Electronic Supplementary Information (ESI[†])

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

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

^a Key Laboratory of Energetic Materials of Anhui Province, College of Chemistry and Materials Science, Huaibei Normal University, Huaibei 235000, P. R. China

*E-mail: dongliu@chnu.edu.cn

Table of Contents

Experimental Section S3
General procedure
Preparation of <i>trans</i> -1-(3-pyridyl)-2-(4-pyridyl)-ethylene (1)
Preparation of $\{[Ag_2(1,4-ndc)(1)_2] \cdot 2H_2O\}_n$ (1a)
UV irradiation of 1a
Isolation of 1,2-bis(3-pyridyl)-3,4-bis(4-pyridyl)cyclobutane (2)
Preparation of $\{[Zn(1,4-ndc)(1)]_2 \cdot H_2O\}_n$ (1b)
UV irradiation of 1b
Isolation of 1,3-bis(3-pyridyl)-2,4-bis(4-pyridyl)cyclobutane (3)
X-ray diffraction crystallography
References
Table S1. Summary of Crystallographic Data for 1, 1a, 2, 1b and 3
Fig. S1 PXRD patterns of 1, 1a, reacted 1a, 2, 1b, reacted 1b and 3
Fig. S2 The ¹ H NMR spectra of 1, UV irradiated sample of 1, 1a, reacted 1a, 2, 1b, reacted 1b
and 3 in d_6 -DMSO at ambient temperature ······S11
Fig. S3 The ¹³ C NMR spectra of 1, 2 and 3 in d_6 -DMSO at ambient temperature S15
Fig. S4 HRMS spectra of 1, 2 and 3·····S17
Fig. S5 The TGA curves for 1a and 1b ······S18
Fig. S6 UV-vis absorption spectra of 1, 2 and 3 ······S19
Table S2. UV-vis absorption data for 1, 2 and 3······S19

Experimental Section

General procedure. Reagents and solvents were purchased from TCI Co., Ltd., and Sigma-Aldrich Co. All the chemicals were used without any further purification. PXRD patterns were obtained using a PANalytical X'Pert PRO MPD system (PW3040/60). Thermal analysis were performed with a Perkin_Elmer TGA-7 thermogravimetric analyser at a heating rate of 10 °C/min and a flow rate of 100 cm³/min (N₂). ¹H NMR (400 MHz) and ¹³C NMR (150 MHz) spectra were recorded in DMSO- d_6 at room temperature. High-resolution mass spectra (HRMS) were obtained by ESI. Infrared (IR) samples were prepared as KBr pellets, and spectrum was obtained in the 4000–400 cm⁻¹ range using a Nicolet Avatar 360 FT-IR spectrophotometer. UV-vis absorption spectra were obtained with a Shimadzu UV-3600 spectrophotometer.

Preparation of *trans*-1-(3-pyridyl)-2-(4-pyridyl)-ethylene (1). A 150 mL round-bottom flask was charged with 3-iodopyridine (6.154 g, 30 mmol), distilled 4-vinylpyridine (3.682 g, 35 mmol), PdCl₂(PPh₃)₂ (0.651 g, 3 mol%) and triethylamine (3.335 g, 33 mmol) in 40 mL of DMF. The solution was heated at 140°C for a period of 20 h. The resulting mixture was poured onto cold water and extracted with dichloromethane. The organic layer was washed with NaOH solution and dried with Na₂SO₄. The organic solution was evaporated in vacuo to give a yellow solid which was recrystallized from MeOH to give pure **1** as colorless crystals. Yield: 4.641 g (85% yield based on 3-iodopyridine). IR (KBr, cm⁻¹): 3419m, 1598s, 1551s, 1493m, 1417s, 1292m, 1249w, 1218m, 1123m, 1024m, 990m, 971s, 881m, 817s, 750s, 540s. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.82 (s, 1H), 8.57 (d, *J* = 4.8 Hz, 2H), 8.51 (d, *J* = 4.4 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.55 (d, *J* = 4.4 Hz, 2H), 7.43 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.38 (d, *J* = 16.8 Hz, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 150.48, 149.70, 149.20, 144.18, 133.64, 132.29, 129.96, 128.34, 124.19, 121.36. HRMS (ESI, m/z) calcd. for C₁₂H₁₀N₂ [M+H]⁺ 183.0917, found 183.0918.

Preparation of $\{[Ag_2(1,4-ndc)(1)_2]\cdot 2H_2O\}_n$ (1a). To a 50 mL Teflon-lined autoclave was loaded AgNO₃ (0.170 g, 1 mmol), 1,4-H₂ndc (0.216 g, 1 mmol), 1 (0.182 g, 1 mmol) and H₂O (25 mL). The Teflon-lined autoclave was sealed and heated in an oven to 160°C for 12 h, and then cooled to ambient temperature at a rate of 5°C h⁻¹ to form colorless block crystals of **1a**. Yield: 0.345 g (83%)

yield based on Ag). IR (KBr, cm⁻¹): 3413m, 1601s, 1560s, 1507w, 1412s, 1327s, 1296m, 1259m, 1222m, 1126w, 1026m, 966s, 872m, 818s, 697s, 546s, 460m. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.79 (s, 1H), 8.75 (dd, *J* = 6.8, 3.6 Hz, 1H), 8.53 (d, *J* = 5.2 Hz, 2H), 8.48 (d, *J* = 4.8 Hz, 1H), 8.07 (d, *J* = 6.4 Hz, 2H), 7.66 (dd, *J* = 6.4, 3.2 Hz, 1H), 7.57 (s, 1H), 7.54 (d, *J* = 5.2 Hz, 2H), 7.41 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.36 (d, *J* = 16.8 Hz, 1H).

UV irradiation of 1a. Powdered crystalline sample of 1a (0.208 g, 0.25 mmol) in between quartz sheets was irradiated with a 20 W LED lamp ($\lambda_{em} = 365$ nm) for approximately 6 h. The irradiation resulted in dimerization of 1 to give 2 in 100% yield. IR (KBr, cm⁻¹): 3383m, 1602s, 1557s, 1506w, 1480m, 1416s, 1329s, 1297m, 1258m, 1222m, 1128w, 1029m, 968s, 873m, 817s, 705s, 545s, 461m. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.75 (dd, *J* = 6.8, 3.6 Hz, 1H), 8.41 (s, 1H), 8.31 (d, *J* = 4.8 Hz, 2H), 8.23 (d, *J* = 4.8 Hz, 1H), 8.06 (s, 1H), 7.66 (dd, *J* = 6.4, 3.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 5.2 Hz, 2H), 7.15 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.65 (d, *J* = 10.0 Hz).

Isolation of 1,2-bis(3-pyridyl)-3,4-bis(4-pyridyl)cyclobutane (2). А mixture of Na₂(H₂edta) · 2H₂O (0.372 g, 1 mmol), NaOH (0.080 g, 2 mmol), H₂O (30 mL), CH₂Cl₂ (30 mL) and the aforementioned photoreacted 1a were placed in a 100 mL flask and stirred for 3 h. The organic phase was separated from the reaction mixture and the aqueous layers were extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was washed with NaOH solution and H_2O , and dried with anhydrous Na₂SO₄. Finally, the organic phase was concentrated to dryness in vacuo to give 2 as colorless powder. Yield: 0.078 g (86% yield based on 1a). Slow evaporation of a saturated EtOH solution within a period of 2 days produced colorless single crystals of 2. IR (KBr, cm⁻¹): 3413m, 1600s, 1556s, 1496m, 1415s, 1284m, 1225m, 1121m, 1023m, 992m, 962m, 886m, 848m, 817s, 748s, 540s. ¹H NMR (400 MHz, DMSO- d_6) δ 8.44 (s, 1H), 8.34 (d, J = 4.8 Hz, 2H), 8.26 (d, *J* = 4.8 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 5.2 Hz, 2H), 7.19 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.69 (d, J = 9.6 Hz, 2H). ¹³C NMR (150 MHz, DMSO-d₆) δ 149.96, 149.68, 148.80, 147.95, 135.80, 135.24, 123.76, 123.53, 45.14, 43.40. HRMS (ESI, m/z) calcd. for $C_{12}H_{10}N_2$ [M+H]⁺ 365.1761, found 365.1763.

Preparation of $\{[Zn(1,4-ndc)(1)]_2 \cdot H_2O\}_n$ (1b). To a 50 mL Teflon-lined autoclave was loaded

Zn(NO₃)₂·6H₂O (0.297 g, 1 mmol), 1,4-H₂ndc (0.216 g, 1 mmol), **1** (0.182 g, 1 mmol) and H₂O (30 mL). The Teflon-lined autoclave was sealed and heated in an oven to 160°C for 12 h, and then cooled to ambient temperature at a rate of 5°C h⁻¹ to form colorless block crystals of **1b**. Yield: 0.419 g (89% yield based on Zn). IR (KBr, cm⁻¹): 3491m, 1614s, 1556s, 1511m, 1457m, 1433s, 1398s, 1227s, 1205m, 1128w, 1062m, 964s, 839m, 797s, 696s, 551s, 460m. ¹H NMR (400 MHz, DMSO- d_6) δ 8.82 (s, 1H), 8.79 (dd, *J* = 6.8, 3.6 Hz, 2H), 8.58 (d, *J* = 5.2 Hz, 2H), 8.52 (d, *J* = 4.4 Hz, 1H), 8.10 (s, 3H), 7.70 (dd, *J* = 6.8, 3.2 Hz, 2H), 7.60 (s, 1H), 7.58 (d, *J* = 5.2 Hz, 2H), 7.44 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.40 (d, *J* = 16.8 Hz, 1H).

UV irradiation of 1b. Powdered crystalline sample of 1b (0.235 g, 0.25 mmol) in between quartz sheets was irradiated with a 20 W LED lamp ($\lambda_{em} = 365$ nm) for approximately 8 h. The irradiation resulted in dimerization of 1 to give 3 in 100% yield. IR (KBr, cm⁻¹): 3507m, 1614s, 1557s, 1512m, 1460m, 1431s, 1400s, 1338s, 1220s, 1201m, 1065m, 1031s, 828m, 794s, 694s, 555s, 460m. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.79 (dd, *J* = 6.0, 3.2 Hz, 2H), 8.47 (s, 1H), 8.34 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 4.8 Hz, 1H), 8.10 (s, 2H), 7.69 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 4.8 Hz, 2H), 7.18 (dd, *J* = 7.2, 5.2 Hz, 1H), 4.72 (d, *J* = 7.6 Hz, 1H), 4.65 (d, *J* = 7.6 Hz, 1H).

Isolation of 1,3-bis(3-pyridyl)-2,4-bis(4-pyridyl)cyclobutane (3). А mixture of Na₂(H₂edta)·2H₂O (0.372 g, 1 mmol), NaOH (0.080 g, 2 mmol), H₂O (30 mL), CH₂Cl₂ (30 mL) and the aforementioned photoreacted 1b were placed in a 100 mL flask and stirred for 3 h. The organic phase was separated from the reaction mixture and the aqueous layers were extracted with CH₂Cl₂ (3 x 30 mL). The combined organic phase was washed with NaOH solution and H₂O, and dried with anhydrous Na₂SO₄. Finally, the organic phase was concentrated to dryness in vacuo to give 3 as colorless powder. Yield: 0.078 g (86% yield based on 1b). Slow evaporation of a saturated EtOH solution over a period of 2 days produced colorless single crystals of 3. IR (KBr, cm⁻¹): 3416m, 1599s, 1556s, 1498m, 1416s, 1286m, 1224m, 1123m, 1024m, 993m, 962m, 887m, 849m, 816s, 747s, 541s. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.47 (s, 1H), 8.34 (d, *J* = 5.2 Hz, 2H), 8.27 (d, J = 4.8 Hz, 1H) 7.64 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 5.2 Hz, 2H), 7.19 (dd, J = 8.0, 4.8 Hz, 1H), 4.72 (d, J = 7.6 Hz, 1H), 4.65 (d, J = 8.0 Hz, 1H). HRMS (ESI, m/z) calcd. for $C_{12}H_{10}N_2$ [M+H]⁺

X-ray diffraction crystallography: All measurements were collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) by using the Φ/ω scan technique. Absorption correction was based on symmetry equivalent reflections using the SADABS program. Single crystals of 1, 1a, 2, 1b and 3 suitable for X-ray analysis were obtained directly from the above preparations. The crystal structures of 1, 1a, 2, 1b and 3 were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXL-97 program.¹ For 1, the refinement in the suggested spacegroup $P2_1/n$ was attempted but not successful. The PLATON program indicated that no obvious spacegroup change is needed. PXRD further confirmed the structural model of 1. The O2 and O4 atoms of 1,4-ndc in 1b was found to be disordered over two sites with an occupancy factor of 0.64/0.36 for O2/O2' and 0.67/0.33 for O4/O4'. All non-hydrogen atoms refined anisotropically. The H atoms of the water molecules in 1a and 1b were located from the Fourier map and included in the final refinement by use of geometrical restraints with the O-H distances being fixed at 0.85 Å and $U_{iso}(H)$ equivalent to 1.5 times of $U_{eq}(O)$. The H atoms of the water molecule in **1b** were found to be disordered over two sites. All other H atoms were introduced at the calculated positions and included in the structure-factor calculations.

References

 (a) G. M. Sheldrick, SHELXS-97, Program for the refinement of crystal structures, University of Göttingen, Germany. 1997. (b) G. M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, University of Göttingen, Germany. 1997.

Compound	1	1a	2	1b	3
chemical formula	$C_{12}H_{10}N_2$	C ₃₆ H ₃₀ Ag ₂ N ₄ O ₆	C24H20N4	C ₄₈ H ₃₄ N ₄ O ₉ Zn ₂	C ₂₄ H ₂₀ N ₄
formula weight	182.22	830.38	364.44	941.57	364.44
crystal system	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	Рс	PError!	Pbca	$P2_{1}/n$	$P2_{1}/n$
<i>a</i> (Å)	7.3773(15)	8.4010(17)	12.112(2)	13.855(3)	9.2988(19)
<i>b</i> (Å)	5.7410(11)	9.3598(19)	16.437(3)	11.031(2)	10.402(2)
<i>c</i> (Å)	12.670(4)	20.446(4)	19.547(4)	14.277(3)	10.241(2)
α (°)	90.00	86.38(3)	90.00	90.00	90.00
β (°)	115.92(2)	82.42(3)	90.00	111.23(3)	96.58(3)
γ (°)	90.00	81.59(3)	90.00	90.00	90.00
$V(Å^3)$	482.6(2)	1574.9(6)	3891.5(12)	2033.9(8)	984.1(3)
Z	2	2	8	2	2
$D_c (g/cm^3)$	1.254	1.751	1.244	1.538	1.230
F(000)	192	832	1536	964	384
μ (MoKa,cm ⁻¹)	0.076	1.299	68757	1.245	17540
total no. of reflns	17010	26717	4466	36008	2254
no. of unique reflns	2168	7057	3384	4671	1658
no. of obsd. reflns	1806	433	253	3516	127
$R_{ m int}$	0.0221	0.0373	0.0388	0.0726	0.0373
R_1^a	0.0458	0.0497	0.0505	0.0550	0.0502
wR_2^b	0.1252	0.1048	0.1425	0.1217	0.1338
GOF^c	1.069	1.087	1.034	1.083	1.032
CCDC number	1522971	1522972	1522973	1522974	1522975

Table S1. Summary of Crystallographic Data for 1, 1a, 2, 1b and 3

 ${}^{a} R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. \ {}^{b} wR = \{ \sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2} \}^{1/2}. \ {}^{c} GOF = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2},$

where n is the number of reflections and p is total number of parameters refined.





(c)



Fig. S1 (a) PXRD pattern of **1** (from single crystal data: red; as-synthesis: black). (b) PXRD patterns of **1a** (from single crystal data: red; as-synthesis: black) and the photoproduct of **1a** (blue). (c) PXRD pattern of **2** (from single crystal data: red; as-synthesis: black). (d) PXRD patterns of **1b** (from single crystal data: red; as-synthesis: black) and the photoproduct of **1b** (blue). (e) PXRD pattern of **3** (from single crystal data: red; as-synthesis: black).

(e)

















S13



Fig. S2 The ¹H NMR spectra of 1 (a), UV irradiated sample of 1 (b), 1a (c), reacted 1a (d), 2 (e),
1b (f), reacted 1b (g) and 3 (h) in d₆-DMSO at ambient temperature.





Fig. S3 The ¹³C NMR spectra of 1 (a), 2 (b) and 3 (c) in d_6 -DMSO at ambient temperature.



Fig. S4 HRMS spectra of 1 (a), 2 (b) and 3 (c).



Fig. S5 The TGA curves for 1a and 1b.



Fig. S6 UV-vis absorption spectra of 1, 2 and 3.

Compound	1	2	3
λ_{max} / nm	300	206	207
А	0.613	0.506	0.505
b / cm	1	1	1
c / mol·L ⁻¹	10-5	10-5	10-5
$\epsilon / L \cdot mol^{-1} \cdot cm^{-1}$	6.13×10^{4}	$5.06 imes 10^4$	$5.05 imes 10^4$

 Table S2. UV-vis absorption data for 1, 2 and 3.