View Article Online View Journal

CrystEngComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Chen, Y. Hou, Q. Zhou, H. Zhang and D. Liu, *CrystEngComm*, 2017, DOI: 10.1039/C7CE00573C.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/crystengcomm

Journal Name



Regiospecific [2+2] photocycloadditions of an unsymmetrical olefin in the solid state based on metal-mediated assemblies

Received 00th January 20xx, Accepted 00th January 20xx

Jing-Min Chen,^a Yi-Xuan Hou,^a Qian-Kun Zhou,^a Hao Zhang,^a and Dong Liu*^a

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 13 April 2017. Downloaded by University of Newcastle on 14/04/2017 01:02:19.

An unsymmetrical olefin in two coordination polymers underwent solid state [2+2] photocycloaddition reactions in quantitative yields. The reactions afforded the *head-to-head* and *head-to-tail* photodimer isomers of cyclobutane derivatives with absolute regiospecificities.

As one of the most important and most frequently used photochemical reactions for organic synthesis, [2+2] photocycloaddition has attracted considerable attention.¹ This is because the products that afforded by photochemical [2+2] cycloaddition reactions are often difficult or impossible to achieve by conventional organic synthetic methodologies.¹ Schmidt's postulate According to for а [2+2] photocycloaddition reaction, each pair of olefinic bonds in the olefin molecules should be aligned parallel with a separation less than 4.2 Å.² To this end, many photochemical [2+2] cycloaddition reactions can be conducted in solutions based on random molecular collision. However, when the solutionbased [2+2] photocycloaddition reactions are occurred between two molecules of unsymmetrical olefins, the reactions usually afford regio- and stereo- isomeric cyclobutane mixtures.³ Owing to the similar physical and chemical properties of these isomers, their mixtures are difficult to be separated and purified. Although the selectivities can be remarkably enhanced by using suitable templates, such solution-based reactions are still hard or unable to produce absolute regiospecific products in quantitative yields.³

Fortunately, reactions proceeded in the solid state provide valuable opportunities to generate remarkable regio- or stereo-specific organic compounds with high yields.⁴⁻⁹ However, the reactivity of a solid-state compound is difficult to

control, owing to its structure demands of close packing in nature.⁴⁻⁹ If the reactive functional groups in adjacent molecules are separated by a long distance in the solid state, these groups cannot move freely to suitable orientations for a reaction to occur.^{4f} Furthermore, for an unsymmetrical olefin, although one of the two photoproducts may be favourably obtained through the photocycloaddition of a well-designed solid, the other isomer is not easy to be prepared through tiny changes of reaction conditions.¹⁰ Therefore, the utilization of crystal engineering to govern the assembly and packing of organic molecules is of particular importance to control chemical reactivity and regiospecificity in the solid state.¹⁰

The dipyridyl compound *trans*-1-(3-pyridyl)-2-(4-pyridyl)ethylene (1) is an unsymmetrical olefin. Each pair of the adjacent molecules of 1 may be aligned to be photoreactive in the *head-to-head* or *head-to-tail* modes with the regulation of suitable noncovalent interactions. After UV irradiation, the molecules of 1 with different arrangements would transform to 1,2-bis(3-pyridyl)-3,4-bis(4-pyridyl)cyclobutane (2) or 1,3bis(3-pyridyl)-2,4-bis(4-pyridyl)cyclobutane (3), respectively (Scheme 1).



Scheme 1 Possible [2+2] photocycloadditions based on the *head-to-head* and *head-to-tail* arranged molecules of 1.

Compound **1** was prepared *via* a modified procedure based on a Heck reaction¹¹ between 3-iodopyridine and 4vinylpyridine. To test whether the pure compound **1** is photoreactive, single crystals of the olefin were obtained by

^{a.}Key Laboratory of Energetic Materials of Anhui Province, College of Chemistry and Materials Science, Huaibei Normal University, 100 DongShan Road, Huaibei 235000, Anhui (P. R. China). E-mail: dongliu@chnu.edu.cn

⁺ Electronic Supplementary Information (ESI) available: Details of synthesis, details of crystal structure refinement, selected bond distances and angles, PXRD patterns, ¹H NMR spectra, ¹³C NMR spectra, HRMS spectra, TGA curves, UV-vis absorption spectra and X-ray crystallographic files in CIF format. CCDC 1522971-1522975. For ESI and crystallographic data in CIF or other electronic format see DOI: See DOI: 10.1039/x00xx00000x

COMMUNICATION

slow evaporation of a saturated MeOH solution within two days. A perspective view of the packing mode of **1** as determined by single crystal X-ray diffraction is shown in Fig. 1. The molecules of **1** in the crystal lattice are not parallel aligned and the distances between the nearest neighbor olefinic bonds are 6.66 or 7.31 Å. Such an arrangement of **1** does not meet Schmidt's topochemical criteria for a photochemical [2+2] cycloaddition.² Powder X-ray diffraction (PXRD) pattern, ¹H NMR, ¹³C NMR and HRMS spectra indicated the good phase purity of **1** (Fig. S1-4, ESI⁺). When a powdered crystalline sample in this form was exposed to UV irradiation for one day using a 20 W LED lamp ($\lambda_{em} = 365$ nm), **1** was confirmed to be photostable from ¹H NMR spectrum (Fig. S2, ESI⁺).



Fig. 1 View of the packing mode of 1 along the *b*-axis.

In the past decades, dipyridyl compounds have proved effective for incorporation into coordination assemblies due to their good coordination abilities.¹² Thus, as a dipyridine, **1** may be parallel arranged within short separations for photoreactions in head-to-head or head-to-tail fashions through the modification of appropriate coordination bonds. Since the enhancement of the photoreactivity of 1 through metal-mediated assemblies has not been investigated previously, we herein report the utilization of metal ions to tune the orientations of the molecules of 1 for the excellently regiocontrolled syntheses of two different photodimer isomers 2 and 3. In some particularly elegant work, Biradha and coworkers have skillfully utilized Ag(I) ions to prepare photodimer isomers of unsymmetrical olefins in appropriate conditions.^{10e,f} However, the preparation of two regiospecific cyclobutane isomers from [2+2] photocycloadditions of an unsymmetrical olefin via adjusting of different metal ions has not been investigated until now.

Compound $\{[Ag_2(1,4-ndc)(1)_2]\cdot 2H_2O\}_n$ (1a) was obtained by the reaction of AgNO $_3$, 1,4-naphthalenedicarboxylic acid (1,4-H₂ndc) and 1 via self-assembly using distilled water as solvent under hydrothermal conditions. The purity of 1a was confirmed by PXRD and ¹H NMR spectroscopy (Fig. S1-2, ESI⁺). Thermogravimetric analysis (TGA) indicated that 1a is stable up to 200 °C (Fig. S5, ESI⁺). Single-crystal analysis revealed that 1a crystallizes in the triclinic space group Pī. Each asymmetric unit consists of two Ag(I) ions, one 1,4-ndc²⁻ anion, two molecules of 1 and two discrete water molecules. In 1a, Ag(I) ions are bridged by 1 to generate a one-dimensional (1D) zigzag chain. Each pair of neighboring chains, related by center of symmetry, are linked by argentophilic forces^{13,14} to form a ladder-like structure (Fig. 2). The positive charges of Ag(I) ions in 1a are balanced by 1,4-ndc2- anions. It is noted that the molecules of 1 in the double chain are arranged in a head-tohead fashion and the distances between adjacent Ag(I) ions are 3.15 and 3.34 Å, respectively. These separations guarantee Page 2 of 6

the dinuclear Ag(I) units good templates to actine the neighboring molecules of **1** within relatively short distance. As a consequence of the assembly process, two adjacent olefinic bonds of **1** within the double chain are parallel to each other with a separation of 3.72 Å (dashed purple lines in Fig. 2), which satisfy the distance criterion for a solid state photochemical [2+2] cycloaddition.²

To evaluate the photoreactivity of 1a, a powdered crystalline sample of 1a was exposed to UV irradiation for 6 h. The irradiation resulted in dimerization of 1 to give 2 in guantitative yield, as evident by ¹H NMR spectroscopy. The ¹H NMR spectrum shows complete disappearance of the signals for the olefinic protons at 7.57 and 7.41 ppm and the emergence of a sharp signal at 4.65 ppm due to cyclobutane protons (Fig. S2, ESI⁺). In some especially graceful work, MacGillivray and co-workers have employed a ditopic carboxylic acid to hold a pair of photoreactive molecules of 1 in a head-to-head configuration through hydrogen bonding interactions. Irradiation with light leads to the formation of a head-to-head photodimer of 1.15a Another photoreactive solid involving **1** is (bta²⁻)·2(3,4-Hbpe⁺) (bta = 1,2,4,5benzenetetracarboxylic acid).^{15b} Owing to the limitation of its intrinsic structure, photoreaction of (bta2-)·2(3,4-Hbpe+) could only form of a mixture of two isomers.15b However, photoreactive coordination complex containing 1 has not been reported previously.¹⁶



Fig. 2 The ladder-like structure of 1a. All hydrogen atoms and solvent water molecules are omitted for clarity. The cyan, red and blue balls represent Ag, O and N atoms, respectively.

In order to determine the structure of the photodimer, the cyclobutane was isolated through extraction from reacted **1a** using CH₂Cl₂ and Na₂H₂edta/NaOH solution. The extraction afforded **2** as a colorless powder, which was characterized by NMR spectroscopy and HRMS (Fig. S2-4, ESI⁺). X-ray crystallography further determined the stereochemistry of **2**. **2** crystallizes in the orthorhombic space group *Pbca*. Each asymmetric unit contains one molecule of **2**. As shown in Fig. **3**, **2** is a *head-to-head* photodimer based on **1**. PXRD pattern indicated that the single crystal used in the structure determination was representative of the bulk sample (Fig. S1, ESI⁺).



Fig. 3 X-ray molecular structure of 2.

ea lime cera a gh to rear a share cera a sha

Published on 13 April 2017. Downloaded by University of Newcastle on 14/04/2017 01:02:19.

Journal Name

The successful isolation of the head-to-head photodimer 2 encouraged us to obtain the head-to-tail product 3. However, the preparation of head-to-tail photoproducts from unsymmetrical dipyridyl-substituted olefins is a challenge because the *head-to-tail* packing mode of unsymmetrical dipyridine molecules is not easy to predict. Considering the coordination chemistry of common metal ions, we found that the assembly of a mixture of dicarboxylate, dipyridine and Zn(II) salt can provide potential opportunity to generate threedimensional (3D) framework with large cavities.¹² To stabilize the architecture, the cavities can be filled by one or more crystallographic equivalent frameworks.¹² If the adjacent frameworks are packed with inversion symmetry, the molecules of unsymmetrical dipyridine in adjacent frameworks may be arranged in a *head-to-tail* fashion. Therefore, Zn(NO₃)₂ was selected as a starting material to react with 1,4-H2ndc and 1. Fortunately, another photoreactive coordination compound $\{[Zn(1,4-ndc)(1)]_2 \cdot H_2O\}_n$ (1b) was obtained.



Fig. 4 (a) The single 3D framework of **1b**. All hydrogen atoms and solvent water molecules are omitted for clarity. The cyan, red and blue balls represent Zn, O and N atoms, respectively. (b) Simplified four-fold interpenetrating architecture of **1b**. (c) View of the close contacts of olefinic bonds between interpenetrating frameworks of **1b**.

1b crystallizes in the monoclinic space group $P2_1/n$. Each asymmetric unit consists of one Zn(II) ion, one 1,4-ndc²⁻ anion, one molecule of **1** and one half of lattice water molecule. In **1b**, each Zn(II) ion is bridged by two 1,4-ndc²⁻ anions to form a $[Zn(1,4-ndc)]_n$ chain extending along the *c* axis. Meanwhile, the $[Zn(1,4-ndc)]_n$ chains are linked by the molecules of **1** to afford a 3D diamondoid framework of $[Zn(1,4-ndc)(1)]_n$ with 1D channels that run along the *b* axis (Fig. 4a). The void space of the single net of **1b** is filled by mutual interpenetration of three crystallographic equivalent networks, forming a four-fold interpenetrating 3D diamondoid architecture (Fig. 4b). The topology of **1b** is similar with that of { $[Cd_3(btre)(1,2,3-btc)_2(H_2O)_3]\cdot 3H_2O_n$ (btre = 1,2-bis(1,2,4-triazol-4-yl)ethane; 1,2,3-btc = 1,2,3-benzenetricarboxylate).¹⁷ However, owing to

COMMUNICATION

the steric hindrance of the trinuclear cluster $[Cd_3(H_2O_1(COO_1A], {[Cd_3(btre)(1,2,3-btc)_2(H_2O)_3] \cdot 3H_2O}_n Cannot 0^{39/C7} generate interpenetrating architecture. The void space of this complex is occupied lattice water molecules.¹⁷ PXRD pattern and ¹H NMR spectrum confirm the single crystal model is representative of the bulk product (Fig. S1-2, ESI⁺). According to the TGA curve,$ **1b**is found to be stable up to 355 °C (Fig. S5, ESI⁺). A closer view of the four-fold entanglement in**1b**indicates that each pair of adjacent molecules of**1**in neighboring coordination frameworks is closely aligned in a*head-to-tail*arrangement. The separation between neighboring olefinic bonds is 3.84 Å (dashed purple lines in Fig. 4c). Such a metal-organic directed arrangement of**1**appears to provide appropriate conditions for a photoinduced [2+2] cycloaddition.²

When a crystalline sample of **1b** was subjected to UV irradiation for 8 h, 100% conversion of olefinic bonds to cyclobutane rings was observed. The formation of **3** was confirmed by complete disappearance of the olefinic signals at 7.60 and 7.40 ppm and the appearance of a new set of peaks at 4.72 and 4.65 ppm due to cyclobutane protons (Fig. S2, ESI⁺). To confirm the stereochemistry of the photoproduct, colorless powder of **3** was extracted from the reacted sample of **1b**. Slow solvent evaporation over a period of two days produced colorless blocks of **3**. A crystal structure analysis confirmed the *head-to-tail* conformation of **3** (Fig. 5). Compound **3** crystallizes in the monoclinic space group $P2_1/n$. Each asymmetric unit contains one half molecule of **3**. The purity of **3** was further verified by PXRD, NMR spectroscopy and HRMS (Fig. S1-4, ESI⁺).



Fig. 5 X-ray molecular structure of 2.

As two isomers, **2** and **3** exhibit distinct structural differences. There are eight *head-to-head* isomeric molecules in each crystal lattice of **2**. Thus, the space that occupied by each molecule of **2** is approximately 486.4 Å³ since its cell volume is 3891.5 Å³. For **3**, 984.1 Å³ of the cell volume is filled by two *head-to-tail* isomeric molecules. Therefore, each molecule of **3** should occupy a space of 492.1 Å³. Apart from the difference between relative arrangements of pyridyl groups, the shapes of cyclobutane groups in **2** and **3** are also different. The four carbon atoms of cyclobutane group in **2** is obviously folded. However, nearly coplanar carbon atoms of cyclobutane group are existed in **3**.

UV-vis absorption spectra of **1-3** indicated that the maximum absorption peaks of these three organic compounds are observed at 300, 206 and 207 nm, respectively (Fig. S6, ESI⁺). According to the absorbances and concentrations of these compounds, the molar absorption coefficients of **1-3** can

be calculated as 6.13 \times 10^4, 5.06 \times 10^4 and 5.05 \times 10^4 L·mol^ 1·cm^-1, respectively.

In summary, we have demonstrated the utilization of metalmediated assemblies to prepare suitable templates for solid state organic syntheses, especially absolutely regiospecific photochemical [2+2] cycloaddition reactions of an unsymmetrical olefin. As other reaction conditions of two systems are the same, the orientations of the olefinic molecules are mainly determined by the coordination modes of different metal ions. Work is in progress to expand this approach to efficiently steer [2+2] photocycloadditions of other unsymmetrical olefins, with a goal to design excellently regio- or stereo-specific reactions for applications in organic synthesis and functional materials.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21201068), the Natural Science Foundation of Anhui Province (1708085MB27), the Key Project of Natural Science Research for Universities of Anhui Province (KJ2016A879), the Innovation Team of the Design and Applications of Advanced Energetic Materials of Anhui Province and the Innovation and Entrepreneurship Training Program for Undergraduates of Anhui Province.

Notes and references

- (a) J. D.Winkler, C. Mazur-Bowen and F. Liotta, *Chem. Rev.*, 1995, **95**, 2003; (b) M. A. Beniddir, L. Evanno, D. Joseph, A. Skiredj and E. Poupon, *Nat. Prod. Rep.*, 2016, **33**, 820; (c) S. Poplata, A. Tröster, Y.-Q. Zou and T. Bach, *Chem. Rev.*, 2016, **116**, 9748.
- 2 G. M. J. Schmidt, Pure Appl. Chem., 1971, 27, 647.
- (a) S. Yamada, N. Uematsu and K. Yamashita, J. Am. Chem. Soc., 2007, **129**, 12100; (b) M. V. S. N. Maddipatla, L. S. Kaanumalle, A. Natarajan, M. Pattabiraman and V. Ramamurthy, Langmuir, 2007, **23**, 7545; (c) V. Ramamurthy and J. Sivaguru, Chem. Rev., 2016, **116**, 9914.
- 4 (a) K. Tanaka and F. Toda, Chem. Rev., 2000, 100, 1025; (b) F. Toda, Organic Solid-State Reactions, Kluwer Academic Publishers, Dordrecht, 2002; (c) I. G. Georgiev and L. R. MacGillivray, Chem. Soc. Rev., 2007, 36, 1239; (d) J. J. Vittal, Coord. Chem. Rev., 2007, 251, 1781; (e) L. R. MacGillivray, G. S. Papaefstathiou, T. Friščić, T. D. Hamilton, D. K. Bučar, Q. L. Chu, D. B. Varshney and I. G. Georgiev, Acc. Chem. Res., 2008, 41, 280; (f) K. Biradha and R. Santra, Chem. Soc. Rev., 2013, 42, 950; (g) G. K. Kole and J. J. Vittal, Chem. Soc. Rev., 2013, 42, 1755.
- 5 (a) A. Michaelides, S. Skoulika and M. Siskos, Chem. Commun., 2004, 2418; (b) W. L. Nie, G. Erker, G. Kehr and R. Fröhlich, Angew. Chem., Int. Ed., 2004, 43, 310; (c) J. Paradies, I. Greger, G. Kehr, G. Erker, K. Bergander and R. Fröhlich, Angew. Chem., Int. Ed., 2006, 45, 7630; (d) Y. Hill and A. Briceňo, Chem. Commun., 2007, 3930; (e) D. Roiban, E. Serrano, T. Soler, I. Grosu, C. Cativielad and E. P. Urriolabeitia, Chem. Commun., 2009, 4681; (f) V. André, A. Hardeman, I. Halasz, R. S. Stein, G. J. Jackson, D. G. Reid, M. J. Duer, C. Curfs, M. T. Duarte and T. Friščić, Angew. Chem., Int. Ed., 2011, 50, 7858; (g) H. X. Xu, S. F. Cheng, X. J. Yang, B. Chen, Y. Chen, L. P. Zhang, L. Z. Wu, W. Fang, C. H. Tung and R. G. Weiss, J. Org. Chem., 2012, 77, 1685.
- 6 (a) X. Y. Wang, Z. M. Wang and S. Gao, Chem. Commun., 2007, 1127; (b) D. Liu, Z. G. Ren, H. X. Li, J. P. Lang, N. Y. Li

Journal Name

Page 4 of 6

and B. F. Abrahams, Angew. Chem., Int. Ed., 2010, 49, 4767: (c) Y.-C. Ou, W.-T. Liu, J.-Y. Li, G.-G. Zhang, the Wang and Mrsc. Tong, Chem. Commun., 2011, 47, 9384; (d) Y.-C. Ou, D.-S. Zhi, W.-T. Liu, Z.-P. Ni and M.-L. Tong, Chem.-Eur. J., 2012, 18, 7357; (e) T. Wu, L.-H. Weng and G.-X. Jin, Chem. Commun., 2012, 48, 4435; (f) Y.-F. Han, G.-X. Jin and F. E. Hahn, J. Am. Chem. Soc., 2013, 135, 9263; (g) D. Liu and J.-P. Lang, CrystEngComm, 2014, 16, 76; (h) D. Liu, H.-F. Wang, B. F. Abrahams and J.-P. Lang, Chem. Commun., 2014, 50, 3173; (i) Y.-F. Han, G.-X. Jin, C. G. Daniliuc and F. E. Hahn, Angew. Chem., Int. Ed., 2015, 54, 4958.

- 7 (a) M. Nagarathinam and J. J. Vittal, Angew. Chem., Int. Ed., 2006, 45, 4337; (b) M. H. Mir, L. L. Koh, G. K. Tan and J. J. Vittal, Angew. Chem., Int. Ed., 2010, 49, 390; (c) R. Medishetty, L. L. Koh, G. K. Kole and J. J. Vittal, Angew Chem., Int. Ed., 2011, 50, 10949; (d) G. K. Kole, T. Kojima, M. Kawano and J. J. Vittal, Angew Chem., Int. Ed., 2014, 53, 2143; (e) R. Medishetty, A. Husain, Z. Bai, T. Runčevski, R. E. Dinnebier, P. Naumov and J. J. Vittal, Angew. Chem., Int. Ed., 2014, 53, 5907; (f) R. Medishetty, S. C. Sahoo, C. E. Mulijanto, P. Naumov and J. J. Vittal, Chem. Mater., 2015, 27, 1821; (g) I.-H. Park, R. Medishetty, H.-H. Lee, C. E. Mulijanto, H. S. Quah, S. S. Lee and J. J. Vittal, Angew Chem., Int. Ed., 2015, 54, 7313.
- 8 (a) T. D. Hamilton, G. S. Papaefstathiou and L. R. MacGillivray, J. Am. Chem. Soc., 2002, 124, 11606; (b) G. S. Papaefstathiou, Z. M. Zhong, L. Geng and L. R. MacGillivray, J. Am. Chem. Soc., 2004, 126, 9158; (c) A. N. Sokolov, D. C. Swenson and L. R. MacGillivray, Proc. Nat. Acad. Sci. U.S.A., 2008, 105, 1794; (d) C. Karunatilaka, D.-K. Bučar, L. R. Ditzler, T. Friščić, D. C. Swenson, L. R. MacGillivray and A. V. Tivanski, Angew. Chem., Int. Ed., 2011, 50, 8642; (e) S. Bhattacharya, J. Stojaković, B. K. Saha and L. R. MacGillivray, Org. Lett., 2013, 15, 744; (f) S. Ghorai, J. C. Sumrak, K. M. Hutchins, D.-K. Bucar, A. V. Tivanski and L. R. MacGillivray, Chem. Sci., 2013, 4, 4304; (g) M. A. Sinnwell and L. R. MacGillivray, Angew. Chem., Int. Ed., 2016, 55, 3477.
- 9 (a) T. Caronna, R. Liantonio, T. A. Logothetis, P. Metrangolo, T. Pilati and G. Resnati, J. Am. Chem. Soc., 2004, 126, 4500; (b) J. F. Eubank, V. C. Kravtsov and M. Eddaoudi, J. Am. Chem. Soc., 2007, 129, 5820; (c) P. Metrangolo, F. Meyer, T. Pilati, G. Resnati and G. Terraneo, Angew. Chem., Int. Ed., 2008, 47, 6114; (d) S. Y. Yang, P. Naumov and S. Fukuzumi, J. Am. Chem. Soc., 2009, 131, 7247; (e) B. R. Bhogala, B. Captain, A. Parthasarathy and V. Ramamurthy, J. Am. Chem. Soc., 2010, 132, 13434; (f) S. Yamada and Y. Nojiri, Chem. Commun., 2011, 47, 9143; (g) S.-Y. Yang, X.-L. Deng, R.-F. Jin, P. Naumov, M. K. Panda, R.-B. Huang, L.-S. Zheng and B. K. Teo, J. Am. Chem. Soc., 2014, 136, 558.
- 10 (a) M. Khan, G. Brunklaus, V. Enkelmann and H. W. Spiess, J. Am. Chem. Soc., 2008, 130, 1741; (b) S. Yamada and Y. Tokugawa, J. Am. Chem. Soc., 2009, 131, 2098; (c) G. K. Kole, G. K. Tan and J. J. Vittal, Org. Lett., 2010, 12, 128; (d) K. M. Hutchins, J. C. Sumrak and L. R. MacGillivray, Org. Lett., 2014, 16, 1052; (e) S. Samai, P. Ghosh and K. Biradha, Chem. Commun., 2013, 49, 4181; (f) M. Garai, K. Maji, V. V. Chernyshev and K. Biradha, Cryst. Growth Des., 2016, 16, 550.
- (a) R. F. Heck and J. P. Nolley Jr, J. Org. Chem., 1972, 37, 2320;
 (b) F. Berthiol, M. Feuerstein, H. Doucet and M. Santelli, Tetrahedron Lett., 2002, 43, 5625.
- 12 (a) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247; (b) M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782; (c) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869.
- 13 (a) Q. Chu, D. C. Swenson and L. R. MacGillivray, Angew. Chem., Int. Ed., 2005, 44, 3569; (b) K. M. Hutchins, T. P. Rupasinghe, L. R. Ditzler, D. C. Swenson, J. R. G. Sander, J. Baltrusaitis, A. V. Tivanski and L. R. MacGillivray, J. Am. Chem.

Journal Name

View Article Online DOI: 10.1039/C7CE00573C

CrystEngComm Accepted Manuscript

Soc., 2014, **136**, 6778; (c) R. C. Laird, M. A. Sinnwell, N. P. Nguyen, D. C. Swenson, S. V. S. Mariappan and L. R. MacGillivray, *Org. Lett.,* 2015, **17**, 3233.

- 14 (a) X.-Y. Li, H.-F. Su, K. Yu, Y.-Z. Tan, X.-P. Wang, Y.-Q. Zhao, .D. Sun and L. Zheng, *Nanoscale*, 2015, **7**, 8284; (b) Z. Wang, R. Senanayake, C. M. Aikens, W.-M. Chen, C.-H. Tung and D. Sun, *Nanoscale*, 2016, **8**, 18905; (c) D. Sun, G.-G. Luo, N. Zhang, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2011, **47**, 1461; (d) Z. Wang, X.-Y. Li, L.-W. Liu, S.-Q. Yu, Z.-Y. Feng, C.-H. Tung and D. Sun, *Chem.-Eur. J.*, 2016, **22**, 6830; (e) X.-Y. Li, H.-F. Su, R.-Q. Zhou, S. Feng, Y.-Z. Tan, X.-P. Wang, J. Jia, M. Kurmoo, D. Sun and L.-S. Zheng, *Chem. -Eur. J.*, 2016, **22**, 3019; (f) H.-Y. Zhuo, .H.-F. Su, Z.-Z. Cao, W. Liu, S.-A. Wang, L. Feng, G.-L. Zhuang, S.-C. Lin, M. Kurmoo, C.-H. Tung, D. Sun and L.-S. Zheng, *Chem. -Eur. J.*, 2016, **22**, 17619.
- 15 (a) D. B. Varshney, G. S. Papaefstathiou and L. R. MacGillivray, Chem. Commun., 2002, 1964; (b) M. Linares and A. Briceño, New J. Chem., 2010, 34, 587.
- 16 (a) D. M. Shin, I. S. Lee, Y. K. Chung and M. S. Lah, *Inorg. Chem.*, 2003, **42**, 5459; (b) S. Wang, S. Xiong, Z. Wang and J. Du, *Chem. –Eur. J.*, 2011, **17**, 8630.
- 17 Y.-F. Peng, S. Zhao, K. Li, L. Liu, B.-L. Li, B. Wu, *CrystEngComm*, 2015, **17**, 2544.

J. Name., 2013, **00**, 1-4 | **5**

CrystEngComm Accepted Manuscript

Graphic Contents Entry

An unsymmetrical olefin in two coordination polymers undergo solid-state [2+2] photocycloadditions to afford absolute regiospecific photodimer isomers in quantitative yields.

