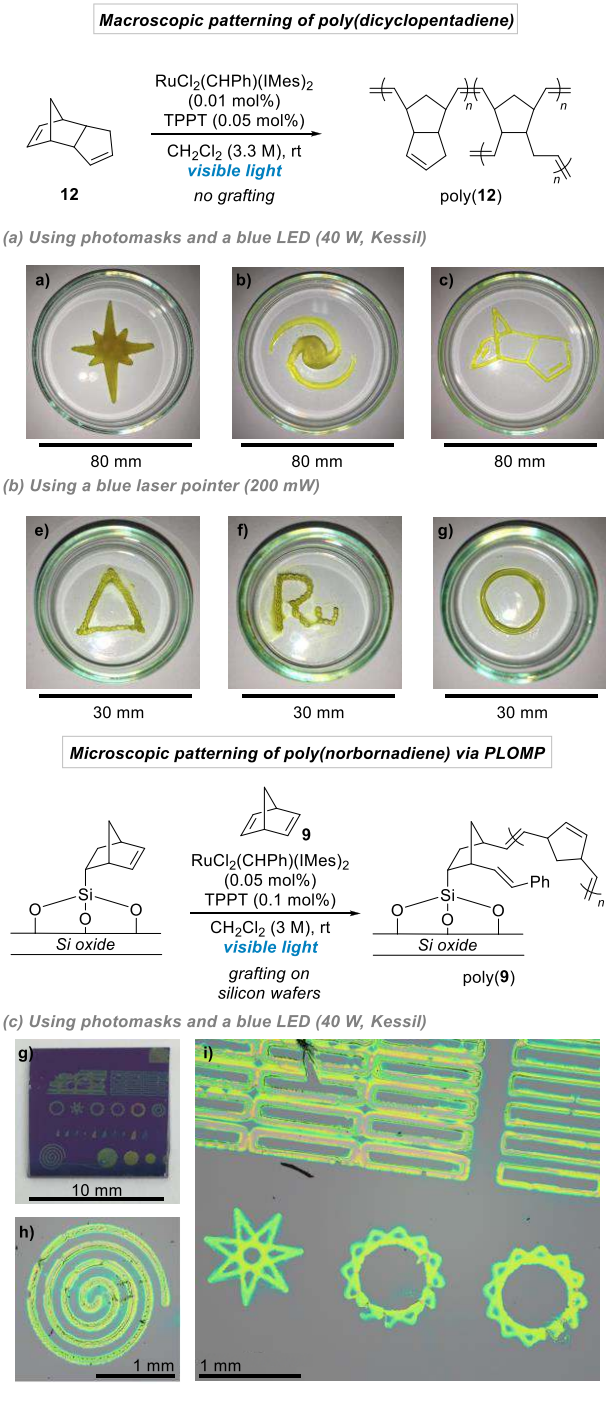

Figure 3. Polymer patterning and photolithographic olefin metathesis polymerization (PLOMP) using visible light.

high resolution photomasks, an attractive alternative is the use of high resolution light sources, such as lasers, which should provide a straightforward way to reach pinpoint resolution and find new applications in photolithography.[24] As proof of concept, we could successfully induce similar patterning from dicyclopentadiene solutions using a simple blue laser pointer (200 mV). In these cases, the patterns are directly and conveniently "drawn" from the bulk solution in a few minutes, either manually (Figure 3d,e) or using an orbital shaker providing constant movement (Figure 3f).

The two afore-described techniques allow the convenient fabrication of macroscopic patterned polymers through spatially resolved ROMP promoted by visible light and without the need for grafting of the monomers. As for microscopic patterning, we also demonstrate the efficiency of our system for PLOMP applications.[12] Although photolithography is now a commonly used technique in microfabrication, such systems based on olefin metathesis are still rare. To this end, 1 cm × 1 cm silicon wafers were first prefunctionalized with a norbornene unit to ensure grafting of the growing polymer onto the surface.[12a] Those prefunctionalized silicon wafers were then used as support to perform the spatially resolved polymerization of norbornadiene on a microscale by simply irradiating a solution of the monomer, $RuCl_2(CHPh)(IMes)_2$ and TPPT in dichloromethane with a regular blue LED light bulb (blue Kessil lamp, 40 W) through high resolution photomasks (Figure 3g).

After developing in dichloromethane, patterns of poly(norbornadiene) with resolutions down to 30−40 μm could be successfully printed over silicon wafers within 10 min of irradiation (Figure 3h,i). These results are accomplished using readily available visible-light sources, and are complementary to Fourkas' positive photoresist,[12a] as well as Grubbs' negative photoresist system,[12b] both of which use UV light, while giving access to similar resolutions.

In conclusion, we have reported the development of an efficient and user-friendly system for olefin metathesis controlled by visible light. The combination of a latent bis(NHC)-ruthenium complex and an oxidizing pyrylium photocatalyst efficiently promotes olefin metathesis under visible light, providing high levels of temporal and spatial resolution. In particular, applications in polymer patterning and photolithographic olefin metathesis polymerization are also demonstrated. Further studies to broaden the scope and applications of this system, as well as to gain more insights into its mechanism, are currently ongoing in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b13663.

Experimental procedures, characterization, copies of ^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

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Notes

The authors declare the following competing financial interest(s): A provisional patent has been submitted covering this work.

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REFERENCES

(1) (a) Grela, K. *Olefin Metathesis: Theory and Practice*; Wiley: Hoboken, NJ, 2014. (b) Grubbs, R. H.; Wenzel, A. G. *Handbook of Metathesis*, 2nd ed.; Wiley-VHC: Weinheim, 2015. (c) Trnka, T. M.; Grubbs, R. H. The Development of L_2X_2Ru = CHR Olefin Metathesis Catalysts: An Organometallic Success Story. *Acc. Chem. Res.* **2001**, *34*, 18−29. (d) Hoveyda, A. H.; Zhugralin, A. R. The remarkable metal-catalysed olefin metathesis reaction. *Nature* **2007**, *450*, 243−250. (e) Ogba, O. M.; Warner, N. C.; O'Leary, D. J.; Grubbs, R. H. Recent advances in ruthenium-based olefin metathesis. *Chem. Soc. Rev.* **2018**, *47*, 4510−4544. (f) Katz, T. J. Olefin Metathesis and Related Reaction Initiated by Carbene Derivatives of Metals in Low Oxidation States. *Angew. Chem., Int. Ed.* **2005**, *44*, 3010−3019.

(2) Higman, C. S.; Lummiss, J. A. M.; Fogg, D. E. Olefin Metathesis at the Dawn of Implementation in Pharmaceuticals and Specialty-Chemicals Manufacturing. *Angew. Chem., Int. Ed.* **2016**, *55*, 3552−3565.

(3) (a) Blanco, V.; Leigh, D. A.; Marcos, V. Artificial switchable catalysts. *Chem. Soc. Rev.* **2015**, *44*, 5341−5370. (b) Choudhury, J. Recent developments on artificial switchable catalysis. *Tetrahedron Lett.* **2018**, *59*, 487−495.

(4) For recent reviews on externally regulated polymerizations, see: (a) Leibfarth, F. A.; Mattson, K. M.; Fors, B. P.; Collins, H. A.; Hawker, C. J. External Regulation of Controlled Polymerizations. *Angew. Chem., Int. Ed.* **2013**, *52*, 199−210. (b) Teator, A. J.; Lastovickova, D. N.; Bielawski, C. W. Switchable Polymerization Catalysts. *Chem. Rev.* **2016**, *116*, 1969−1992. (c) Ogawa, K. A.; Goetz, A. E.; Boydston, A. J. Developments in Externally Regulated Ring-Opening Metathesis Polymerization. *Synlett* **2016**, *27*, 203−214. (d) Teator, A. J.; Bielawski, C. W. Remote Control Grubbs Catalysts That Modulate Ring-Opening Metathesis Polymerizations. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 2949−2960.

(5) For reviews on latent olefin metathesis catalysis, see: (a) Szadkowska, A.; Grela, K. Initiation at Snail's Pace: Design and Applications of Latent Olefin Metathesis Catalysts Featuring Chelating Alkylidene Ligands. *Curr. Org. Chem.* **2008**, *12*, 1631−1647. (b) Monsaert, S.; Lozano Vila, A.; Drozdzak, R.; Van Der Voort, P.; Verpoort, F. Latent olefin metathesis catalysts. *Chem. Soc. Rev.* **2009**, *38*, 3360−3372. For recent reviews on light-promoted olefin metathesis, see: (c) Vidavsky, Y.; Lemcoff, N. G. Light-induced olefin metathesis. *Beilstein J. Org. Chem.* **2010**, *6*, 1106−1119. (d) Eivgi, O.; Lemcoff, N. G. Turning the Light On: Recent Developments in Photoinduced Olefin Metathesis. *Synthesis* **2018**, *50*, 49−63.

(6) (a) Stoll, R. A.; Hecht, S. Artificial Light-Gated Catalyst Systems. *Angew. Chem., Int. Ed.* **2010**, *49*, 5054−5075. (b) Neilson, B. N.; Bielawski, C. W. Illuminating Photoswitchable Catalysis. *ACS Catal.* **2013**, *3*, 1874−1885. (c) Göstl, R.; Senf, A.; Hecht, S. Remote-controlling chemical reactions by light: Towards chemistry with high spatio-temporal resolution. *Chem. Soc. Rev.* **2014**, *43*, 1982−1996.

(7) For recent representative examples using ruthenium catalysts, see: (a) Wang, D.; Wurst, K.; Knolle, W.; Decker, U.; Prager, L.; Naumov, S.; Buchmeiser, M. R. Cationic Ru^{II} Complexes with N-Heterocyclic Carbene Ligands for UV-Induced Ring-Opening Metathesis Polymerization. *Angew. Chem., Int. Ed.* **2008**, *47*, 3267−3270. (b) Wang, D.; Wurst, K.; Buchmeiser, M. R. Cationic versus Neutral Ru^{II} − N-heterocyclic Carbene Complexes as Latent Precatalysts for the UV-Induced Ring-Opening Metathesis Polymerization. *Chem. - Eur. J.* **2010**, *16*, 12928−12934. (c) Keitz, B. K.; Grubbs, R. H. A Tandem Approach to Photoactivated Olefin Metathesis: Combining a Photoacid Generator with an Acid Activated Catalyst. *J. Am. Chem. Soc.* **2009**, *131*, 2038−2039. (d) Khalimon, A. Y.; Leitao, E. M.; Piers, W. E. Photogeneration of a Phosphonium Alkylidene Olefin Metathesis Catalyst. *Organometallics* **2012**, *31*, 5634−5637. (e) Ben-Asuly, A.; Aharoni, A.; Diesendruck, C. E.; Vidavsky, Y.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. Photoactivation of Ruthenium Olefin Metathesis Initiators. *Organometallics* **2009**, *28*, 4652−4655. (f) Levin, E.; Mavila, S.; Eivgi, O.; Tzur, E.; Lemcoff, N. G. Regioselective Chromatic Orthogonality with Light-Activated Metathesis Catalysts. *Angew. Chem., Int. Ed.* **2015**, *54*, 12384−12388. (g) Sutar, R. L.; Levin, E.; Butilkov, D.; Goldberg, I.; Reany, O.; Lemcoff, N. G. A Light-Activated Olefin Metathesis Catalyst Equipped with a Chromatic Orthogonal Self-Destruct Function. *Angew. Chem., Int. Ed.* **2016**, *55*, 764−767. (h) Teator, A. J.; Shao, H.; Lu, G.; Liu, P.; Bielawski, C. W. A Photoswitchable Olefin Metathesis Catalyst. *Organometallics* **2017**, *36*, 490−497.

(8) For reviews on photoredox catalysis, see: (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322−5363. (b) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. Single-Electron Transmetalation via Photoredox/Nickel Dual Catalysis: Unlocking a New Paradigm for sp^3-sp^2 Cross-Coupling. *Acc. Chem. Res.* **2016**, *49*, 1429−1439. (c) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116*, 10075−10166. (d) Skubi, K. L.; Blum, T. R.; Yoon, T. P. Dual Catalysis Strategies in Photochemical Synthesis. *Chem. Rev.* **2016**, *116*, 10035−10074.

(9) (a) Ogawa, K. A.; Goetz, A. E.; Boydston, A. J. Metal-Free Ring-Opening Metathesis Polymerization. *J. Am. Chem. Soc.* **2015**, *137*, 1400−1403. (b) Goetz, A. E.; Boydston, A. J. Metal-Free Preparation of Linear and Cross-Linked Polydicyclopentadiene. *J. Am. Chem. Soc.* **2015**, *137*, 7572−7575. (c) Goetz, A. E.; Pascual, L. M. M.; Dunford, D. G.; Ogawa, K. A.; Knorr, D. B., Jr.; Boydston, A. J. Expanded Functionality of Polymers Prepared Using Metal-Free Ring-Opening Metathesis Polymerization. *ACS Macro Lett.* **2016**, *5*, 579−582.

(10) For our previous work on controlling cobalt-catalyzed cycloadditions with photoredox catalysis, see: (a) Ruhl, K. E.; Rovis, T. Visible Light-Gated Cobalt Catalysis for a Spatially and Temporally Resolved [2+2+2] Cycloaddition. *J. Am. Chem. Soc.* **2016**, *138*, 15527−15530. (b) Ravetz, B. D.; Ruhl, K. E.; Rovis, T. External Regulation of Cobalt-Catalyzed Cycloaddition Polymerization with Visible Light. *ACS Catal.* **2018**, *8*, 5323−5327. (c) Ravetz, B. D.; Wang, J. Y.; Ruhl, K. E.; Rovis, T. Photoinduced Ligand-to-Metal Charge Transfer Enables Photocatalyst-Independent Light-Gated Activation of Co(II). *ACS Catal.* **2019**, *9*, 200−204.

(11) For general references on photolithography, see: (a) Bratton, D.; Yang, D.; Dai, J. Y.; Ober, C. K. Recent progress in high resolution lithography. *Polym. Adv. Technol.* **2006**, *17*, 94−103. (b) Madou, M. J. *Fundamentals of Microfabrication and Nanotechnology*, 3rd ed., CRC Press: Boca Raton, FL, 2011; ISBN 9780849331800. (c) Xu, H.; Kosma, V.; Giannelis, E. P.; Ober, C. K. In pursuit of Moore's Law: Polymer Chemistry in Action. *Polym. J.* **2018**, *50*, 45−55.

(12) For two examples of photolithographic ring opening metathesis polymerization, see: (a) Harris, R. F.; Ricci, M. J.; Farrer, R. A.; Praino, J.; Miller, S. J.; Saleh, B. E. A.; Teich, M. C.; Fourkas, J. T. Photolithographic Patterning of Ring-Opening Metathesis Catalysts on Silicon. *Adv. Mater.* **2005**, *17*, 39−42. (b) Weitekamp, R. A.; Atwater, H. A.; Grubbs, R. H. Photolithographic Olefin Metathesis Polymerization. *J. Am. Chem. Soc.* **2013**, *135*, 16817−16820.

(13) For a review on switchable polymerization catalysts, see: Teator, A. J.; Lastovickova, D. N.; Bielawski, C. W. Switchable Polymerization Catalysts. *Chem. Rev.* **2016**, *116*, 1969−1992.

(14) For a recent review, see: (a) Chen, M.; Zhong, M.; Johnson, J. A. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. *Chem. Rev.* **2016**, *116*, 10167−10211. For selected examples, see: (b) Fors, B. P.; Hawker, C. J. Control of a Living Radical Polymerization of Methacrylates by Light. *Angew. Chem., Int. Ed.* **2012**, *51*, 8850−8853. (c) Anastasaki, A.; Nikolaou, V.; Zhang, Q.; Burns, J.; Samanta, S. R.; Waldron, C.; Haddleton, A. J.; McHale, R.; Fox, D.; Percec, V.; Wilson, P.; Haddleton, D. M. Copper(II)/Tertiary Amine Synergy in Photoinduced Living Radical Polymerization: Accelerated Synthesis of ω-Functional and α,ω-Heterofunctional Poly(acrylates). *J. Am. Chem. Soc.* **2014**, *136*, 1141−1149. (d) Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J. Metal-Free Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* **2014**, *136*, 16096−16101. (e) Pan, X.; Malhotra, N.; Simakova, A.; Wang, Z.; Konkolewicz, D.; Matyjaszewski, K. Photoinduced Atom Transfer

DOI: 10.1021/jacs.8b13663
J. Am. Chem. Soc. 2019, 141, 6791−6796

Radical Polymerization with ppm-Level Cu Catalyst by Visible Light in Aqueous Media. *J. Am. Chem. Soc.* **2015**, *137*, 15430−15433.
(15) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. A Novel Class of Ruthenium Catalysts for Olefin Metathesis. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490−2493.
(16) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. Synthesis and Activity of Ruthenium Alkylidene Complexes Coordinated with Phosphine and N-Heterocyclic Carbene Ligands. *J. Am. Chem. Soc.* **2003**, *125*, 2546−2558.
(17) Conrad, J. C.; Yap, G. P. A.; Fogg, D. E. Concise Route to Highly Reactive Ruthenium Metathesis Catalysts Containing a Labile Donor and an N-Heterocyclic Carbene (NHC) Ligand. *Organometallics* **2003**, *22*, 1986−1988.
(18) (a) Eelman, M. D.; Blacquiere, J. M.; Moriarty, M. M.; Fogg, D. E. Shining New Light on an Old Problem: Retooling MALDI Mass Spectrometry for Organotransition-Metal Catalysis. *Angew. Chem., Int. Ed.* **2008**, *47*, 303−306. (b) Bailey, G. A.; Fogg, D. E. Confronting Neutrality: Maximizing Success in the Analysis of Transition-Metal Catalysts by MALDI Mass Spectrometry. *ACS Catal.* **2016**, *6*, 4962−4971.
(19) For a study on the reaction of NHCs with one-electron oxidants, see: Ramnial, T.; McKenzie, I.; Gorodetsky, B.; Tsang, E. M. W.; Clyburne, J. A. C. Reactions of *N*-Heterocyclic carbenes (NHCs) with one-electron oxidants: possible formation of a carbene cation radical. *Chem. Commun.* **2004**, 1054−1055.
(20) (a) Antoni, P. W.; Hansmann, M. M. Pyrylenes: A New Class of Tunable, Redox-Switchable, Photoexcitable Pyrylium−Carbene Hybrids with Three Stable Redox-States. *J. Am. Chem. Soc.* **2018**, *140*, 14823−14835. For radical addition to the 4-position of TPPT, see: (b) Branchi, B.; Bietti, M.; Ercolani, G.; Izquierdo, M. A.; Miranda, M. A.; Stella, L. The Role of Aromatic Radical Cations and Benzylic Cations in the 2,4,6-Triphenylpyrylium Tetrafluoroborate Photosensitized Oxidation of Ring-Methoxylated Benzyl Alcohols in CH_2Cl_2 Solution. *J. Org. Chem.* **2004**, *69*, 8874−8885.
(21) At this time, we cannot discount potential pathways due to catalyst decomposition.
(22) Similar patterning could be obtained with: norbornadiene **9**, 1,5-cyclooctadiene **10** and 5-ethylidene-2-norbornene **11**; see Supporting Information for details.
(23) The amount of monomer consumed that is not present in the final patterned polymer was estimated at 7% by analysis of the wash using an external reference.
(24) Rühe, J. And There Was Light: Prospects for the Creation of Micro- and Nanostructures through Maskless Photolithography. *ACS Nano* **2017**, *11*, 8537−8541.

DOI: 10.1021/jacs.8b13663
J. Am. Chem. Soc. 2019, 141, 6791−6796