

Chemistry Europe

European Chemical

Societies Publishing

Chemistry A European Journal



Accepted Article

Title: Visible-light-induced Heptacene Generation under Ambient Conditions: Utilization of Single-crystal Interior as an Isolated Reaction Site

Authors: Hironobu Hayashi, Nao Hieda, Mitsuaki Yamauchi, Yee Seng Chan, Naoki Aratani, Sadahiro Masuo, and Hiroko Yamada

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.202002155

Link to VoR: https://doi.org/10.1002/chem.202002155



COMMUNICATION

Visible-light-induced Heptacene Generation under Ambient Conditions: Utilization of Single-crystal Interior as an Isolated Reaction Site

Hironobu Hayashi,*^[a] Nao Hieda,^[a] Mitsuaki Yamauchi,^[b] Yee Seng Chan,^[a] Naoki Aratani,^[a] Sadahiro Masuo,*^[b] Hiroko Yamada*^[a]

[a]	Dr. H. Hayashi, N. Hieda, Y. S. Chan, Prof. Dr. N. Aratani, Prof. Dr. H. Yamada	
	Division of Materials Science	
	Nara Institute of Science and Technology (NAIST)	
	8916-5 Takayama-cho, Ikoma 630-0192 (Japan)	
	E-mail: hhayashi@ms.naist.jp, hyamada@ms.naist.jp	
[b]	Dr. M. Yamauchi, Prof. Dr. S. Masuo	
	Department of Applied Chemistry for Environment	
	KwanseiGakuin University	
	2-1 Gakuen, Sanda, Hyogo 669-1337, Japan	
	E-mail: masuo@kwansei.ac.jp	
	Supporting information for this article is given via a link at the end of the document.	

Abstract: The photo-induced generation of unstable molecules generally requires stringent conditions to prevent oxidation and the concomitant decomposition of the products. The visible-light-induced conversion of two heptacene precursors to heptacene was studied. Single crystals of bis- and mono-a-diketone-type heptacene precursors (7-DK2 and 7-DK1, respectively), were prepared to investigate the effect of precursor structure on reactivity. The photoirradiation of a 7-DK2 single crystal cleaved only one α -diketone group, forming an intermediate bearing a pentacene subunit, while that of a 7-DK1 single crystal gave rise to characteristic absorption peaks of heptacene and their increase in intensity with photoirradiation time, indicating the generation of heptacene without decomposition. Heptacene production was not observed when the precursors were photoirradiated in solution, implying that the single crystal interior provided isolation from the external environment, thus preventing heptacene oxidation.

Performing chemical reactions within single crystals or molecular cages is challenging but significant, because their specific packing and void spaces enable highly selective reactions. Indeed, a number of efficient reactions inside porous materials have been achieved.^{1–7} Moreover, single-crystal-to-single-crystal transformations can be realized by controlling external conditions such as light, temperature, and chemical reactants, as demonstrated by the creation of photoswitchable materials^{8,9} and two-dimensional networks.^{10–12} In the above-mentioned studies, generally the whole crystal is exposed to external stimuli to achieve efficient reactions. In this study, we focused on another potential use of the single crystal interior: the possibility of isolating a reaction site from the external environment, thereby allowing an unstable product to remain intact.^{13–21}

A polyacene was chosen as the unstable compound for the study. Polyacenes, composed of multiple linearly fused benzene rings, have drawn considerable attention because of their potential utility as organic semiconductor materials. Their intrinsic optical and electronic properties, stemming from their zigzagedge, render them suitable candidates for exploring magnetism in graphene nanostructures.²² At the same time, however, the zigzag-edged structure of polyacenes results in ultra-narrow highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps with increasing acene length, which causes a decrease in stability. Furthermore, polyacenes are poorly soluble, due to their uncomplicated structure, which lacks functional groups. A successful strategy for the synthesis of polyacenes is the Strating-Zwanenburg reaction, $^{\rm 23}$ whereby $\alpha\text{-}$ diketone groups undergo visible-light-induced photodecarbonylation at the final stage to generate polyacenes. Quantitative conversion from precursors to polyacenes can be achieved by simple photoirradiation with only gaseous byproducts. A number of polyacenes have been synthesized via the Strating-Zwanenburg reaction and characterized by matrix-isolation techniques at low temperatures, or via state-of-the-art on-surface synthesis under ultra-high vacuum conditions, enabling experimental investigation of their electronic properties.22,24-28 However, the generation of polyacenes via visible-light-induced photodecarbonylation of α-diketone groups is in stark contrast with the fact that polyacenes are unstable against photoirradiation because of their high HOMO levels. Heptacene generation by thermally-induced cycloreversion from diheptacenes under an argon stream²⁹ and by thermal decarbonylation of monoketone heptacene precursors,³⁰ have been reported, thereby establishing that heptacene can persist in the solid state for an extended period of time. However, such conversions necessitate anaerobic conditions. Consequently, the generation of polyacenes via visible-light irradiation and ambient conditions is considerably challenging, while its success would provide a facile access to the fundamental properties of polyacenes.

The isolation of generated polyacenes from the external environment prevents their oxidation. In this context, we have successfully demonstrated the photoconversion of a crystalline phase α -diketone-type pentacene precursor into pentacene, with the use of a 488 nm CW laser.^{31,32} Importantly, the CW laser selectively irradiates the interior of a single crystal, suggesting its potential utility as an isolated site for unstable compounds. This

COMMUNICATION

effective technique was applied herein for the generation of heptacene under ambient conditions.

Two heptacene precursors, bearing two or one α -diketone group, **7-DK2**²² and **7-DK1**²⁵ (Figure 1), respectively, were prepared according to literature procedures, in order to investigate the structural effect on the conversion, when it is accompanied by a large structural change in the crystal. Upon photoirradiation, **7-DK2** can be converted to heptacene *via* an intermediate bearing a pentacene subunit, while **7-DK1** can be converted to heptacene without generating an intermediate.



Figure 1. α -Diketone-type heptacene precursors and their expected photoconversion to heptacene.

The absorption spectra of **7-DK2** and **7-DK1** in toluene exhibited broad peaks at approximately 430–500 nm, which were assigned to the $n-\pi^*$ transition of the α -diketone moiety (Figure 2). Considering that the anthracene moiety does not absorb beyond approximately 400 nm, photoirradiation at 450–500 nm can selectively excite the $n-\pi^*$ transition in the precursors.



Figure 2. UV-vis absorption spectra of 7-DK1 (blue) and 7-DK2 (red) in toluene.

First, photoconversion of the precursors in toluene under N₂ atmosphere was investigated to confirm the instability of heptacene and, hence, the significance of the solid state conversion. A blue LED (470 ± 10 nm, 200 mW cm⁻²) was used as a light source for the photoconversion. In the case of **7-DK2**, as the photoirradiation progressed, new peaks at 490, 546, and 593 nm appeared and grew in intensity (Figure 3). The color of the solution changed from yellow to purple, suggesting the conversion of **7-DK2** to the pentacene-containing intermediate.³¹ However, further photoirradiation, and/or photoirradiation at a higher power (400 mW cm⁻²), could not convert the intermediate to heptacene, affording precipitates of the intermediates instead.

This result implies that the $n-\pi^*$ transition of the intermediate could not be efficiently excited further, as the generated pentacene moiety displays an intense absorption in the same region as the n- π^* transition, which prevents the intermediates from further photoconversion to heptacene. By contrast, the photoirradiation of 7-DK1 (470±10 nm, 200 mW cm⁻²) afforded orange precipitates, accompanied by a small increase in absorption at 481 and 518 nm. The characterization of these precipitates was not pursued at present, however, analysis of their absorption spectra suggests that they are likely to be a mixture of diheptacene, heptacenequinone and related oxidized species.²⁹ The presence of oxygen molecules in the system is unavoidable even with prolonged N_2 bubbling. Thus, the generated heptacenes immediately undergo dimerization and/or oxidation reactions, demonstrating the difficulty in heptacene isolation in solution even under anaerobic conditions.



Figure 3. UV-vis absorption spectra changes during photoirradiation of (a) **7-DK2** and (b) **7-DK1** in toluene under N₂ atmosphere. Conditions for photoirradiation: LED lamp with 470 \pm 10 nm (200 mW cm⁻²). Images show the color of **7-DK2** and **7-DK1** solutions before and after photoirradiation.

For photoconversion in the solid state, single crystals of 7-DK2 and 7-DK1 were prepared by the diffusion of hexane vapor into a dichloromethane solution of the precursors. Block crystals³⁴ were obtained from the 7-DK2 solution, while needle crystals³⁵ were grown from the 7-DK1 solution (Figure 4a,d). In both cases, the dihedral angle between the two aromatic regions bridged by the α -diketone-containing moiety was 108° (Figure 4b,e). In the crystals, the **7-DK2** molecules are densely packed through $\pi - \pi$ interactions, CH- π interactions, and hydrogen bonding. The benzene moieties are stacked in the crystals with a $\pi-\pi$ distance of 3.88 Å (Figure 4c). Similarly, 7-DK1 molecules are packed through CH- π interactions and hydrogen bonding. Importantly, 7-DK1 molecules on their own cannot provide a sufficiently dense space packing, thus the inclusion of dichloromethane molecules occurs in the packing (Figure 4f). Therefore, the intermolecular interactions between 7-DK2 molecules are expected to be stronger than those of 7-DK1, suggesting that the significant structural change accompanying the photoconversion is more favorable for 7-DK1 compared with 7-DK2.

Finally, photoconversion in the crystals was investigated (see experimental details in Supporting Information). Briefly, in this experiment, the coverslip on which the single crystal was placed onto the stage of an inverted microscope. The light source from a 488 nm CW laser was introduced through an objective lens. For the observation of the single crystal absorption spectra, a halogen lamp with a Köhler illumination system was used as the incident light. Note that the absorption spectra in the regions of 450–700 nm and 650–1000 nm were measured separately, as a different spectral measurement system was employed.

COMMUNICATION



Figure 4. Optical images of (a) 7-DK2 and (d) 7-DK1 single crystals. Singlecrystal X-ray structures of (b) 7-DK2 and (e) 7-DK1. Thermal ellipsoids represent 50% probability. Solvent molecules are omitted for clarity (7-DK1). Packing structure of (c) 7-DK2 and (f) 7-DK1 single crystals with space filling model. Hydrogen atoms are omitted for clarity.

In the transmission image of the 7-DK2 crystal (Figure 5a), a red emission was observed during photoirradiation, and the focal point became dark-orange after photoirradiation. Spectroscopic analysis of the 7-DK2 crystal indicated increasing absorption at 565 and 607 nm as the photoirradiation progressed (Figure 5c). Considering the results obtained for the photoirradiation in solution, these observed peaks were confidently assigned to the intermediate containing a pentacene subunit. The observed red emission additionally supports the formation of a pentacene moiety.³¹ Notably, absorptions corresponding to the aggregation of the intermediate, which should appear at 625 nm and 663 nm, were not observed, unlike in the case of pristine pentacene.³¹ This is likely as a result of the remaining bulky a-diketone groups preventing pentacene stacking. Further photoirradiation, and/or irradiation at a higher energy (200 µW) exhibited the same trend as seen in solution. Specifically, no significant peaks were observed in the region of 700-1000 nm (Figure 5d), indicating the cleavage of a single α -diketone molety in **7-DK2**, without the formation of heptacene. On the contrary, photoirradiation of the 7-DK1 crystal yielded differing results (Figure 5b). Upon photoirradiation, a broad peak appeared in the range of 550-700 nm (Figure 5e). More interestingly, characteristic peaks with vibronic structures were observed at 652, 721, 791, and 820 (shoulder) nm, along with a broad absorption peak at approximately 900 nm (Figure 5f). According to a previous report, heptacene films deposited on a sapphire at 16 K exhibited a broad absorption in the range of 700-800 nm with the maximum absorption at roughly 800 nm,²⁹ while the absorption spectrum of heptacene, obtained by heating a solution of diheptacene in 1methylnaphthalene, displayed characteristic peaks at 623, 682, 753, and 792 (shoulder) nm.²⁹ Thus, the peaks observed for the

7-DK1 crystal during photoirradiation could be assigned to heptacene, strongly suggesting the generation of heptacene in the crystal. This result is in contrast with that observed in solution, where the generated heptacene was immediately decomposed and/or dimerized. Indeed, no significant changes in the spectrum were noted during the measurement. The broad peak at approximately 900 nm is attributable to heptacene aggregation $via \pi - \pi$ stacking in the crystal, although the degree of aggregation appears to be low.³²



Figure 5. Transmission images of (a) 7-DK2 and (b) 7-DK1 crystals before (left), during (middle), and after (right) photoirradiation. UV-vis-NIR absorption spectra recorded during photoirradiation of (c, d) 7-DK2 and (e, f) 7-DK1 crystals under an ambient atmosphere. Conditions for photoirradiation: 488 nm CW laser with 50 μ W.

It should be mentioned that recent studies have reported good thermal stability of heptacene up to 420 °C. In addition, it has been reported that no significant changes in the spectrum of heptacene were observed after it was stored in a glove box for six weeks. One matter for concern is the dimerization of heptacene in the solid state. However, the probability for the dimerization event is strongly dependent on the packing structure.29,30 Specifically, heptacene gradually undergoes cyclodimerization to diheptacene in the solid state, in the case of heptacene generated by the thermal decomposition of diheptacene.²⁹ This is likely due to the face-to-face packing of heptacenes, resulting from minor structural rearrangements in the solid state during the conversion. On the other hand, considering that only minor structural rearrangements in the solid state are possible during the conversion process, the packing structure of 7-DK1 would impede the dimerization process. These factors contribute to the increase in heptacene absorption intensity with photoirradiation duration.

Additionally, conversion from the α -diketone precursor to heptacene requires considerable structural modifications, from the bent to the planar structure. Thus, the structural and optical

COMMUNICATION

advantages of 7-DK1, along with its limited interactions between the molecules in the crystal, would facilitate conversion to heptacene. As mentioned, the generation and characterization of heptacene has only been achieved under stringent conditions.22,25,27,29 Accordingly, the visible-light-induced generation of photo-unstable heptacenes presents as being an "unreasonable" strategy. However, herein, the intensity of heptacene absorption had unquestionably increased with increasing photoirradiation time, even under ambient conditions. This result strongly indicated that the generated heptacene molecules in the crystal were protected from oxidation, while the possibility of heptacene decomposition cannot be entirely excluded. The favorable thermal stability of heptacene following the conversion would provide for further applications, such as organic field-effect transistors and organic solar cells. Notably, comparable results were obtained for three individual crystals of 7-DK1, when subjected to the same conditions, guaranteeing the reliability of this approach.

In summary, we have demonstrated the visible-lightinduced generation of heptacene under ambient conditions. Pivotal to the success of this method was the selective irradiation of the crystal interior, with the generated heptacenes being shielded by heptacene precursors on the outer regions of the crystal. This strategy provides efficient access to otherwise inaccessible compounds. We believe that this approach is of general relevance for the synthesis and characterization of unstable molecules.

Acknowledgements

This work was partly supported by CREST JST (No. JPMJCR15F1) and Grants-in-Aid for Scientific Research (Nos. JP17H03042, JP19H04584, JP18K14190, JP18H01958, JP18K14195, and JP20H02816).

Keywords: heptacene • single crystal • photoconversion • isolated reaction site • precursor approach

- [1] M. Yoshizawa, M. Tamura, M. Fujita, Science 2006, 312, 251–254.
- [2] Z. Huang, P. S. White, M. Brookhart, *Nature* **2010**, *465*, 598–601.
- [3] M. Yoshizawa, J. K. Klosterman, M. Fujita, Angew. Chem. Int. Ed. 2009, 48, 3418–3438.
- [4] H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, *Science* **2006**, 327, 846–850.
- [5] H.-L. Jiang, D. Feng, T.-F. Liu, J.-R. Li, H.-C. Zhou, J. Am. Chem. Soc. 2012, 134, 14690–14693.
- [6] M. Zhao, S. Ou, C.-D. Wu, Acc. Chem. Res. 2014, 47, 1199–1207.
- [7] D. Yang, B. C. Gates, ACS Catal. 2019, 9, 1779–1798.
- [8] S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* 2007, 446, 778–781.
- [9] R. O. Al-Kaysi, A. M. Müller, C. J. Bardeen, J. Am. Chem. Soc. 2006, 128, 15938–15939.
- [10] C. Hu, U. Englert, Angew. Chem. Int. Ed. 2006, 45, 3457–3459.
- [11] P. Kissel, R. Erni, B. Schweizer, M. D. Rossell, B. T. King, T. Bauer, S. Götzinger, A. D. Schlüter, J. Sakamoto, *Nat. Chem.* 2012, *4*, 287–291.
- [12] P. Kissel, D. J. Murray, W. J. Wulftange, V. J. Catalano, B. T. King, *Nat. Chem.* 2014, 6, 774–778.
- [13] D. J. Cram, E. Tanner, R. Thomas, Angew. Chem. Int. Ed. 1991, 30, 1024–1027.
- [14] R. Warmuth, M. A. Marvel, Angew. Chem. Int. Ed. 2000, 39, 1117–1119.
- [15] M. Ziegler, J. L. Brumaghim, K. N. Raymond, *Angew. Chem. Int. Ed.* 2000, 39, 4119–4121.

- [17] T. Iwasawa, R. J. Hooley, Jr J. Rebek, Science 2007, 317, 493–496.
- [18] P. Mal, B. Breiner, K. Rissanen, J. R. Nitschke, *Science* 2009, 324, 1697– 1699.
- [19] N. Nishimura, K. Kobayashi, J. Org. Chem. 2010, 75, 6079–6085.
- [20] S. Horiuchi, T. Murase, M. Fujita, *J. Am. Chem. Soc.* 2011, *133*, 12445–12447.
 [21] M. Yamashita, Y. Sei, M. Akita, M. Yoshizawa, *Nat. Commun.* 2014, *5*,
- [21] M. Yamashita, Y. Sei, M. Akita, M. Yoshizawa, Nat. Commun. 2014, 5, 4662.
- [22] J. I. Urgel, S. Mishra, H. Hayashi, J. Wilhelm, C. A. Pignedoli, M. D. Giovannantonio, R. Widmer, M. Yamashita, N. Hieda, P. Ruffieux, H. Yamada, R. Fasel, *Nat. Commun.* **2019**, *10*, 861.
- [23] J. Strating, B. Zwanenburg, A. Wagenaar, A. C. Udding, *Tetrahedron Lett.* 1969, 10, 125–128.
- H. Yamada, Y. Yamashita, M. Kikuchi, H. Watanabe, T. Okujima, H. Uno, T. Ogawa, K. Ohara, N. Ono, *J. Chem.–Eur. J.* 2005, *11*, 6212–6220.
- [25] R. Mondal, B. K. Shah, D. C. Neckers, J. Am. Chem. Soc. 2006, 128, 9612–9613.
- [26] C. Tönshoff, H. F. Bettinger, Angew. Chem. Int. Ed. 2010, 49, 4125–4128.
- [27] M. Zugermeier, M. Gruber, M. Schmid, B. P. Klein, L. Ruppenthal, P. Müller, R. Einholz, W. Hieringer, R. Berndt, H. F. Bettinger, J. M. Gottfried, *Nanoscale* 2017, 9, 12461–12469.
- [28] B. Shen, J. Tatchen, E. Sanchez-Garcia, H. F. Bettinger, Angew. Chem. Int. Ed. 2018, 57, 10506–10509.
- [29] R. Einholz, T. Fang, R. Berger, P. Grüninger, A. Früh, T. Chassé, R. F.
 Fink, H. F. Bettinger, *J. Am. Chem. Soc.* 2017, *139*, 4435–4442.
- [30] A. Jancarik, G. Levet, A. Gourdon, Chem.-Eur. J. 2019, 25, 2366-2374.
- [31] S. Masuo, K. Tanaka, M. Oe, H. Yamada, *Phys. Chem. Chem. Phys.* 2014, *16*, 13483–13488.
- [32] M. Yamauchi, Y. Miyamoto, M. Suzuki, H. Yamada, S. Masuo, *Phys. Chem. Chem. Phys.* **2019**, *21*, 6348–6353.
- [33] J. I. Urgel, H. Hayashi, M. D. Giovannantonio, C. A. Pignedoli, S. Mishra, O. Deniz, M. Yamashita, T. Dienel, P. Ruffieux, H. Yamada, R. Fasel, *J. Am. Chem. Soc.* **2017**, *139*, 11658–11661.
- [34] Crystallographic data for **7-DK2**: C₃₄H₁₈O₄, M_W = 490.48, Monoclinic, space group C2/c, a = 21.829(5), b = 8.367(2), c = 13.012(3) Å, β = 98.919(5)°, V = 2347.8(10) Å³, T = 90 K, Z = 4, reflections measured 5298, 1743 unique. The final R₁ was 0.0559 (*I* > 2*σ*(*I*)), and the final wR on F² was 0.1841 (all data), GOF = 0.998.
 [35] Crystallographic data for **7-DK1**: C₃₂ 5H₁₉O₂Cl. M_W = 476.93, Monoclinic.

Crystallographic data for **7-DK1**: C_{32.5}H₁₉O₂Cl, M_W = 476.93, Monoclinic, space group *P*2₁/*c*, *a* = 18.385(15), *b* = 6.379(5), *c* = 24.22(2) Å, β = 127.879(10)°, *V* = 2242(3) Å³, *T* = 90 K, *Z* = 4, reflections measured 9756, 3212 unique. The final *R*₁ was 0.0978 (*I* > 2 σ (*I*)), and the final *wR* on *F*² was 0.2408 (all data), GOF = 1.022.

COMMUNICATION

Entry for the Table of Contents



The single-crystal interior provided a reaction site isolated from the external environment thus preventing oxidation of unstable products. Visible-light-irradiation of the inner region of a mono- α -diketone-type heptacene precursor crystal resulted in characteristic heptacene absorption peaks, suggesting successful heptacene generation under ambient conditions.