

### Article

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# A Preferential Photoreaction in a Porous Crystal, Metal–Macrocycle Framework (MMF): Pd<sup>II</sup>-Mediated Olefin Migration over [2+2] Cycloaddition

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**ABSTRACT:** A nano-sized confined space with well-defined functional surfaces has great potential to control the efficiency and selectivity of catalytic reactions. Herein we report that a 1,6-diene, which normally forms an intramolecular [2+2] cycloadduct under photo-irradiation, preferentially undergoes a photo-induced olefin migration in a porous crystal, metal-macrocycle framework (MMF), and alternatively [2+2] cycloaddition is completely inhibited in the confined space. A plausible reaction mechanism for olefin migration triggered by the photo-induced dissociation of the Pd-Cl bond is suggested based on UV-vis diffuse reflectance spectroscopy, single-crystal XRD, and MS-CASPT2 calculation. The substrate scope of the photo-induced olefin migration in MMF was also examined using substituted allylbenzene derivatives.

#### INTRODUCTION

Nano-sized confined spaces often provide an excellent platform for highly efficient and selective reactions, as typified by enzymes involved in preferential catalytic reactions in biological systems, and also as seen in a significant number of reports on in-space reactions using synthetic nano-spaces of molecular cages<sup>1</sup> and porous solids<sup>2</sup> such as zeolites, metal-organic frameworks (MOFs), and covalent-organic frameworks. Molecular reactivity is generally sensitive to a change in chemical surrounding. For instance, a porous coordination network was found to completely suppress the polymerization of an olefin and alternatively facilitate another oxidation reaction.<sup>3a</sup> Another notable example is that encapsulation of a molecule in MOF brings the reactivity from nucleophilic to electrophilic.<sup>3b</sup> Thus, synthetic, confined nano-spaces potentially play roles in inhibiting a usual reaction pathway and activating an alternative reaction pathway.

In this context, attention is currently focused on photoreactions in confined spaces,<sup>4a-c</sup> for instance, related to photo-activation of inert coordination compounds,<sup>4d</sup> stabilization of photo-labile molecules,<sup>4e</sup> and regio- and stereo-selective photoreactions.<sup>4f,g</sup> From another perspective, if a photoreaction is inhibited and an alternative reaction is photo-induced in a confined space, it would be possible to switch photoreaction pathways even under the same photo-irradiation conditions. Herein, we report that a photo-induced olefin migration of a 1,6-diene 1 to produce **1b** is preferentially promoted in a porous crystal, metal– macrocycle framework (MMF),<sup>5</sup> whereas the diene **1** exclusively produced an intramolecular [2+2] cycloadduct (1a) in solution under a similar photo-irradiation condition (Figure 1). We discuss the effects of the inner surfaces of the MMF channels with Pd<sup>II</sup> centers on the reactivity of diene 1 by UV-vis diffuse reflectance spectroscopy, singlecrystal XRD, and MS-CASPT2 calculations as well as a model reaction using a simpler olefin compound 3.



**Figure 1.** Two photoreaction pathways of **1** for [2+2] cycloaddition in solution and olefin migration in MMF.

Recently, we have reported a porous crystal, metalmacrocycle framework (MMF), formed from four structural isomers of trinuclear  $Pd^{II}$  complexes of a macrocyclic hexamine L.<sup>5a</sup> This porous crystal has one-dimensional channels with a 1.4 × 1.9 nm<sup>2</sup> dimension with five enanti



**Figure 2.** (a) Self-assembly of four structural isomers of Pd<sub>3</sub>LCl<sub>6</sub>, (*P*)-*syn*, (*M*)-*syn*, (*P*)-*anti*, and (*M*)-*anti*, into MMF with a single-crystalline channel. (b) A partial MMF channel structure with readily accessible Pd centers as highlighted in red circles. (c) Site-selective uptake of 1 (39% occupancy). The side chain with a terminal olefin of 1 was highly disordered in the channel. MMF: stick and ball model, 1: CPK model. C: gray, N: blue, O: red, Cl: green, Pd: yellow. The enlarged figure (right) shows two hydrogen bonds formed between 1 and two Pd<sup>II</sup> centers.

omeric pairs of molecular binding sites (Figure 2a,b). The structural features allowed for site-selective arrangement of guest molecules *via* hydrogen bonding,<sup>5b,c</sup> *in-situ* X-ray snapshot observation of molecular arrangement processes,<sup>5d</sup> and size-specific reactions with acid catalysts immobilized on the channel surface.<sup>5f</sup> In this study, we focused on the exposed and therefore readily accessible Pd<sup>II</sup> centers (Figure 2b) to clarify the mechanism of the Pd<sup>II</sup>-mediated photoreactions.

#### **RESULTS AND DISCUSSION**

Preferential Photoreaction in MMF. 1,6-Diene 1 was initially examined for a photochemical intramolecular [2+2] cycloaddition reaction. As previously reported,<sup>6</sup> the diene 1 quantitatively underwent [2+2] cycloaddition in CD<sub>3</sub>CN to exclusively generate a desired cycloadduct 1a (Table 1, Entry 3). Then, the encapsulation of 1 into MMF channels was carried out by soaking MMF crystals in a solution of 1 in CH<sub>2</sub>CN (6 mM) and left to stand for several days at 20 °C. The single-crystal X-ray diffraction (SXRD) analysis of a resulting crystal demonstrated that 1 was site-selectively adsorbed via two hydrogen bonds to the bottom corners of the channel with 39% occupancy (Figure 2c). The number of encapsulated molecules was estimated to be 0.5 per a unit-space after crystal digestion in DCl-DMSO- $d_6$  by NMR spectroscopy (Figure S<sub>2</sub>). This result is comparable to that of the SXRD analysis (39% occupancy for the two binding sites per a unit-space), which suggests that most of encapsulated molecules were adsorbed to the inner surfaces of MMF channels.

Next, an MMF crystal including 1 obtained as above was picked up, covered with fluorolube<sup>®</sup> to prevent solvent evaporation, and then irradiated with a 300 W Xenon lamp (280–630 nm). Under this condition, no [2+2] cycloadducts were detected, but olefin migration exclusively proceeded to produce an internal olefin 1b in 22% conversion (Table 1, Entry 1). In contrast, this olefin migration did not proceed in the dark even at 70 °C (Entry 2), indicating that the olefin migration of 1 was photo-induced in the MMF channels. In addition, it is worthy noted that the crystallinity of MMF was maintained to some extent even after photoirradiation for 5 h as proven by XRD analyses (Figures S6 and S7).

#### Table 1. Photoreactions of 1 in various reaction media

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Entry	Condition <sup>a</sup>	Time	Conversion <sup>b</sup> (1, 1a, 1b, <sup>c</sup> %)
1	in $MMF^d$	5 h	78 nd 22
2	in MMF <sup>e</sup> without photo- irradiation	5 h	>99 nd nd
3	in CD <sub>3</sub> CN <sup>f</sup>	3 min	nd 87 <sup>h</sup> nd
4	in CD <sub>3</sub> CN <sup>f</sup> with suspended MMF	3 min	nd 82 <sup><i>h</i></sup> nd
5	in CD <sub>3</sub> CN (frozen) <sup>g</sup>	60 min	93 6 <sup>h</sup> nd
6	in CD <sub>3</sub> OD (not frozen) <sup>g</sup>	10 min	nd 91 <sup>h</sup> nd
7	molecular crystal of $1^d$	60 min	98 2 nd

<sup>*a*</sup>Photo-irradiation with a 300 W Xenon lamp (280–630 nm) at room temperature. <sup>*b*</sup>The conversion rates were estimated based on the ratios of **1**, **1a**, and **1b** (Entries 1, 2, and 7) or on the comparison with the signal of 1,1,2,2-tetrachloroethane as the internal standard (Entries 3–6). <sup>*c*</sup>The E/Z ratios of the products were over 10. <sup>*d*</sup>The sample was warmed up to 70 °C due to the photo-irradiation. <sup>*e*</sup>The reac-

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tions were conducted at room temperature and at 70 °C.  ${}^{f}$ The reaction was conducted at room temperature.  ${}^{g}$ The reaction was conducted at -78 °C.  ${}^{h}$ The rest of the compounds was decomposed. nd = not detected.

In all the control experiments with trinuclear Pd<sup>II</sup> complexes [Pd<sub>3</sub>LCl<sub>6</sub>] or each component of MMF (L or PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> only) instead of MMF crystals, diene 1 afforded a photoinduced [act] graleadduct to only (Scho



induced [2+2] cycloadduct 1a only (Scheme S2). Moreover, MMF crystals without soaking treatment suspended in solution had no effects on the photo-induced [2+2] cycloaddition (Entry 4). This marked difference in the reaction pathway under photo-irradiation suggests that the olefin migration proceeds only in the confined space of MMF. For comparison, compound 2, which does not undergo olefin migration due to the presence of two methyl groups at the allylic position and is expected to readily cyclize by the Thorpe-Ingold effect, was incorporated into MMF crystals (containing 1.2 molecules per a unit-space; Figures S11 and S12) and examined for the photoreaction. The result showed that no reactions occurred in the MMF channels (Figure S13), whereas compound 2 produced a [2+2] cycloadduct in 83% conversion in solution (Scheme S5).

Inhibition of [2+2] Cycloaddition in MMF. One possible reason why the photo-induced [2+2] cycloaddition with 1 or 2 was inhibited in MMF is a photo-shielding effect by the MMF framework. Azobenzene encapsulated in MMF underwent isomerization with lower efficiency (23% conversion in 5 h; Figure S17) than a photoreaction in solution (99% conversion in 2 h; Scheme S7) under the same photo-irradiation condition, suggesting the photoshielding in the applied area being irradiated is likely to be effective to some extent for suppressing the excitation of 1 or 2 in MMF. Another possible reason is the limited mobility of the substrates in the confined space. In particular, the space-specific, internal close solvation of their side chain moiety may inhibit the flexible conformational changes required for forming the transition state of the intramolecular cycloaddition (Figures S37-S39). The photo-induced [2+2] cycloaddition of 1 without MMF smoothly proceeded in CD<sub>2</sub>CN at room temperature (Table 1, Entry 3) or in CD<sub>3</sub>OD even at temperature as low as -78 °C (Table 1, Entry 6). However, the reaction extremely slowed down in frozen CD<sub>2</sub>CN at -78 °C and also in the crystal state at room temperature (Table 1, Entries 5 and 7). Taken all together, the decrease in the mobility of solvent molecules in MMF channels appears to restrict the conformational changes of 1 required for the intramolecular [2+2] cycloaddition.

# Table 2. Comparison between photoreactions of 3 in solution and in MMF



Entry	Medium	Light source (nm)	Time (h)	Conversion <sup><i>a</i></sup> ( <b>3</b> , <b>3a</b> , <sup><i>b</i></sup> %)
1	in CD <sub>3</sub> CN	280–630 <sup>°</sup>	2	70 <sup>g</sup> nd
2		$450 \pm 10^{c,e}$	2	>99 nd
3		no irradiation <sup>c</sup>	72	>99 nd
4	in MMF	280-630 <sup>d</sup>	3	nd >99
5		$450 \pm 10^{c,e}$	15	40 60
6		no irradiation <sup>c</sup>	15	>99 nd
7		no irradiation <sup>f</sup>	2	93 7

<sup>*a*</sup>The conversion rates were estimated based on the comparison with the signal of 1,1,2,2-tetrachloroethane as the internal standard (Entries 1–3), or based on the ratios of **3** and **3a** (Entries 4–7). <sup>*b*</sup>The *E/Z* ratios of the products were over 10. <sup>*c*</sup>Photo-irradiation was carried out with a 300 W Xenon lamp (280–630 nm) at room temperature. <sup>*d*</sup>Photo-irradiation was carried out with a 300 W Xenon lamp (280–630 nm). The sample was warmed up to 70 °C due to the photo-irradiation. <sup>*e*</sup>A band-path filter was used (HWHM = 10 nm). <sup>*f*</sup>The reaction was conducted at 65 °C. <sup>*g*</sup>Approximately 30% of **3** was decomposed. nd = not detected.

Photo-induced Olefin Migration in MMF. To confirm if the reaction is promoted by direct photo-excitation of the olefin moiety, the photoreactions with a simple olefin 3, which does not undergo [2+2] cycloaddition, were examined. The photoreaction of 3 in solution without MMF showed decomposition, and did not produce an olefin-migrated product 3a at all (Table 2, Entry 1). On the other hand, the reaction of 3 in MMF crystals (containing 3.4 molecules of **3** per a unit-space; Figures S19 and S20) under photo-irradiation (280-630 nm) produced 3a quantitatively (Entry 4). The same is true of photo-irradiation at  $450 \pm 10$  nm (Entries 2 and 5) although the reaction rate was significantly slowed down in MMF. Importantly, this indicates that the olefin migration reaction in MMF was not promoted by the photo-excitation of olefin itself. As a matter of course, no reactions proceeded without photoirradiation at room temperature (Entries 3 and 6), and only the trace amount of 3a was detected when heated at 65 °C without irradiation (Entry 7). Therefore, the photoirradiation was considered to affect the reaction in a way different from that by direct excitation of olefins.



**Figure 3.** (a) A DRUV-Vis spectrum of MMF. (b) A calculated spectrum of a model complex (MS-CASPT<sub>2</sub>). (c) The chemical structure and the Pd-Cl  $\sigma^*$  orbital of a model complex.

The mechanism of olefin migration reaction was then theoretically examined with a focus on the photochemical reactivity of the Pd centers, as it is well known that the olefin migration is promoted by acids, bases, photoirradiation, or metal catalysts.<sup>7</sup> Olefin migration reactions are, in general, initiated by photo-excitation of olefin moieties at a wavelength shorter than 260 nm (over 300 kJ/mol) and proceed *via* [1,3]-sigmatropic rearrangement. Based on an assumption that Pd-Cl bonds become labile by photo-irradiation to facilitate ligand exchange and thereby activation of substrates on the Pd centers on the inner surface of MMF,8 the reaction mechanism was investigated both experimentally and theoretically. The diffuse reflectance UV-vis (DRUV-Vis) spectrum of MMF crystals showed broad absorption around 290 and 390 nm (Figure 3a). Multi-state complete-active-space secondorder perturbation theory (MS-CASPT2) calculations9 with a model complex (PdCl<sub>2</sub> complex of N,N'-diethyl-1,2phenylenediamine) suggested electron transitions at 295 and 457 nm, which basically agreed with the experimental data (Figure 3b). These absorption bands were thus assigned as transitions to a Pd-Cl  $\sigma^*$  orbital of the Pd complex, which indicates a significant relationship with Pd-Cl cleavage (Figure 3c).

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Single-crystal XRD analysis was proven to be available for the direct observation of the Pd-Cl perturbation after photo-irradiation. As a result, the electron density of Cl atoms on the ceiling of MMF channels was significantly decreased after photo-irradiation for 2 h at -180 °C (Figure 4). This observation suggests that the Pd-Cl bond was partially cleaved, presumably followed by ligand exchange, under photo-irradiation. In addition, Raman spectroscopy also supported the photo-activation of the Pd-Cl bond (Figure S40).<sup>10</sup> Thus, it was concluded based on these results that the Pd centers on the inner surfaces of MMF channels were activated by photo-dissociation of the Pd-Cl bond to promote the olefin migration reaction. This was significantly more effective than heating only (Table 2, Entries 4 and 7). The activated Pd centers should be labile and capable of binding to the terminal double bond of a substrate, and then olefin migration would take place by one of the known transition-metal mediated mechanisms of olefin migration such as alkyl and allyl mechanisms.<sup>7a</sup> On the other hand, the *in situ* generation of active metal sites demonstrated here is also consistent with recent application of labile or unsaturated coordination sites in MOFs to catalysis, gas storage, and separation.<sup>11</sup>



**Figure 4.** (a) Crystal structure of a unit-space of MMF. (b) 2D electron density maps of a PdCl<sub>2</sub> center which is a macrocyclic component on the ceiling sites, before and after the photo-irradiation. Positive electron density around the PdCl<sub>2</sub> center is represented as a contour map in green solid lines, and the border between positive and negative electron densities in blue dotted lines.

**Substrate Scope of Photo-induced Olefin Migration.** Finally, we examined the photoreaction of several other olefins **4–9** with a substituent on the benzene ring of allylbenzene in MMF to examine the substrate scope of the photo-induced olefin reaction (Table 3). The substrates were first encapsulated by soaking MMF crystals in a CH<sub>3</sub>CN solution containing an olefin substrate, and then the resulting crystals were collected and irradiated with a Xenon lamp for 1 h. As a result, all the substrates 4-9 were converted into internal olefins 4a-9a in moderate conversion yields (41-82%, Table 3). For instance, the position of the electron-donating methoxy group had only a little effect on the reactivity (Table 3, Entries 1-3), and electronwithdrawing substituents such as bromo and trifluoromethyl groups were also acceptable (Table 3, Entries 4, 5). Moreover, the migration reaction took place even on multiply functionalized substrates 8 and 9 although the rate of conversion slightly decreased (Table 3, Entries 6, 7). These results indicate that the photo-induced olefin migration in MMF can be applied to allylbenzene derivatives regardless of the kind of substituents on the aromatic ring.

It is well known that some of 2-propenylbenzene (allylbenzene) and 1-propenylbenzene derivatives are useful for several applications such as fragrance industry and pharmaceutical chemistry. For instance, compounds **3** and **8** are naturally occurring compounds and named estragole and safrole, respectively, and their isomers, anethole (**3a**) and isosafrole (**8a**), have been studied for testing their biological activities. In addition, anethole (**3a**) and isosafrole (**8a**) are also known to be key intermediates for preparing important bioactive compounds and pharmaceuticals.<sup>7a</sup> Therefore the development of a new method for the olefin migration reaction of allylbenzene derivatives must be a promising way to expand their potential applications.



Table 3. Photochemical reactivity of substituted al-lylbenzene derivatives in MMF

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<sup>*a*</sup>Photo-irradiation was carried out with a 300 W Xenon lamp (280–630 nm) at room temperature, and the irradiation warmed the sample up to 70 °C. <sup>*b*</sup>The *E/Z* ratios of the products were over 10 in each case. <sup>*c*</sup>The conversion was estimated based on the ratios of substrate and product.

# CONCLUSION

In this study, photo-induced olefin migration reaction of 1,6-diene which preferentially takes place in the MMF channels instead of intramolecular [2+2] cycloaddition expected from the reactivity in solution was well characterized, and the Pd-mediated mechanism triggered by the photo-activation of PdCl, centers on the inner surfaces of MMF was established experimentally and theoretically. The reaction preference in the confined space of MMF turned out to be due to the significant changes in the chemical surroundings, the molecular mobility and the local concentration effects on the reaction efficiency at the activated Pd centers as well as the photo-shielding effect by MMF. The activation-inhibition strategy in a confined space demonstrated here is therefore expected to open new opportunities for finding a hidden photoreaction pathway as well as for developing precisely controlled catalytic photoreactions.12 Moreover, such unexpected molecular behaviors in a confined space with a well-defined surface structure would provide an important clue to space-specific, efficient and selective reactions, as realized in natural enzymatic systems, which have high potential for metal-catalyzed reactions such as bond activation, cross-coupling, and redox reactions.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures including characterization of compounds.

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# Notes

No competing financial interests have been declared.

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#### REFERENCES

(1) (a) Koble, T. S.; Wassenaar, J.; Reek, J. N. H. *Chem. Soc. Rev.* **2008**, *37*, 247. (b) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. *Chem. Soc. Rev.* **2014**, *43*, 1734. (c) Brown, C. J.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. *Chem. Rev.* **2015**, *115*, 3012. (d) Zarra, S.; Wood, D. M.; Roberts, D. A., Nitschke, J. R. *Chem. Soc. Rev.* **2015**, *44*, 419. (e) Chen. L.-J.; Yang, H.-B.; Shionoya, M. *Chem. Soc. Rev.* **2017**, *46*, 2555. (f) Kang, J.; Rebek Jr., J. *Nature* **1997**, *385*, 50. (g) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251.

(2) (a) Davis, M. E. *Nature* 2002, *417*, 813. (b) Lee, J.-Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* 2009, *38*, 1450. (c) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* 2009, *38*, 1248. (d) Uemura, T.; Yanai, N.; Kitagawa, S. *Chem. Soc. Rev.* 2009, *38*, 1228. (e) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* 2004, *43*, 2334. (f) Cook, T. R; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* 2013, *113*, 734. (g) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* 2013, *341*, 974. (h) Diercks, C. S.; Yaghi, O. M. *Science* 2017, *355*, eaal1585.

(3) (a) Inokuma, Y.; Nishiguchi, S.; Ikemoto, K.; Fujita, M. *Chem. Commun.* **2011**, *47*, 12113. (b) Bauer, G.; Ongari, D.; Xu, X.; Tiana, D.; Smit, B.; Ranocchiari, M. *J. Am. Chem. Soc.* **2017**, *139*, 18166.

(4) (a) Cohen, M. D.; Schmidt, G. M. J. J. Chem. Soc. **1964**, 1996. (b) Ramamurthy, V.; Gupta, S. Chem. Soc. Rev. **2015**, *44*, 119. (c) Ramamurthy, V.; Sivaguru, J. Chem. Rev. **2016**, *116*, 9914. (d) Yoshizawa, M.; Miyagi, S.; Kawano, M.; Ishiguro, K.; Fujita, M. J. *Am. Chem. Soc.* **2004**, *126*, 9172. (e) Yamashina, M.; Sei. Y; Akita, M.; Yoshizawa, M. Nat. Commun. **2014**, *5*, 4662. (f) Schultz, A. G.; Taveras, A. G., Taylor, R. E.; Tham, F. S.; Kullnig, R. K. J. Am. Chem. Soc. **1992**, *114*, 8725. (g) Nakamura, A.; Inoue, Y. J. Am. Chem. Soc. **2003**, *125*, 966.

(5) (a) Tashiro, S.; Kubota, R.; Shionoya, M. J. Am. Chem. Soc. 2012, 134, 2461. (b) Kubota, R.; Tashiro, S.; Umeki, T.; Shionoya, M. Supramol. Chem. 2012, 24, 867. (c) Tashiro, S.; Umeki, T.; Kubota, R.; Shionoya, M. Angew. Chem., Int. Ed. 2014, 53, 8310. (d) Kubota, R.; Tashiro, S.; Shiro, M.; Shionoya, M. Nat. Chem. 2014, 6, 913. (e) Tashiro, S.; Shionoya, M. Bull. Chem. Soc. Jpn. 2014, 87, 643. (f) Tashiro, S.; Yonezawa, H.; Kubota, R.; Umeki, T.; Shionoya, M. Chem. Commun. 2016, 53, 7657.

(6) Müller, C.; Bauer, A.; Maturi, M. M.; Cuquerella, M. C.; Miranda, M. A.; Bach, T. J. Am. Chem. Soc. **2011**, *133*, 16689.

(7) (a) Hassam, M.; Taher, A.; Arnott, G. E.; Green, I. R.; van Otterlo, W. A. L. *Chem. Rev.* 2015, *11*5, 5462. (b) Harrod, J. F.; Chalk, A. J. *Nature* 1965, 205, 280. (c) Lindsey Jr, R. V.; Cramer, R. *J. Am. Chem. Soc.* 1966, *88*, 3534.

(8) (a) Dilorenzo, K. K.; Gilbert, R. M.; Hoggard, P. E. J. Coord. Chem. 2010, 63, 558. (b) Perumareddi, J. R.; Adamson, A. W. J. Phys. Chem. 1968, 72, 414.

(9) (a) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlei, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483. (b) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218. (c) Finley, J.; Malmqvist, P.-Å.; Roos, B. O.; Serrano-Andrés, L. Chem. Phys. Lett. **1998**, 288, 299.

(10) Wang, H.; Shen, S.; Wang, L.; Zheng, X. J. Phys. Chem. B **2010**, *114*, 16847.

(11) (a) Corma, A.; García, H.; Xamena, F. X. L. *Chem. Rev.* **2010**, 110, 4606. (b) Dincă, M.; Long, J. R. *Angew. Chem., Int. Ed.* **2008**, 47, 6766. (c) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, 112, 724.

(12) The catalytic use of MMF for this photoreaction is of concern to this work, so that the reusability of MMF was preliminarily tested. So far we have not observed significant reactivity of MMF yet for the photo-induced olefin migration of **3** in the se-

cond cycle probably due to the collapse of pore entrances. The details of the catalytic properties and the mechanism of this photoreaction will be reported elsewhere.

