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Photodimerization of a 1D hydrogen-bonded zwitter-ionic lead(II) complex and its isomerization in solution†

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A pair of bpe–H⁺ ligands in a zwitter-ionic complex undergoes photochemical cycloaddition quantitatively accompanied by proton transfer and the cyclobutane ring isomerizes slowly in solution to two more isomers, catalyzed by CF_3CO_2H acid.

The criteria for the solid-state photochemical [2 + 2] cycloaddition reaction have been well established.[1,2] However it is still a challenge to stack a pair of double bonds in the crystal lattice by design. A number of weak interactions have been discovered to align the double bonds in the crystal lattice in a congenial manner for the [2 + 2] cycloaddition reactions which normally yield stereospecific products quantitatively, in contrast to the reaction in solution.[3] The strength and directionality of the hydrogen bonds have been elegantly exploited by MacGillivray and coworkers to align the double bonds in 4,4′-bipyridylethylene (bpe) with clip-like templates such as resorcinol and its derivatives in the crystal lattice.[3,4] Coordination metal complexes have also been used for this purpose.[5–7] To the best of our knowledge, hydrogen-bonded metal complexes have rarely been used to align the C=C bonds for photochemical dimerization reactions.[8a] Herein we report the photoreactivity of a hydrogen-bonded zwitter-ionic Pb(II) complex accompanied by proton transfer from bpe–H⁺ to the $CF_3CO_2^-$ ligand upon the [2 + 2] cycloaddition reaction between a pair of well-aligned bpe–H⁺ ligands and isomerization of cyclobutane derivative during the crystallization of photodimerized product. The triflouroacetic acid (TFA) obtained in the reaction catalyzes the isomerization of the *rctt*-tpcb isomer to *rcct*-tpcb and *rtct*-tpcb quantitatively in solution (tpcb = tetrakis(4-pyridyl)cyclobutane).

Colorless block-like crystals of zwitter-ionic lead(II) complex $[Pb(bpe-H)_2(O_2CCF_3)_4]$, (**1**) were obtained by diffusing bpe solution into a solution of $Pb(O_2CCH_3)_2 \cdot 3H_2O$ and TFA.‡ Single crystal X-ray diffraction studies reveal that the Pb(II) is coordinated to four $CF_3CO_2^-$ ligands and two monoprotonated bpe ligands to have highly distorted geometry with an O_4N_2 donor set. Of the four $CF_3CO_2^-$, two are in chelating mode. The Pb–O bond distances vary from 2.641(5) to 2.885(5) Å. The zwitter-ionic complexes are assembled through complementary N–H···O hydrogen bonding between the protonated imine nitrogen atoms and O1 of the monodentate trifluoroacetate ligand to furnish a zigzag hydrogen-bonded chain propagating along the *c*-direction as shown in Fig. 1. A crystallographic twofold axis is present at the Pb(II) while the center of the hydrogen-bonded bpe–H⁺ pair lies on

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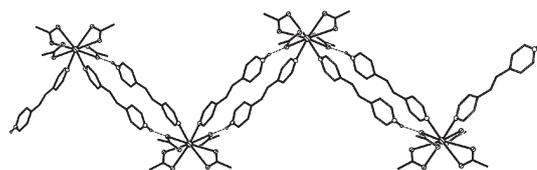*Fax: +65 6779 1691; Tel: +65 6516 2975*

Fig. 1 A portion of the zigzag hydrogen-bonded polymer **1**. The C–H hydrogen atoms, disordered atoms and fluorine atoms are not shown for clarity.

an inversion center. As a result, the bpe–H⁺ pairs are stacked in parallel with π···π interactions between the adjacent pyridyl groups and the distance between the centroids of the pyridyl groups is 3.63 Å. The distance between the centers of the adjacent C=C bonds, 3.87 Å, indicates that these pairs are favorable for a [2 + 2] photochemical cycloaddition reaction. Although a cobalt(II) complex containing the bpe–H⁺ ligand has been reported, the bpe–H⁺ were not aligned as expected.[8a] In another cobalt(II) complex,[8b] a pair of bpe units were aligned using O–H···N hydrogen bonding similar to **1**.

The powdered crystalline complex **1** was subjected to UV irradiation for a period of 12 h and quantitative photoreactivity is evident from the ¹H and ¹³C NMR spectra of the irradiated product **2**. The ¹H NMR spectrum of **2** in d_6-DMSO shows complete disappearance of the olefinic protons at 7.75 ppm and the appearance of cyclobutane protons at 4.85 ppm and a shift in the signals of the bipyridyl protons from 8.74 and 7.84 ppm to 8.47 and 7.43 ppm, indicating the formation of stereo-specific *rctt*-tpcb in 100% yield.[9] The single crystals of **1** became a gel after irradiation for 1–5 h, but became a powder after 12 h exposure to UV irradiation. The gel-like material has TFA as confirmed by mass spectrometric analysis. The formation of TFA during the photodimerization reaction can only be explained by the transfer of a proton from bpe–H⁺ to the $CF_3CO_2^-$ ligand.

Recrystallization of **2** in methanol yielded single crystals, **2a**.‡ The molecular structure and connectivity in **2a** is more or less predicted from the structure of **1** after the elimination of TFA. In **2a** the Pb(II) has highly distorted trigonal bipyramidal coordination with the axial positions occupied by the oxygen atoms of the $CF_3CO_2^-$ anion and the equatorial positions by two nitrogen atoms from two tpcb ligands along with an active lone pair. Each tpcb ligand is bridging two Pb(II) ions through two N atoms and two more pyridyl rings are non-bonded with the expected *rctt* stereochemistry at the cyclobutane ring.[3] This connectivity results in a highly corrugated 1D coordination polymeric structure as shown in Fig. 2. However, the pyridyl rings in the 1,2-positions of the cyclobutane ring are involved in the connectivity rather than
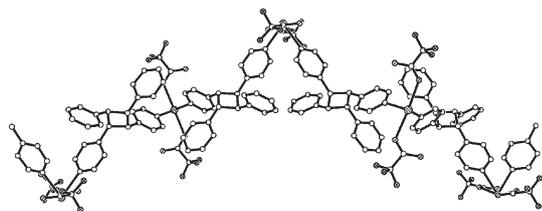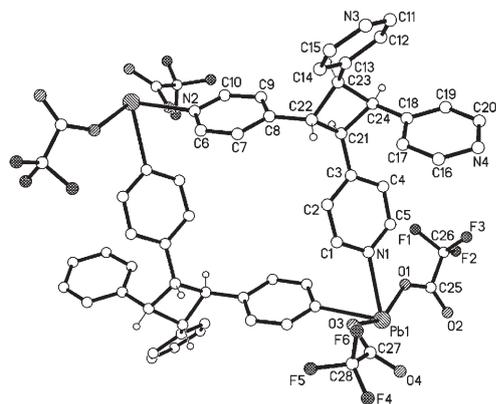
Fig. 2 A portion of the 1D coordination polymeric structure of **2a**. The C–H hydrogen atoms and disordered F atoms are not shown for clarity.

the expected 1,3-positions based on the packing of **1**. Since the structure, composition, connectivity, *etc.* of the coordination polymers are greatly influenced by the recrystallization conditions,[10] it is not surprising that the connectivity in **2a** is different from that of the irradiated product, **2**.

A mixture of yellow half-sphere crystals with diamond-like facets (**2a**) and cream colored long blocks (**3**) were obtained after four days by diffusing diethylether into a methanolic solution of **2**. The crystal structure determination of **3** revealed that the molecular formula is the same as **2a** but the connectivity and stereochemistry at the tpcb ligand is completely different as displayed in Fig. 3.‡

The stereochemistry at the tpcb cyclobutane ring in **3** is *rcct* which is surprisingly different from that observed in **2a**. Three pyridyl rings of the *rcct*-tpcb ligand are bonded intermolecularly to


(a)
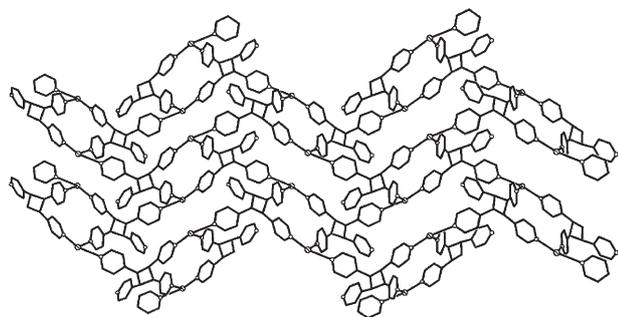
(b)

Fig. 3 (a) A perspective view of the repeating unit of **3** showing the numbering scheme and stereochemistry at the cyclobutane ring. (b) A portion of the 2D coordination polymeric structure in the (101) plane. The hydrogen atoms and $CF_3CO_2^-$ anions in (b) are not shown for clarity.

three Pb(II) ions while the fourth pyridyl ring with N4 atoms is uncoordinated. Two pyridyl rings containing N1 and N2 atoms from two *rcct*-tpcb ligands are bonded to two Pb(II) ions forming a dimer which has a square grid shape. The third pyridyl ring containing N3 connects these squares by bonding to the neighboring Pb(II) ions to provide a T-shaped geometry at the metal center and forming a highly corrugated 2D coordination polymer in the (101) plane as shown in Fig. 3b. The overall 2D coordination polymeric structure can be described as zigzag folded origami made from a sheet.

Despite the change in the connectivity between the tpcb ligand and Pb(II) anticipated during crystallization, the change in the stereochemistry at the cyclobutane ring is rather unexpected. The ^{1}H NMR spectrum of a fresh solution of **2** in d_6-DMSO shows chemical shifts at 8.47 (doublet), 7.43 (doublet) and 4.85 ppm due to the *rctt* isomer only. However, signals due to the *rcct* and *rtct* isomers start appearing on standing the solution at room temperature for two days and a ^{1}H NMR spectrum recorded after four days is shown in Fig. 4. The ^{1}H NMR spectrum clearly indicates the formation of the *rtct* isomer (peaks labelled b) from the chemical shifts at 8.52 (doublet) and 7.44 (doublet, overlapped with c) and 3.88 (singlet) ppm respectively. The chemical shifts are in good agreement with the reported data.[9,11,12] On the other hand, the chemical shift pattern of the *rcct* isomer (c) is rather complex due to the low symmetry of the isomer. For this *rcct* isomer (c) the expected six doublets from the pyridyl groups in the range 6.98–8.58 ppm and three triplets from the cyclobutane C–H protons in the range 4.50–5.09 ppm are also observed.

Contamination of TFA in the solution containing photoconverted product **2** is suspected to have catalyzed the conversion of *rctt*-tpcb to other stereoisomers. A small amount of TFA was added to the fresh solution of **2** in CD_3OD and the intensities of the signals due to *rtct* and *rcct* isomers were found to increase by 10% in the ^{1}H NMR spectrum, as compared to the unadulterated solution after two days. It appears that the protonation of the free pyridyl nitrogen atom in the tpcb ligand is responsible for the isomerization of *rctt*-tpcb.

The isomerization of *rctt*-1,2,3,4-tetrakis(4-methyl-4-pyridinium)-cyclobutane and similar cyclobutane derivatives were investigated by Horner and Hünig.[12] The strain associated with a four membered ring contributes to the inherent reactivity in
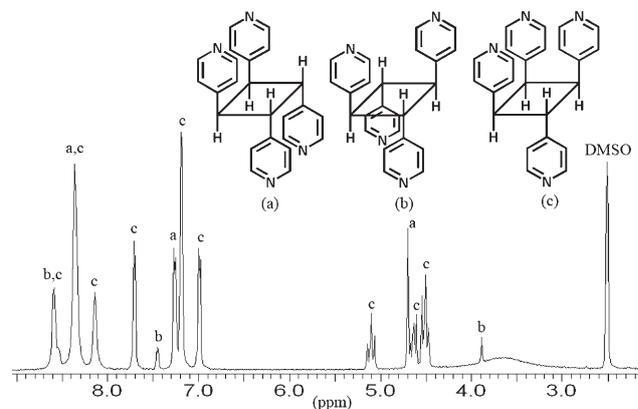
Fig. 4 ^{1}H NMR spectrum of the photodimerized product of **2** in d_6-DMSO recorded after four days. The inset shows the structures of cyclobutane isomers *rctt* (a), *rtct* (b), *rcct* (c).

solution.[9a] Alkylation of the pyridyl ring followed by deprotonation–reprotonation by the base and aqueous acid produced a mixture of the two steroisomers.[12] The mechanism involved in the isomerization of **2** may be very similar to that discussed by these authors. The di-protonated *rctt*-tpcb ring of **2** in solution is expected to prompt a similar rearrangement in solution. Reprotonation of the cyclic conjugated intermediate is expected to produce the *rcct*-tpcb isomer and further similar reaction to produce the *rtct*-tpcb isomer. Our preliminary experiments show that such isomerization does not occur in [{(F_3CCO_2)(μ-O_2CCH_3)Zn}$_2$(*rctt*-tpcb)][6d] on the addition of TFA, indicating that free uncoordinated pyridyl nitrogen is essential for protonation which subsequently leads to isomerization reactions.

A zwitter-ionic metal complex has been serendipitously observed for the first time to align the C=C bonds in monoprotonated bpe ligands in the crystal lattice to satisfy the Schmidt's alignment criterion for the solid-state reaction. Quantitative photodimerization reaction occurs when **1** was subjected to UV radiation for 12 h. The [2 + 2] cycloaddition is accompanied by transfer of proton from bpe–H$^+$ to the $CF_3CO_2^-$ ligand followed by the elimination of TFA from the Pb(II) complex. Due to the reorganization of structures during crystallization, the connectivity of the crystallized product of [Pb(*rctt*-tpcb)(O_2CCF_3)$_2$] is slightly different from the predicted structure based on the packing of **1**, and the compound **2a** is a 1D coordination polymer with two uncoordinated pyridyl groups. The *rctt* isomer formed in the photodimerized product isomerized to the *rtct* and *rcct* isomers in a variety of solvents as evident from ^{1}H NMR studies. The crystal structure of [Pb(*rcct*-tpcb)(O_2CCF_3)$_2$], **3**, is composed of zigzag folded 2D coordination polymeric sheets. This is the first crystal structure of a metal complex containing the unusual *rcct*-tpcb isomer. The TFA in a solution of [Pb(*rctt*-tpcb)(O_2CCF_3)$_2$], **2**, has been found to catalyze the isomerization of *rctt*-tpcb to the *rtct* and *rcct* isomers.

Notes and references

‡ Synthesis of **1**: A 2 mL THF solution of 4,4′-bipyridylethylene, bpe (0.09 g, 0.5 mmol), was layered over a solution of Pb(OAc)$_2$·3H$_2$O (0.189 g, 0.5 mmol) and TFA (0.171 g, 1.5 mmol) in 2 mL MeOH with 4 mL CH$_3$CN as a middle buffer layer. Colorless distorted block crystals were formed after 2 days which were decanted and dried. Yield: 0.24 g (46%). ^{1}H NMR (300 MHz, d_6-DMSO, 298 K, TMS): δ = 8.74 (d, 4H, Py–H), 7.84 (d, 4H, Py–H), 7.75 (s, 2H, CH=CH). Elemental analysis (%) calcd. for $C_{32}H_{26}N_4$ F$_{12}O_8$ Pb (1025.73), C, 37.47; H, 2.16; N, 5.46. Found: C, 37.42;H, 2.19;N, 5.42%.

UV Irradiation of **1**: 10 mg of the crystalline powder was packed in between two pyrex glass slides and irradiated for 12 h (Luzchem photoreactor) using the wavelength 350 nm. $δ_H$ (300 MHz; d_6-DMSO; 298 K, TMS) 8.47 (d, 4H, Py–H), 7.43 (d, 4H, Py–H), 4.85 (s, 4H, CH–CH).

Crystal Data for **1**: $C_{32}H_{22}F_{12}N_4O_8$Pb, M = 1025.73, monoclinic, space group $C2/c$, a = 11.916(4) Å, b = 15.793(6) Å, c = 19.578(7) Å, $β$ = 101.828(8)°, V = 3606(2) Å^3, Z = 4, $ρ_{calc}$ = 1.889 g cm^{-3}, $μ$ = 4.796 mm^{-1}, T = 296 K. Final R indices [$I > 2σ(I)$], R1 = 0.039, wR2 = 0.100, GoF on F^2 = 1.032.

Crystal Data for **2a**: $C_{28}H_{20}F_6N_4O_4$Pb, M = 797.67, cubic, space group $Ia\bar{3}d$, a = 34.8486(8) Å, V = 42321.0(8) Å^3, Z = 48, $ρ_{calc}$ = 1.502 g cm^{-3}, $μ$ = 4.849 mm^{-1}, T = 223 K. Final R indices [$I > 2σ(I)$], R1 = 0.0575, wR2 = 0.1584, GoF on F^2 = 1.051.

Crystal Data for **3**: $C_{28}H_{20}F_6N_4O_4$Pb, M = 797.67, monoclinic, space group $P2_1/n$, a = 15.8071(8) Å, b = 10.1994(5) Å, c = 18.290(1) Å, $β$ = 95.518(2)°, V = 2935.1(3) Å^3, Z = 4, $ρ_{calc}$ = 1.805 g cm^{-3}, $μ$ = 5.826 mm^{-1}, T = 296 K. Final R indices [$I > 2σ(I)$], R1 = 0.043, wR2 = 0.101, GoF on F^2 = 1.018.

The bpe–H$^+$ are disordered in **1** and were successfully resolved. The F atoms of CF_3 are disordered in all three structures and they were appropriately modelled in the least-square refinements. Crystal data were collected on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated MoKα radiation. CCDC 640883 for **1**, 640884 for **2** and 640885 for **3**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714355a

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