Supporting Information for

Research on Single-Crystal-to-Single-Crystal Photoaddition and Extension of the Schmidt's Rule in Topological Chemistry

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Experimental Section

Synthesis of 1,4-bpeb

(1,4-bis[2-(4-pyridyl)ethenyl]benzene) was synthesized by a modified method according to reference¹. The ratio of γ -picoline to terephthalaldehyde was increased from 2.1 to 3. The crude product was collected and washed with ethanol.

Synthesis of $\{Zn_2(\mu_3-OH)(1,3,5-btc)(1,4-bpeb)\} \cdot 4.5H_2O\}_n$

H₃btc (0.20 mmol, 0.042 g), 1,4-bpeb (0.20 mmol, 0.057 g) and Zn(Ac)₂ (0.20 mmol, 0.037 g) were added to a 25 mL beaker, then deionized water (10 mL) was added, and the mixture was stirred vigorously. Then, treated with ultrasonic stirring for 10 min until the solution was well mixed, and then the mixture was heated from 25°C to 180°C by programmed temperature control at a rate of 5°C/h and then maintained at 180°C for 96 h. Finally, the temperature was slowly reduced to 25°C after 31 h to obtain pale yellow block crystals (0.087 g, yield 60%). The crystals suitable for X-ray diffraction (1 and 2), were separated by filtration, washed with distilled water and dried in air. Elemental analysis: $C_{29}H_{29}N_2O_{11.5}Zn_2$, found (calculated) C 48.07 (48.35), H 4.14 (4.06), N 4.04 (3.89)%. FT-IR (KBr, cm⁻¹): 1608(s), 1570(s), 1551(w), 1515(s), 1436(s), 1373(s), 1343(m), 1231(w), 1202(s), 1102(m), 1070(s), 1031(s), 988(w), 970(m), 957(m), 909(w), 875(m), 833(s), 798(m), 761(s), 718(s), 619(s), 553(s). Powder X-ray diffraction measurement showed that the product was of pure phase.

UV irradiation

Single crystal 3 was obtained with 133 mW·h·cm⁻² UV irradiation of a crystal

with a UV spot light source (HOYA EXECURE 4000, multi-wavelength, the main peak is 365 nm) for 7 hours. Single crystal **4** was obtained with 210 mW·h·cm⁻² UV irradiation of a crystal with a 250 W UV high-pressure mercury lamp for 4 hours.

Powder sample: approximately 0.1 g of **1** was evenly spread on a watch glass, placed under a UV source (OPAS XLite 500Q Drawer), and irradiated with UV light for 24 h and 48 h. The powder on the glass was turned over every 4 h to make it evenly irradiated. The UV source energy density was about 54 mW·h·cm⁻², and the distance between the UV light source and the sample was 80 mm.

NMR Measurement of UV Irradiation Product

The powder of the complex (86 mg, 0.12 mmol) was UV irradiated with OPAS XLite 500Q Drawer for 96 hours (approximately 99 mW·h·cm⁻²), and stirred every 8 hours during irradiation. Put the irradiated powder, Na₂(H₂edta) (180 mg, 0.48 mmol), 12 ml H₂O, and 15 ml CH₂Cl₂ in a 150 mL round bottom flask and stirred for 2 days. The upper layer was the water layer (light yellow), and the lower layer was the organic layer (dark yellow). Separated them with a separatory funnel. Added 2 mol/L NaOH solution into the water phase in the separatory funnel until pH = 10 - 11, then the water solution turned into pink. Washed it with 3 × 6 ml of CH₂Cl₂. Merged the CH₂Cl₂ solutions and rotary evaporated it, a pink powder was obtained. Washed the powder with 2 mol/L NaOH solution and deionized water respectively for three times, a powder of 24 mg was obtained (theoretical yield 34.1 mg).

 $_1$ H NMR spectra were measured with the powder in D₆-DMSO on a Bruker Avance II 400M. After UV irradiation, the peaks c (7.35 ppm) and d (7.16 ppm) of the ethylene weakened, and two new peaks of cyclobutane appeared at around c' (4.82 ppm) and d' (4.67 ppm). The conversion rate calculated based on the H integral area is approximately 24.5%. (**Fig. S1**)

Single crystal X-ray structure determination

All data were collected in a nitrogen flow cooled with liquid nitrogen. The data of **1** was collected on a Bruker APEX area-detector diffractometer ($\lambda = 0.71073$ Å), and **2** was collected on a Rigaku XtaLAB Synergy diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å). The data of **3** and **4** were collected on an Oxford Gemini S Ultra with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å). Absorption corrections were performed with SADABS (Bruker, 2002) or CrysAlisPro (Rigaku Oxford Diffraction, 2022). All single crystal primary structures were solved and refined by full matrix least squares refinement using the Olex2 program. All the non-hydrogen atoms, except for those with occupancy rates below 0.3, were refined anisotropically on F^2 . The H atoms on the coordination sites were accurately geometrically positioned. Table 1 summarizes the crystal parameters for the four compounds.

PXRD, IR, UV-vis, Fluorescence measurements and Elemental analysis

X-ray powder diffraction was performed on an Ultima-IV, Thermo Fisher Scientific Co., Ltd, using Cu-K α radiation ($\lambda = 1.54184$ Å), the measurements were

performed at a test voltage of 40 kV, a test current of 15 mA and a scan angle of $5\sim50^{\circ}$, and the powder diffraction data of 1 was simulated by MERCURY 2022.1.0. (Fig. S2)

Elemental analyses (C, H, N) were measured on a Vario EL III elemental analyzer. IR spectroscopy was performed on a Nicolet iS50 (KBr compression, wavelength range 4000~400 cm⁻¹). (**Fig. S3, 4**)

The solid state diffuse reflectance UV-vis spectra were measured on a Cary-5000 (Agilent Technologies) UV-visible spectrometer. (**Fig. S5**)

The solid fluorescence emission and excitation spectra were measured on a Hitachi F-7000 FL spectrophotometer. The excitation wavelength was 380 nm, the test excitation slit width and emission slit width were 5.0 nm, and the PMT voltage was 700 V. (**Fig. S6-S8**)

Thermogravimetric analysis was obtained by testing on a Simultaneous Thermal Analyzer 449F5 in N_2 with a 10°C/min heating rate, in the temperature range 30-800°C. (Fig. S9)

Table 1. Crystallographic data of 1~4					
	1	2	3	4	
CCDC No	2258569	2258570	2258571	2258572	
Formula	$C_{29}H_{29}N_2O_{11.5}Zn_2$	$C_{29}H_{29.8}N_2O_{11.9}Zn_2$	$C_{29}H_{27.8}N_2O_{10.9}Zn_2$	$C_{29}H_{27.7}N_2O_{10.85}Zn_2$	
F.W.	720.28	727.49	709.47	708.57	
Crystal system	triclinic	triclinic	triclinic	triclinic	
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	
<i>F</i> (000)	738.0	746.0	726.0	725.0	
T/K	189(2)	100(2)	233(2)	233(2)	
a (Å)	9.3469(4)	9.3510(2)	9.1845(3)	8.7170(10)	
<i>b</i> (Å)	9.9760(4)	9.9976(2)	9.9874(3)	9.9589(12)	
<i>c</i> (Å)	17.9902(8)	18.0428(4)	18.5249(5)	19.6815(14)	
α (°)	79.7430(10)	80.100(2)	79.721(2)	78.835(9)	
β (°)	86.7290(10)	87.289(2)	86.064(2)	84.141(9)	
γ (°)	67.2950(10)	67.583(2)	68.155(3)	69.710(11)	
V (Å ³)	1522.64(11)	1535.78(6)	1551.94(8)	1571.1(3)	
Z, D_c (g.cm ⁻³)	2, 1.571	2, 1.573	2, 1.518	2, 1.498	
μ (mm ⁻¹)	1.640	2.496	2.431	2.400	
Refl. /unique	13358/6954	34341/6003	22035/6122	10747/6160	
Data/restraints/ parameters	6954/248/765	6003/230/748	6122/542/698	6160/552/703	
Rint	0.0207	0.0416	0.0515	0.0861	
R1 [I > $2\sigma(I)$]	0.0463	0.0534	0.0770	0.0890	
ω R2 (all data)	0.1335	0.1435	0.2374	0.3068	
$\Delta \rho (e \text{\AA}^{-3})$	0.80/-0.81	1.47/-1.06	1.67/-0.87	1.32/-1.13	

Tables

Table 2.	Selected	bond	lengths	(Å)	and	bond	angles	(°) of 1
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		1			
Zn(1)-O(1)	2.021(19)	Zn(1)-N(1)	2.097(5)	$Zn(2)-O(7)^{i}$	1.9545(18)
Zn(1)-O(4) ⁱⁱ	1.968(3)	$Zn(1)-O(7)^{i}$	1.9545(18)	Zn(2)-O(2)	1.9601(19)
Zn(1)-O(7)	1.991(3)	Zn(2)-O(6) ⁱⁱⁱ	1.917(2)	$Zn(2)-N(2)^{iv}$	2.006(5)
O(6)-Zn(2) ⁱⁱⁱ	1.917(2)				
O(7)-Zn(1)-O(7) ⁱⁱ	84.26(8)	$O(6)^{iv}$ -Zn(2)-O(2)	114.36(9)	O(1)-Zn(1)-Zn(1) ⁱ	104.71(6)
O(4) ⁱⁱ -Zn(1)-O(7)	109.52(9)	$O(7)^{i}$ -Zn(2)-O(2)	107.89(8)	$N(1)$ - $Zn(1)$ - $Zn(1)^{i}$	146.91(15)
$O(4)^{ii}$ -Zn(1)-O(1)	136.98(9)	$O(6)^{iv}$ -Zn(2)-N(2) ⁱⁱⁱ	110.57(18)	O(2)-Zn(2)-N(2) ⁱⁱⁱ	103.71(14)
O(7)-Zn(1)-O(1)	113.34(8)	$Zn(1)-O(7)-Zn(1)^{i}$	95.74(8)	$Zn(2)^{i}-O(7)-Zn(1)$	120.53(9)
$O(4)^{ii}$ -Zn(1)-N(1)	90.98(12)	$O(7)^{i}$ -Zn(2)-N(2) ⁱⁱⁱ	111.05(16)	$Zn(2)^{i}-O(7)-Zn(1)^{i}$	110.24(8)
O(7)-Zn(1)-N(1)	103.0(16)	O(1)-Zn(1)-O(7) ⁱ	89.83(11)	O(7)-Zn(1)-Zn(1) ⁱ	40.16(5)
O(1)-Zn(1)-N(1)	83.08(15)	N(1)-Zn(1)-O(7) ⁱ	89.76(7)	$O(6)^{iv}$ -Zn(2)-O(7) ⁱ	109.16(8)
$O(7)^{i}$ -Zn(1)-Zn(1) ⁱ	40.16(5)	$O(4)^{ii}$ -Zn(1)-Zn(1) ⁱ	103.18(6)		

Symmetry transformations used to generate equivalent atoms: ⁱ2-*x*, 1-*y*, 1-*z*; ⁱⁱ1+*x*, -1+*y*, +*z*; ⁱⁱⁱ1-*x*, 1-*y*, 1-*z*; ^{iv}1+*x*, 1+*y*, -1+*z*; ^v-1+*x*, 1+*y*, +*z*; ^{vii}-1+*x*, -1+*y*, 1+*z*; ^{vii}-1-*x*, 3-*y*, -*z*.

Table 3. Selected bond lengths (Å) and bond angles (°) of 2

2						
Zn(1)-O(4) ⁱⁱ	1.982(2)	Zn(1)-N(1)	2.097(3)	$O(7)^{i}$ -Zn(2)	1.9651(15)	
Zn(1)-O(7)	2.003(18)	$Zn(1)-O(7)^{i}$	2.162(16)	Zn(2)-O(2)	1.9709(17)	
Zn(1)-O(1)	2.028(15)	Zn(2)-O(6) ⁱⁱⁱ	1.929(19)	$Zn(2)-N(2)^{iv}$	1.984(3)	
O(6)-Zn(2) ⁱⁱⁱ	1.929(19)					
O(7)-Zn(1)-O(7) ⁱⁱ	89.68(6)	$O(6)^{iv}$ -Zn(2)-O(2)	114.34(8)	O(1)-Zn(1)-Zn(1) ⁱ	104.68(5)	
O(4) ⁱⁱ -Zn(1)-O(7)	109.58(7)	$O(7)^{i}$ -Zn(2)-O(2)	107.49(7)	$N(1)$ - $Zn(1)$ - $Zn(1)^{i}$	146.63(9)	
$O(4)^{ii}$ -Zn(1)-O(1)	136.90(8)	$O(6)^{iv}$ -Zn(2)-N(2) ⁱⁱⁱ	112.21(11)	O(2)-Zn(2)-N(2) ⁱⁱⁱ	106.15(10)	
O(7)-Zn(1)-O(1)	113.35(7)	$Zn(1)-O(7)-Zn(1)^{i}$	95.5(7)	$Zn(2)^{i}-O(7)-Zn(1)$	120.17(8)	
$O(4)^{ii}$ -Zn(1)-N(1)	91.26(9)	$O(7)^{i}$ -Zn(2)-N(2) ⁱⁱⁱ	107.64(9)	$Zn(2)^{i}-O(7)-Zn(1)^{i}$	110.44(7)	
O(7)-Zn(1)-N(1)	102.6(10)	O(1)-Zn(1)-O(7) ⁱ	89.68(6)	O(7)-Zn(1)-Zn(1) ⁱ	44.23(5)	
O(1)-Zn(1)-N(1)	83.16(9)	N(1)-Zn(1)-O(7) ⁱ	171.43(10)	$O(6)^{iv}$ -Zn(2)-O(7) ⁱ	108.71(7)	
$O(7)^{i}$ -Zn(1)-Zn(1) ⁱ	40.26(5)	$O(4)^{i}$ -Zn(1)-Zn(1) ⁱ	103.12(6)			

Symmetry transformations used to generate equivalent atoms: ⁱ2-*x*, 1-*y*, 1-*z*; ⁱⁱ1+*x*, -1+y, +z; ⁱⁱⁱ1+*x*, 1+y, -1+z; ^{iv}1-*x*, 1-*y*, 1-*z*; ^v-1+*x*, 1+y, +z; ^{vi}-1+*x*, -1+y, 1+z.

Figures



Fig. S1. 1H NMR spectra of bpeb and (bpeb)₂ extracted from UV irradiated 1.





Fig. S4 IR (UV 0 h, 24 h and 48 h) of 1



Fig. S5 UV diffuse reflectance spectrum (UV 0 h and 48 h) of 1



Fig. S6 Solid fluorescence spectrum (UV 0 h and 48 h) of 1



Fig. S7 Solid-state fluorescence spectra of 1



Fig. S8 Solid-state fluorescence spectra of 1 and 1,4-bpeb



Fig. S9 Thermogravimetric analysis of 1