

# Template-controlled topochemical photodimerization based on “organometallic macrocycles” through single-crystal to single-crystal transformation†

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**Organometallic macrocycles 2a and 2b undergo [2 + 2] photochemical cycloaddition to form 3a and 3b in quantitative yield, accompanied by a single-crystal to single-crystal transformation.**

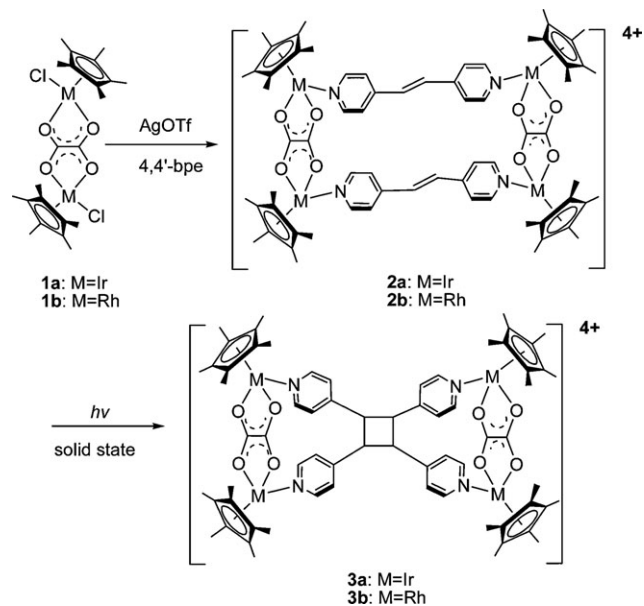
Topochemical photodimerization for cyclobutane or even ladderane ring formation is currently attracting significant attention.<sup>1</sup> Over recent years, extensive studies have been made on the template-controlled solid-state photochemical [2 + 2] cycloadditions<sup>2</sup> for carbon–carbon coupling by using organic molecules as well as some metal ions.<sup>3</sup> Among these photodimerizations, solid-state supramolecular transformations including single-crystal to single-crystal (SCSC) remains quite rare, although a few transition metal-ion complexes used as linear templates to direct [2 + 2] photodimerizations have appeared in the literature recently.<sup>3,4</sup>

We and others have recently reported a series of tetranuclear iridium and rhodium supramolecules containing pentamethylcyclopentadienyl ligands in combination with  $\mu$ -Cl or  $\mu$ -oxalato dinuclear bridging units as short edges.<sup>5</sup> In these complexes, the distances between the two pyridyl-based ligands are close to each other because of the presence of  $\pi \cdot \cdot \pi$  interactions and fall within the ranges for [2 + 2] photoreaction. By taking into account the dimensions of the tetranuclear rectangle macrocycles, we wondered if the  $\mu$ -oxalato dinuclear iridium complexes could be used as “organometallic clip” linear templates to direct [2 + 2] photodimerizations in the solid state.

Following this idea, tetranuclear complexes bearing the 4,4'-bpe [4,4'-bpe = *trans*-1,2-bis(4-pyridyl)ethylene] ligand, [Cp\*<sub>4</sub>M<sub>4</sub>( $\mu$ -bpe)<sub>2</sub>( $\mu$ - $\eta^2$ - $\eta^2$ -C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>](OTf)<sub>4</sub> (**2a**: M = Ir, **2b**: M = Rh) were designed and synthesized. As shown in Scheme 1, the tetranuclear rectangle macrocycle that contains the 4,4'-bpe ligand, formulated as [Cp\*<sub>4</sub>Ir<sub>4</sub>( $\mu$ -bpe)<sub>2</sub>( $\mu$ - $\eta^2$ - $\eta^2$ -C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>](OTf)<sub>4</sub> **2a** was prepared as yellow crystals *via* **1a**<sup>5c,7</sup> with two equivalents of AgOTf and subsequent reaction with 4,4'-bpe in methanol at room temperature (ratio = 1 : 1).† The <sup>1</sup>H NMR spectrum showed four singlets at  $\delta$  1.61, 7.59, 8.11 and 8.27 ppm in 60 : 8 : 8 : 4 intensity ratio, due to Cp\*, olefinic and the

pyridyl protons, respectively. In addition, the structure was determined by single-crystal X-ray analysis.§

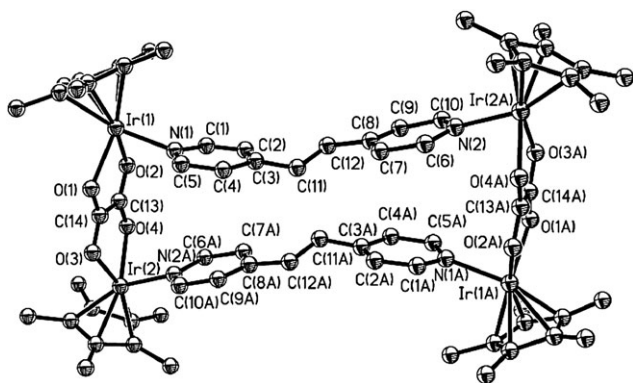
As shown in Fig. 1, the crystal structure reveals that the complex **2a** cation, which lies about an inversion center, possesses a rectangular structure bridged by two oxalate ligands and two molecules of 4,4'-bpe with dimensions of 5.558 × 13.251 Å. The average Ir–O and Ir–N bond lengths are 2.162 and 2.133 Å. Each metal adopts a six-coordinate geometry where the pyridyl nitrogen atoms of 4,4'-bpe and oxygen atoms of oxalato ligands occupy the apical positions, assuming that the Cp\* ligand functions as a three-coordinate ligand. The structures show that the two 4,4'-bpe ligands of **2a** are close to each other due to a significant face-to-face  $\pi \cdot \cdot \pi$  interaction. In this arrangement, the double bonds of the two 4,4'-bpe ligands lie parallel to each other with a distance of 3.23 Å. These geometries are congenial for the [2 + 2] cycloaddition to take place in the solid state according to the topochemical postulate of Schmidt [2 + 2] photoreaction. Moreover, cross-plane photoreactions are prevented by the absence of any contacts between the olefins belonging to adjacent molecules in the crystal stacking. As a result, the double bonds of the assembly are the sole olefins of the solids that confirm to the topochemical principle.<sup>2</sup>



Scheme 1 Synthesis of **2a,b** and **3a,b**.

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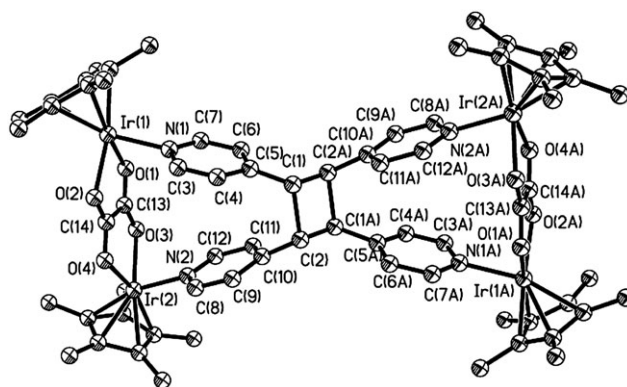
† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b717554j



**Fig. 1** Cation structure of **2a** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ir(1)–N(1) 2.135(14), Ir(1)–O(2) 2.148(9), Ir(1)–O(1) 2.185(10), Ir(2)–O(4) 2.139(10), Ir(2)–O(3) 2.167(10), O(3)–C(14) 1.242(18), O(4)–C(13) 1.267(17), O(2)–C(13) 1.250(16), O(1)–C(14) 1.227(16), C(11)–C(12) 1.300(18); N(1)–Ir(1)–O(2) 84.2(4), N(1)–Ir(1)–O(1) 86.4(5), O(2)–Ir(1)–O(1) 75.5(4), O(4)–Ir(2)–O(3) 76.6(4), C(13)–O(2)–Ir(1) 113.7(10), C(14)–O(1)–Ir(1) 114.5(11), C(12)–C(11)–C(3) 114(3), C(11)–C(12)–C(8) 118(3). Symmetry transformations used to generate equivalent atoms:  $-x, 1 - y, 2 - z$ .

When single crystals or a powdered crystalline sample of **2a** were subjected to UV irradiation using an Hg lamp for a period of approximately 25 h this resulted in dimerization of 4,4'-bpe to give 4,4'-tpcb (where 4,4'-tpcb = *trans*-tetrakis(4-pyridyl)cyclobutane) in quantitative yield, as evident by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy in  $\text{CD}_3\text{OD}$ .<sup>8</sup> The  $^1\text{H}$  NMR spectrum shows evident disappearance of the sharp singlet for the olefinic protons at  $\delta$  7.59 ppm, the appearance of a sharp singlet at  $\delta$  5.13 ppm due to cyclobutane protons, and a shift in the resonances of the pyridyl protons from  $\delta$  8.27 and 8.11 ppm to  $\delta$  = 8.15, 8.07 ppm and 7.72, 7.37 ppm. In addition, a singlet for cyclobutane carbons also appeared at  $\delta$  45.0 ppm in the  $^{13}\text{C}$  NMR spectrum.† X-Ray crystallographic analysis of **3a** confirmed the formation of new bonds across the vertical strands as shown in Fig. 3.‡ The pyridyl rings are bent towards each other. Similarly to **2a**, the cation of **3a** (Fig. 2) also lies about an inversion center, and each Ir atom is coordinated by one nitrogen atom from 4,4'-tpcb and two oxygen atoms of bridging oxalato ligands with Ir...Ir separations of 5.562 and 13.122 Å, as defined by the iridium centers. As a result, the C1–C2 bond length is 1.87(2) Å, which is longer than the carbon bond length of cyclobutane in other coordination complexes.<sup>4</sup> Optical microscopy revealed that the transparency and shape of the crystals along with their single-crystal nature were retained during the photoreaction, which suggested that the reaction occurred *via* a SCSC transformation.<sup>8</sup>

A rhodium analog **2b** was obtained in 72% yield from the reaction of **1b**<sup>Sc</sup> with 4,4'-bpe in the presence of AgOTf.‡ UV irradiation of **2b** produced the expected cyclobutane in 95% yield after a period of 50 h. The formation of 4,4'-tpcb was characterized by a near complete disappearance of the olefinic singlet at  $\delta$  7.52 ppm and the appearance of a sharp singlet at  $\delta$  5.05 ppm due to cyclobutane protons, in addition, pairs of doublets at  $\delta$  7.30, 7.31, 7.64, 7.65, 8.00, 8.09 for the pyridyl protons also evidenced the transformation (see ESI†).



**Fig. 2** Cation structure of **3a** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ir(1)–N(1) 2.115(8), Ir(1)–O(1) 2.170(7), Ir(1)–O(2) 2.154(7), Ir(2)–O(3) 2.142(7), Ir(2)–O(4) 2.152(7), C(1)–C(2) 1.87(2), C(1)–C(2A) 1.45(2); N(1)–Ir(1)–O(1) 82.5(3), N(1)–Ir(1)–O(2) 84.4(3), O(2)–Ir(1)–O(1) 76.7(3), N(2)–Ir(2)–O(3) 83.2(3), N(2)–Ir(2)–O(4) 83.7(3), C(2A)–C(1)–C(5) 120.0(16), C(2A)–C(1)–C(2) 89.0(15), C(5)–C(1)–C(2) 111.9(13), C(1A)–C(2)–C(10) 118.2(16), C(1A)–C(2)–C(1) 91.0(15), C(10)–C(2)–C(1) 112.6(13). Symmetry transformations used to generate equivalent atoms:  $1 - x, 1 - y, 1 - z$ .

In summary, we have described the use of tetranuclear rectangle macrocycles in topochemical photodimerization reactions. This work demonstrates that a number of other rectangle macrocycle structures may also be used to preorganize the double bonds in the spacer ligands. Work is in progress to obtain new organometallic clip templates based on this approach.

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## Notes and references

† All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were dried and deoxygenated by MBraun Solvent Purification System (4464) and collected just before use.  $[\text{Cp}^*\text{IrCl}_2]_2$ <sup>6</sup> and **1a**<sup>Sc</sup><sup>7</sup> were prepared according to literature methods. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer. Elemental analyses were carried out on a Elementar III Vario EI Analyzer.  $^1\text{H}$  NMR spectra were obtained on Bruker DMX-500 or Bruker DMX-400 spectrometers in  $[\text{D}_6]\text{DMSO}$  or  $\text{CD}_3\text{OD}$  solution.

**2a**: AgOTf (52 mg, 0.2 mmol) was added to a suspension of **1a** (81 mg, 0.1 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then 4,4'-bpe (18 mg, 0.1 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15 h. The solvent was then removed and the residue was extracted with  $\text{CH}_2\text{Cl}_2$ . The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **2a** as yellow crystals (103 mg, 82%). IR (KBr disk):  $\nu/\text{cm}^{-1}$ : 3110.9, 2979.5, 2922.2, 1677.8, 1633.4, 1614.6, 1428.9, 1259.0, 1164.7, 1032.9, 838.5, 641.5.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ , 298 K):  $\delta$  8.27 (d, 8H, Py-H), 8.11 (d, 8H, Py-H), 7.59 (s, 4H, C<sub>7</sub>=CH), 1.61 (s, 60H; Cp\*). Elemental analysis (%): calc. for  $\text{C}_{72}\text{H}_{80}\text{F}_{12}\text{Ir}_4\text{N}_4\text{O}_{20}\text{S}_4 \cdot 4\text{H}_2\text{O}$ : C 34.34, H 3.52, N 2.22, S 5.09; found: C 34.30, H 3.65, N 2.15; S 5.19. **2b** was obtained as yellow crystals from **1b** and 4,4'-bpe by using a procedure similar to that used for **2a**. Yield: 76%. IR (KBr disk):  $\nu/\text{cm}^{-1}$ : 3073.1, 2975.8, 2922.6, 1613.7, 1428.0, 1380.8, 1260.9, 1162.2,

1031.5, 981.7, 836.8, 640.9. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD, 298 K): δ 8.04 (d, 8H, Py-H), 7.67 (d, 8H, Py-H), 7.52 (s, 4H, CH=CH), 1.61 (s, 60H; Cp\*). Elemental analysis (%). calc. for C<sub>72</sub>H<sub>80</sub>F<sub>12</sub>Rh<sub>4</sub>N<sub>4</sub>O<sub>20</sub>S<sub>4</sub>: C 41.39, H 3.86, N 2.68, S 6.14; found (%): C 41.03, H 3.57, N 2.47; S 6.19.

**UV Irradiation of 2a:** A powdered sample of **2a** was placed between two glass slides and was irradiated using a broad Hg lamp (300 W) for approximately 25 h. Yellow crystals of **3a** suitable for X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in dichloroethane. IR (KBr disk):  $\nu/\text{cm}^{-1}$ : 3095.8, 2969.2, 2915.6, 1676.5, 1629.8, 1430.2, 1385.0, 1260.9, 1225.1, 1156.8, 1031.7, 838.3, 794.1, 639.2. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD, 298 K): δ 8.15 (d, 4H, Py-H), 8.07 (d, 4H, Py-H), 7.72 (d, 4H, Py-H), 7.37 (d, 4H, Py-H), 5.13 (s, 4H, CH-CH), 1.61 (s, 60H; Cp\*). <sup>13</sup>C NMR (500 MHz, CD<sub>3</sub>OD, 298 K): δ 174.58 (CO), 153.24 (C-Py), 130.12 (C-Py), 126.87 (C-Py), 88.30 (C-CH<sub>3</sub>), 45.02 (CH-CH), 8.81 (CH<sub>3</sub>).

**UV Irradiation of 2b:** A powdered sample of **2b** was placed between two glass slides and was irradiated using a broad Hg lamp (300 W) for approximately 50 h. Yellow crystals of **3b** were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in dichloromethane. IR (KBr disk):  $\nu/\text{cm}^{-1}$ : 3068.0, 2975.8, 2914.4, 1617.0, 1428.8, 1381.7, 1261.0, 1160.7, 1070.1, 1030.4, 837.5, 640.0.

§ **Crystal data for 2a:** C<sub>72</sub>H<sub>80</sub>F<sub>12</sub>Ir<sub>4</sub>N<sub>4</sub>O<sub>20</sub>S<sub>4</sub>·4H<sub>2</sub>O,  $M_r = 2518.50$ , monoclinic, space group  $P2_1/c$ ,  $a = 13.977(4)$ ,  $b = 24.358(7)$ ,  $c = 14.728(4)$  Å,  $\beta = 105.768(5)^\circ$ ,  $V = 4825(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.733$  g cm<sup>-3</sup>. A total of 20247 of which 8503 reflections were independent ( $R_{\text{int}} = 0.0818$ ). The structure was refined to final  $R_1 = 0.0710$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1993$  for all data,  $\text{GOF} = 1.012$ , and residual electron density max./min. = 1.597 and -0.570 e Å<sup>-3</sup>. **Crystal data for 3a:** C<sub>72</sub>H<sub>80</sub>F<sub>12</sub>Ir<sub>4</sub>N<sub>4</sub>O<sub>20</sub>S<sub>4</sub>·ClCH<sub>2</sub>CH<sub>2</sub>Cl,  $M_r = 2545.39$ , monoclinic, space group  $P2_1/c$ ,  $a = 12.607(3)$ ,  $b = 14.302(3)$ ,  $c = 24.551(6)$  Å,  $\beta = 103.230(4)^\circ$ ,  $V = 4309.5(19)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.962$  g cm<sup>-3</sup>. A total of 17921 of which 7573 reflections were independent ( $R_{\text{int}} = 0.0755$ ). The structure was refined to final  $R_1 = 0.0513$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1168$  for all data,  $\text{GOF} = 0.977$ , and residual electron density max./min. = 1.086 and -0.787 e Å<sup>-3</sup>.

All single crystals were immersed in mother-liquor and sealed in thin-walled glass. Data were collected on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). All the data were collected at room temperature using the  $\omega$  scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on  $F^2$  by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program.<sup>9</sup> In complex **2a**, one of the two triflate anions is slightly disordered so nine bond distances were restrained by DFIX instructions. In **3a**, atom C36 was restrained by ISOR instructions and two bond distances of the 1,2-dichloroethane solvent molecule were restrained. Thus there were eight restraints in this refinement.

CCDC 665361 (**2a**) and CCDC 665362 (**3a**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717554j

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