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High conversion and selectivity of photodimerization under air conditions by supramolecular oxidation restraint within a metallocage-like nanoreactor<sup>†</sup>

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suitable cavity, functional interaction sites and a flexible backbone, could encapsulate 9-anthraldehyde molecules and act as a nanoreactor via supramolecular behavior, avoiding the undesired oxidation forming 9,10-anthraguinone, and also as an efficient catalyst to successfully achieve high conversion of single photodimers under air conditions.

The remarkable photodimerization between two identical or different molecules into photodimers has been one of the most important categories in photochemical reactions.<sup>1-3</sup> Depending on the different numbers of atoms in the formed ring, the modes of photodimerization could be classified as [2 +2], [4 + 4], [4 + 2], [3 + 2], *etc.*, which mainly occurs between the organic molecules containing carbon-carbon double bonds or aromatic molecules with good photoactivity. Therefore, photodimerization could be regarded as a feasible method for the direct formation of C-C bonds and is much greener than other general organic reactions, owing to its atom economy, less toxic/polluting agents involved and lightdriven behavior.4-6 Taking the reaction mechanism into account, the substrates are firstly activated to the excited state or radicals are generated under irradiation and then their high energy and different electronic patterns are exploited for the next combination. The excited state species and radicals usually have short lifetimes and are difficult to regulate during the photochemical reactions. From this point of view,

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The well-designed metal-organic cage Ce-BHP, with a size-

seeking or developing appropriate systems participating in photodimerization as catalysts or reaction media to improve the conversion and selectivity appears to be particularly significant.

On the other hand, photodimerization generally could obtain several isomers within a single system. The accurate control and improvement of its stereoselectivity and regioselectivity have become a topical issue for the intensive research of photodimerization.7-9 In particular, the stereoselectivity and regioselectivity of photodimerization become more complicated in solution, due to the freer and more irregular motion among the molecules. Based on these situations, the introduction of a supramolecular selfassembled structure into the photodimerization system as a molecular reactor to restrict the substrates within welldefined confined space proved to be an efficient approach for the improvement of stereoselectivity the and regioselectivity.10-13 The excellent and well-studied supramolecular architectures in this field were mainly focused on macrocyclic hosts formed through covalent bonds, including cyclodextrins, calixarenes, covalent capsules, and cucurbiturils, which have been widely delineated by the pioneering work of many groups.14-19

Another class of interesting molecular hosts, coordinationdriven metal-organic cages (MOCs), which are self-assembled by metal ions and organic ligands as linkers containing internal cavities with well-defined shapes and sizes, have achieved increasing prominence.<sup>20-24</sup> These materials, as the subunits of artificial supramolecular host platforms, could be easily functionalized with multiple active sites and accurately control the size and shape of the structures via the coordination of specific metal ions with well-designed ligands. The promising functionalities and coordination abilities of MOCs provide them with advantages to mimic protein receptors or enzymes for the effective binding ability of molecules within their microenvironments to stabilize reactive intermediates or catalyze chemical transformations

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avoiding the undesired reaction pathways.<sup>25–28</sup> Therefore, compared with the traditional macrocyclic hosts, the advantages of coordination-driven MOCs mainly are: (1) the coordinated ligands could be easily modified with functional groups as required; (2) the introduction of metal ions into the system could improve the potential activity; (3) the sizes and shapes of structures and cavities could be modulated *via* the assembly of the extensive choice of metal ions and well-designed ligands.

Recently, we reported a flexible ligand-based metalorganic cage by the incorporation of Ce(III) ions synthesized via a vapor diffusion method.<sup>29</sup> The 4f metal atoms in the metal-based complex with alterable valence could perform multiple redox states that facilitate the electron or proton transfer and thus it is regarded potential as photocatalyst.30-32 The functional amide and secondary amino groups of ligands as interaction sites play an important role in the host-guest supramolecular behaviour for the selective recognition of RNA-based nucleoside derivatives with fluorescence response. The self-adaptive behaviour of the flexible ligand backbone presented in this work inspired us to further study the field of photodimerization of 9-anthraldehyde. From the structural point of view, this metal-organic cage, Ce-BHP, contains open windows of 8.52  $\times$  9.56 Å<sup>2</sup> and a well-defined cavity, which are suitable for the accommodation of 9-anthraldehyde molecules with a width of 5.8 Å and a length of 9.2 Å. Additionally, the functional amide and secondary amino groups of ligands in the backbone and the aldehyde group in 9-anthraldehyde exhibit potential hydrogen-bonding, together with  $\pi \cdots \pi$  stacking interactions, to recognize and construct the supramolecular system. Besides, the flexible backbone with self-adaptivity of Ce-BHP facilitates the encapsulation and maintains the stability of the complexation in solution (Fig. 1). Based on these considerations, we envision that Ce-BHP is an ideal candidate as a molecular reactor and a catalyst for the catalysis of photodimerization with feasible selectivity.

The supramolecular interaction between the host Ce-**BHP** and the guest 9-anthraldehyde molecules was investigated by NMR spectroscopy. The <sup>1</sup>H NMR titration spectrum of 9-anthraldehyde (10 mM) in a mixture solution of  $CDCl_3$  and DMSO- $d_6$  (v:v = 1:1) upon the addition of 0.5 mole ratio of Ce-**BHP** (5 mM) to the above solution exhibited downfield shifts of the protons from 11.50 to 11.62 ppm and 8.85 to

Size-suitable cavity

Interaction sites

Flexible backbone





**Fig. 2** (a) Main peaks in the <sup>1</sup>H NMR spectra of the cage Ce-**BHP** upon the addition of 2 mole ratio of 9-anthraldehyde; (b) free 9-anthraldehyde in the mixture solution of  $CDCl_3$ : DMSO- $d_6$  (v: v = 1:1).

8.95 ppm, respectively (Fig. 2), while other peaks have remained unchanged. These protons could be attributed to the aldehyde group and aromatic ring of 9-anthraldehyde and the shifts provided an indicator for the strong interaction between 9-anthraldehyde and the cage Ce-**BHP** *via* supramolecular behavior.<sup>33</sup>

Fluorescence spectroscopy of 9-anthraldehyde in DMF solution upon the addition of Ce-**BHP** was also performed with excitation at 340 nm. Fluorescence titration revealed that the addition of Ce-**BHP** in a solution of 9-anthraldehyde (10.0  $\mu$ M) caused significant emission quenching (Fig. 3). The emission intensity exhibited almost complete quenching when 0.5-fold Ce-**BHP** (5.0  $\mu$ M) was added to the system. The quenching process could probably be attributed to the interaction between the host Ce-**BHP** and the guest 9-anthraldehyde molecules.<sup>34</sup> The titration profiles upon the addition of Ce-**BHP** are consistent with the Hill plot. The best fitting of the titration profiles suggests a 1:2 host-guest behavior, with the association constant ( $K_{ass.}$ -G) being calculated to be 4.33 × 10<sup>9</sup> M<sup>-1</sup>.

ESI-MS suggested that metal–organic cage Ce-**BHP** could be regarded as a stable homogeneous catalyst in solution and 9-anthraldehyde was chosen as the model system to study its photodimerization in the solution. Under typical conditions, the photodimerization was conducted in a test tube by



Fig. 3 (a) The family of normalized fluorescence spectra of 9-anthraldehyde (10.0  $\mu$ M) in DMF solution upon the addition of 1.0, 2.0, 3.0, 4.0 and 5.0  $\mu$ M Ce-BHP, excited at 340 nm; (b) quenching fluorescence with different ratios of Ce-BHP as a host and 9-anthraldehyde as a guest molecule.

adding 0.05 mmol of 9-anthraldehyde and Ce-**BHP** (1 mol%) as a homogeneous catalyst with the addition of tertbutylammonium bromide (TBABr, 5 mol%) in a mixed solution of  $\text{CDCl}_3/\text{DMSO-}d_6$  (1mL/0.2 mL) in a mild environment and under Xe lamp irradiation. After irradiation, the reaction system was directly monitored by <sup>1</sup>H NMR analysis to determine the conversion and selectivity.



Surprisingly, unlike the normal photodimerization, the obtained photoproducts were not postulated to the ideal *syn* and *anti*-dimers *via* the analysis of the <sup>1</sup>H NMR spectrum. Separated by silica-gel column chromatography and further identified by GC-MS and X-ray single crystal analysis, the final photoproducts were confirmed as *anti*-dimers and 9,10-anthraquinone, which was synthesized from the oxidation of 9-anthraldehyde. The *anti*-dimer adducts of 9-anthraldehyde were observed exclusively without the formation of *syn*-dimers upon photodimerization<sup>35,36</sup> and the reaction route is illustrated in Table 1.

Irradiation of 9-anthraldehyde with Ce-**BHP** and TBABr was carried out under the optimal conditions for 8 hours and afforded 92% conversion and 90% selectivity for the main product *anti*-dimer (entry 1). The control experiment shows only 47% conversion and 83% selectivity in the absence of the co-catalyst TBABr; however, without adding the cage Ce-**BHP** into the system, relatively low reaction conversion and selectivity are afforded (entries 3 and 4). These results indicate that the presence of both Ce-**BHP** and TBABr plays a significant role in the catalysis of photodimerization and we deemed that Ce-**BHP** and TBABr act synergistically as catalysts in the catalytic process. Additionally, the photodimerization could not occur without irradiation, and almost no conversion is observed under the typical

conditions in the dark (entry 5). According to previous of the side product 9,10reports, the formation anthracenedione from 9-anthraldehyde needs the participation of oxygen or an oxidizing agent.<sup>37,38</sup> The high selectivity to the target photodimer in the presence of Ce-BHP, together with the results of the control experiments, indicated that the cage structure could be regarded as a molecular reactor to effectively block the oxidation of 9-anthraldehyde during the photocatalysis. In order to this confirm speculation, we carried out the photodimerization under a saturated argon and oxygen atmosphere with other fixed conditions. Almost complete conversion (>99%) to the desired photodimer adduct (selectivity >99%) was observed after 8 h irradiation in an argon atmosphere (entry 6), and only 65% conversion without adding Ce-BHP, suggesting that the presence of Ce-BHP indeed has a positive effect on the increase of the conversion (entry 7). However, 9-anthraldehyde could all convert into the side product 9,10-anthracenedione in an oxygen atmosphere in the absence of Ce-BHP, giving 54% selectivity to afford the photodimer with the addition of a catalytic amount of Ce-BHP (entries 8 and 9). These results exhibited full evidence that the photodimerization occurred within the cavity of the Ce-BHP cage, and Ce-BHP is regarded not only as a homogeneous catalyst for this reaction, but also as a shelter to avoid the formation of the side product 9,10anthracenedione in the catalytic system. The free ligand BHP (4 mol%) resulted in 82% conversion and 64% selectivity, both lower than those of cage Ce-BHP. At this point, the combination of Ce(III) centers and ligands into the metalorganic cage system is a promising approach to achieve high reaction efficiency and selectivity in photodimerization catalysis.

The catalytic efficiency and selectivity depend on the amount of Ce-**BHP** in a certain range and can be reduced by adding 0.5% mol of Ce-**BHP** (entry 12). Fortunately, the single crystals of photoproducts isolated from the catalytic system after the reaction were obtained and the quality of the crystals was sufficient for X-ray structure analysis. From the

Table 1 Ce-BHP-catalyzed and control experiments for the photodimerization of 9-anthraldehyde <sup>a</sup>					
Entry	Catalyst	Condition	Adduct	Conversion <sup><math>b</math></sup> (%)	Selectivity <sup>b</sup> (%)
1	Ce-BHP	Air	TBABr	92	90
2	Ce-BHP	Air	_	47	83
3	_	Air	TBABr	72	45
4	_	Air	_	22	39
5	Ce-BHP	Air, in the dark	TBABr	Trace	Trace
6	Ce-BHP	Ar	TBABr	>99	99
7	_	Ar	TBABr	65	90
8	Ce-BHP	$O_2$	TBABr	>99	54
9	_	$O_2$	TBABr	>99	0
$10^c$	Ligand BHP	Air	TBABr	82	64
11 <sup>c</sup>	Ligand BHP	Air	_	38	46
$12^d$	Ce-BHP	Air	TBABr	84	78

<sup>*a*</sup> Conditions: 9-anthraldehyde (0.05 mmol), TBABr (5 mol%), Ce-**BHP** (1 mol%), CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub> (1mL/0.2 mL), 25 °C, 8 h Xe lamp irradiation. <sup>*b*</sup> Conversion and selectivity are determined by <sup>1</sup>H NMR analysis. <sup>*c*</sup> With 4 mol% free ligand **BHP**. <sup>*d*</sup> With 0.5 mol% catalyst.

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structure, the asymmetric unit contains three independent *anti*-dimer photoproducts and one 9,10-anthracenedione molecule (Fig. 4). This crystal structure with a 3:1 ratio was approximately in accordance with the calculation of the catalytic selectivity (78%) and also provided full evidence for the formation of 9,10-anthracenedione *via* the oxidation in the catalytic system. Additionally, the single crystal of the pure *anti*-dimer product could also be obtained and isolated from the catalytic system after the reaction (Fig. S6†).

Catalytic traces of photodimerization have been further obtained with cage Ce-BHP and the coexistence of TBABr under the optimal conditions at different reaction times. As shown in Fig. 5a, the conversion has increased with the reaction time and remained unchanged after 8 hours. It was worth noticing that there was almost no difference in the selectivity with the increase of reaction time in the presence of cage Ce-BHP. Additionally, the photoreaction process has also been monitored by UV-vis spectroscopy. The substrate 9-anthraldehyde and the side product 9,10-anthracenedione showed main absorption at 398 nm and 322 nm, respectively, while no obvious absorption was observed in the UV-vis range for the pure photodimer product (Fig. 5b). Depending on the difference in UV-vis absorption of these molecules, it was convenient for us to monitor the photoreaction process via the consumption of 9-anthraldehyde and the formation of 9,10-anthracenedione. As shown in Fig. 5c and d, the UV-vis spectral traces of photodimerization both exhibited the decrease of 9-anthraldehyde and the increase of 9,10anthracenedione at 1 h, 4 h and 8 h reaction times with or without addition of cage Ce-BHP, respectively. However, the peak of 9,10-anthracenedione was found to grow slowly in the presence of Ce-BHP, giving a stark contrast to the growth of the peak of 9,10-anthracenedione without Ce-BHP under the same conditions. These results were consistent with the conclusion that the cage structure Ce-BHP could be regarded as an effective molecular reactor to block oxidation of 9-anthraldehyde during the photocatalysis. A proposed mechanism for the photodimerization of 9-anthraldehyde has been shown to illustrate the role of cage Ce-BHP (Fig. S7<sup>†</sup>). First, 9-anthraldehyde molecules were accommodated in cage Ce-BHP to form the 1:2 inclusion complex. Then, Br as the nucleophilic reagent could attack the excited substrates, resulting in a corresponding intermediate, which is expected to both participate in the next steps of



**Fig. 4** The crystal structure and the packing mode of photoproducts isolated from the catalytic system.



**Fig. 5** (a) Catalytic traces of photodimerization with cage Ce-**BHP** and coexistence of TBABr under the optimal conditions at different reaction times; (b) UV-vis spectra of the substrate 9-anthraldehyde (black), pure photodimer product (blue) and side product 9,10-anthracenedione (red); (c) UV-vis spectral traces of photodimerization without cage Ce-**BHP** under 1 h (black), 4 h (red) and 8 h (blue) irradiation; (d) UV-vis spectral traces of photodimerization with cage Ce-**BHP** under 1 h (black), 4 h (red) and 8 h (blue)

photodimerization and oxidation of 9,10-anthracenedione. From a mechanism point of view, the avoidance of 9,10anthracenedione formation is not attributed to the cage's ability to exclude dioxygen, but rather to the restricted generation of a large intermediate product that does not fit cavity Ce-BHP. Therefore, within the of the photodimerization of 9-anthraldehyde exhibited not only high conversion with a catalytic amount of Ce-BHP, but also excellent selectivity based on the remarkable well-confined effect of the Ce-BHP cage under air conditions.

#### Conclusions

(a)

In conclusion, the photodimerization of 9-anthraldehyde in the presence of metal-organic cage Ce-BHP under air conditions has been studied in this work. The size-suitable open windows and cavity of Ce-BHP were able to accommodate 9-anthraldehyde molecules, which was monitored by <sup>1</sup>H NMR and fluorescence titration. GC-MS and X-ray single crystal analyses indicated that the final photoproducts of 9-anthraldehyde were anti-dimers and 9,10anthraquinone synthesized from the oxidation of 9-anthraldehyde. Ce-BHP could be regarded as an ideal molecular reactor to avoid the oxidation of 9-anthraldehyde and an effective catalyst for the formation of anti-dimers with high conversion and selectivity under air conditions via the supramolecular confined effect. Such a strategy could be applied to the construction of more modified molecular reactors to functionalize the catalysis of other photochemical reactions.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references

- 1 N. Hoffmann, Chem. Rev., 2008, 108, 1052-1103.
- 2 S. Poplata, A. Tröster, Y. Q. Zou and T. Bath, *Chem. Rev.*, 2016, **116**, 9748–9815.
- 3 X. D. Huang, J. G. Jia, M. Kurmoo, S. S. Bao and L. M. Zheng, *Dalton Trans.*, 2019, **48**, 13769–13779.
- 4 A. Albini and M. Fagnoni, Green Chem., 2004, 6, 1-6.
- 5 V. Ramamurthy and J. Sivaguru, *Chem. Rev.*, 2016, **116**, 9914–9993.
- 6 V. Ramamurthy and S. Gupta, Chem. Soc. Rev., 2015, 44, 119-135.
- 7 R. Brimioulle, D. Lenhart, M. M. Maturi and T. Bach, *Angew. Chem., Int. Ed.*, 2015, **54**, 3872–3890.
- 8 T. Bach, H. Bergmann, B. Grosch and K. Harms, J. Am. Chem. Soc., 2002, 124, 7982–7990.
- 9 L. S. Kaanumalle and V. Ramamurthy, *Chem. Commun.*, 2007, 1062–1064.
- 10 C. X. Tan, D. D. Chu, X. H. Tang, Y. Liu, W. M. Xuan and Y. Cui, *Chem. Eur. J.*, 2019, 25, 662–672.
- 11 M. Yoshizawa, Y. Takeyama, T. Okano and M. Fujita, J. Am. Chem. Soc., 2003, **125**, 3243–3247.
- 12 Y. Yamauchi, M. Yoshizawa, M. Akita and M. Fujita, J. Am. Chem. Soc., 2010, 132, 960–966.
- 13 J. C. Ji, W. H. Wu, W. T. Liang, G. Cheng, R. Matsushita, Z. Q. Yan, X. Q. Wei, M. Rao, D. Q. Yuan, G. Fukuhara, T. Mori, Y. Inoue and C. Yang, *J. Am. Chem. Soc.*, 2019, 141, 9225–9238.
- 14 B. Chen, S. F. Cheng, G. H. Liao, X. W. Li, L. P. Zhang, C. H. Tung and L. Z. Wu, *Photochem. Photobiol. Sci.*, 2011, 10, 1441–1444.
- 15 Y. Inokuma, M. Kawano and M. Fujita, *Nat. Chem.*, 2011, 3, 349–358.
- 16 B. C. Pemberton, N. Barooah, D. K. Srivatsava and J. Sivaguru, *Chem. Commun.*, 2010, 46, 225–227.
- 17 J. W. Lee, S. Samal, N. Selvapalam, H. J. Kim and K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621-630.

- 18 M. Pattabiraman, A. Natarajan, R. Kaliappan, J. T. Mague and V. Ramamurthy, *Chem. Commun.*, 2005, 4542–4544.
- 19 C. Ke, C. Yang, T. Mori, T. Wada, Y. Liu and Y. Inoue, *Angew. Chem., Int. Ed.*, 2009, **48**, 6675–6677.
- 20 J. Guo, Y. Z. Fan, Y. L. Lu, S. P. Zheng and C. Y. Su, *Angew. Chem.*, *Int. Ed.*, 2020, **59**, 8661–8669.
- 21 R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2015, **115**, 7001–7045.
- 22 M. Yoshizawa, M. Tamura and M. Fujita, *Science*, 2006, 312, 251–254.
- 23 M. D. Pluth, R. G. Bergman and K. N. Raymond, *Science*, 2007, **316**, 85–88.
- 24 X. Jing, C. He, L. Zhao and C. Y. Duan, Acc. Chem. Res., 2019, 52, 100–109.
- 25 L. Zhao, X. Jing, X. Z. Li, X. Y. Guo, L. Zeng, C. He and C. Y. Duan, *Coord. Chem. Rev.*, 2019, **378**, 151–187.
- 26 S. Zarra, D. M. Wood, D. A. Roberts and J. R. Nitschke, *Chem. Soc. Rev.*, 2015, 44, 419-432.
- 27 W. Wang, Y. X. Wang and H. B. Yang, *Chem. Soc. Rev.*, 2016, 45, 2656–2693.
- 28 P. Mal, B. Breiner, K. Rissanen and J. R. Nitschke, *Science*, 2009, **324**, 1697–1699.
- 29 L. Yang, D. P. Zhang, H. Yang, Y. H. Dong, Z. Zhou and S. N. Wang, *Inorg. Chem.*, 2019, 58, 4067–4070.
- 30 M. Fagnoni, D. Dondi, D. Ravelli and A. Albini, *Chem. Rev.*, 2007, **107**, 2725–2756.
- 31 P. D. Frischmann, K. Mahata and F. Würthner, *Chem. Soc. Rev.*, 2013, **42**, 1847–1870.
- 32 L. Yang, C. He, X. Liu, J. Zhang, H. Sun and H. M. Guo, *Chem. Eur. J.*, 2016, **22**, 5253–5260.
- 33 K. Li, L. Y. Zhang, C. Yan, S. C. Wei, M. Pan, L. Zhang and C. Y. Su, J. Am. Chem. Soc., 2014, 136, 4456-4459.
- 34 B. Li, H. T. Fan, S. Q. Zang, H. Y. Li and L. Y. Wang, Coord. Chem. Rev., 2018, 377, 307–329.
- 35 H. Bouas-Laurent, A. Castellan and J.-P. Desvergne, *Chem. Soc. Rev.*, 2001, **30**, 248–263.
- 36 S. Karthikeyan and V. Ramamurthy, *Tetrahedron Lett.*, 2005, **46**, 4495–4498.
- 37 T. L. Wee, L. C. Schmidt and J. C. Scaiano, J. Phys. Chem. C, 2012, 116, 24373–24379.
- 38 R. Kumar, N. Sharma, N. Sharma, A. Sharma and A. K. Sinha, *Mol. Diversity*, 2011, 15, 687–695.