

# 3D→3D interpenetrated and 2D→3D polycatenated Ag(I) networks constructed from 1,4-bis(2-methylimidazol-1-ylmethyl)benzene and dicarboxylates

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(1) Experiment details.....	2
(2) X-ray Crystallography .....	3
(3) Synthesis of 1 and 2 .....	4
(4) Table S1: The selected bond distances and angles for 1 and 2.....	5
(5) Table S2: Crystal data for 1 and 2.....	6
(6) Fig. S1: IR spectra of 1 and 2 .....	7
(7) Fig. S2: XRD patterns of 1 and 2 .....	8
(8) Fig. S3: View of the [Ag <sub>2</sub> (bmimb)] rod passing through the [Ag <sub>2</sub> (bmimb) <sub>2</sub> ] loop. ....	9
(9) Fig. S4: View of the 3D single network built from 2D (6,3)-nets and [Ag <sub>2</sub> (bmimb) <sub>2</sub> ] loops. .....	10
(10) Fig. S5: View of the 26- and 46-membered macrocycles. ....	11
(11) Fig. S6: Comparison of PXRD of 1 and 2 with dehydrated 1' and 2'. ....	12
(12) Fig. S7: The UV-Vis spectra of 1 and 2.....	13
(13) Scheme S1: The <i>anti</i> and <i>syn</i> conformations of bmimb ligand in 1. ....	14

## (1) Experiment details

All the reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra were recorded on a Nicolet AVATAT FT-IR330 spectrometer as KBr pellets in the frequency range 4000-400  $\text{cm}^{-1}$ . The elemental analyses (C, H, N contents) were determined on a CE instruments EA 1110 analyzer. Photoluminescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate. TG curves were measured from 30 to 800  $^{\circ}\text{C}$  on a SDT Q600 instrument at a heating rate 10  $^{\circ}\text{C}/\text{min}$  under the  $\text{N}_2$  atmosphere (100 mL/min). X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-K $\alpha$  radiation. UV/vis diffuse-reflectance spectra were measured from 200 to 800 nm on a carry 5000 UV-vis-NIR spectrophotometer.

## (2) X-ray Crystallography

Single crystals of the complexes **1** and **2** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for **1** and **2** were collected on a Bruker-AXS CCD single-crystal diffractometer with graphite-monochromated Mo K $\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 20 frames each, each frame corresponds to a  $0.3^\circ$  scan in 5 s, followed by spot integration and least-squares refinement. Data were measured using  $\omega$  scans of  $0.3^\circ$  per frame for 10 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.<sup>1</sup> Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.<sup>1</sup> In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97<sup>2</sup> and refined on  $F^2$  by full-matrix least-squares procedures with SHELXL-97.<sup>3</sup> Atoms were located from iterative examination of difference  $F$ -maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times  $U_{eq}$  of the attached C atoms. All structures were examined using the Addsym subroutine of PLATON<sup>4</sup> to assure that no additional symmetry could be applied to the models.

(1) Bruker. *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA, 1998.

(2) G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Gottingen, Germany, 1997.

(3) Sheldrick, G. M. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Gottingen, Germany, 1997.

(4) A. L. Spek, *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

### (3) Synthesis of **1** and **2**

#### *Synthesis of complex [Ag<sub>2</sub>(bmimb)<sub>1.5</sub>(pzdc)·3H<sub>2</sub>O]<sub>n</sub> (**1**).*

A mixture of Ag<sub>2</sub>O (23 mg, 0.1 mmol), bmimb (27 mg, 0.1 mmol) and pzdc (17 mg, 0.1 mmol) was stirred in methanol-DMF mixed solvent (5 mL, v/v: 3/2). Then aqueous NH<sub>3</sub> solution (25%, 2 mL) was dropped into the mixture to give a clear solution under ultrasonic treatment (160 W, 50 °C, 20 min). The resultant solution was allowed to evaporate slowly in darkness at room temperature for several days to give yellow crystals of **1** (yield: 76%, based on Ag). They were washed with a small volume of cold ethanol. Anal. Calc. (found) for Ag<sub>2</sub>C<sub>30</sub>H<sub>35</sub>N<sub>8</sub>O<sub>7</sub>: C, 43.13 (42.33); H, 4.22 (3.94); N, 13.41 (12.94)%. IR (KBr):  $\nu(\text{cm}^{-1}) = 3409$  (s), 1638 (s), 1588 (s), 1530 (m), 1502 (m), 1428 (s), 1385 (m), 1354 (s), 1273 (m), 1197 (w), 1159 (m), 1137 (w), 1110 (m), 1076 (w), 1024 (w), 989 (m), 884 (m), 847 (m), 831 (m), 737 (s), 664 (m), 478 (m).

#### *Synthesis of complex [Ag (bmimb)(mac)<sub>0.5</sub>·0.5H<sub>2</sub>O]<sub>n</sub> (**2**).*

The synthesis of **2** was similar to that of **1**, but using mac (13 mg, 0.1 mmol) instead of pzdc. Yellow crystals of **2** were obtained in 85% yield based on Ag. They were washed with a small volume of cold ethanol. Anal. Calc. (found) for Ag<sub>2</sub>C<sub>36</sub>H<sub>41</sub>N<sub>8</sub>O<sub>6</sub>: C, 48.18 (48.67); H, 4.60 (4.66); N, 12.49 (12.67)%. IR (KBr):  $\nu(\text{cm}^{-1}) = 3420$  (s), 1577 (s), 1501 (m), 1470 (m), 1424 (s), 1273 (m), 1154 (w), 1138 (w), 1078 (w), 984 (w), 738 (s), 665 (s).

**(4) Table S1: The selected bond distances and angles for 1 and 2**

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Compound 1			
Ag1—N6	2.182(6)	Ag2—N4 <sup>ii</sup>	2.153(7)
Ag1—N7 <sup>i</sup>	2.340(5)	Ag2—N2	2.175(6)
Ag1—N8	2.427(5)	Ag2—O3	2.544(5)
Ag1—O4	2.621(5)	Ag2—O2	2.572(5)
Ag1—O1 <sup>i</sup>	2.647(5)		
N6—Ag1—N7 <sup>i</sup>	137.5(2)	N8—Ag1—O1 <sup>i</sup>	86.55(18)
N6—Ag1—N8	140.1(2)	O4—Ag1—O1 <sup>i</sup>	146.95(15)
N7 <sup>i</sup> —Ag1—N8	81.20(18)	N4 <sup>ii</sup> —Ag2—N2	137.5(3)
N6—Ag1—O4	98.88(19)	N4 <sup>ii</sup> —Ag2—O3	130.4(2)
N7 <sup>i</sup> —Ag1—O4	90.28(18)	N2—Ag2—O3	92.0(2)
N8—Ag1—O4	65.25(17)	N4 <sup>ii</sup> —Ag2—O2	84.9(2)
N6—Ag1—O1 <sup>i</sup>	114.06(19)	N2—Ag2—O2	117.0(2)
N7 <sup>i</sup> —Ag1—O1 <sup>i</sup>	67.61(18)	O3—Ag2—O2	70.25(16)
Symmetry codes: (i) $-x+3/2, y+1/2, -z+3/2$ ; (ii) $-x+1, -y+1, -z+2$ .			

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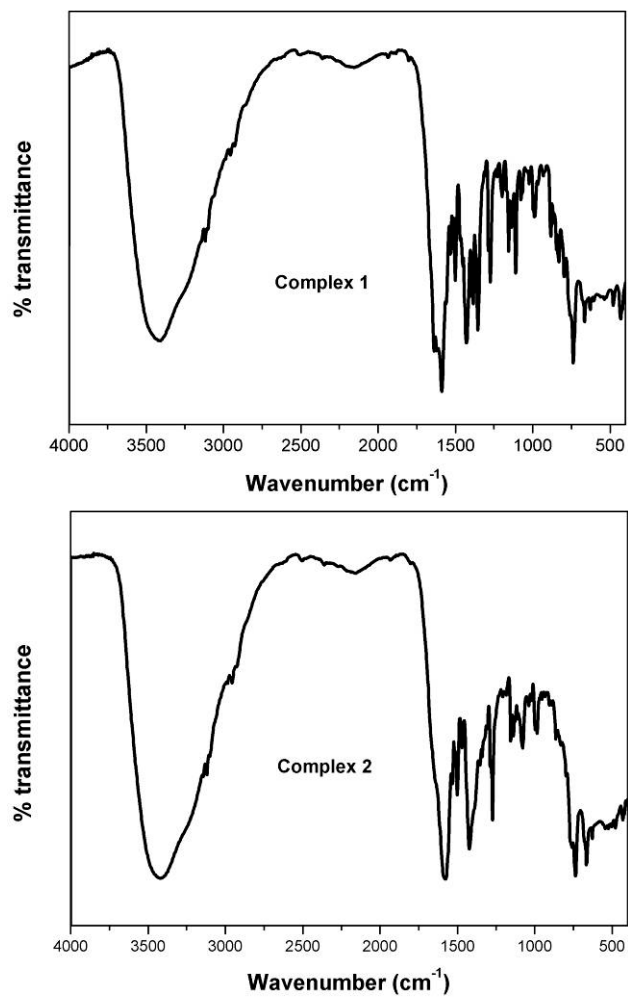
Compound 2			
Ag1—N4 <sup>i</sup>	2.134(7)	Ag1—O2	2.363(6)
Ag1—N2	2.158(7)		
N4 <sup>i</sup> —Ag1—N2	153.8(2)	N2—Ag1—O2	86.7(2)
N4 <sup>i</sup> —Ag1—O2	119.1(2)		
Symmetry code: (i) $x-1/2, y-1/2, z-1$ . (ii) $1-x, y, 1-z$			

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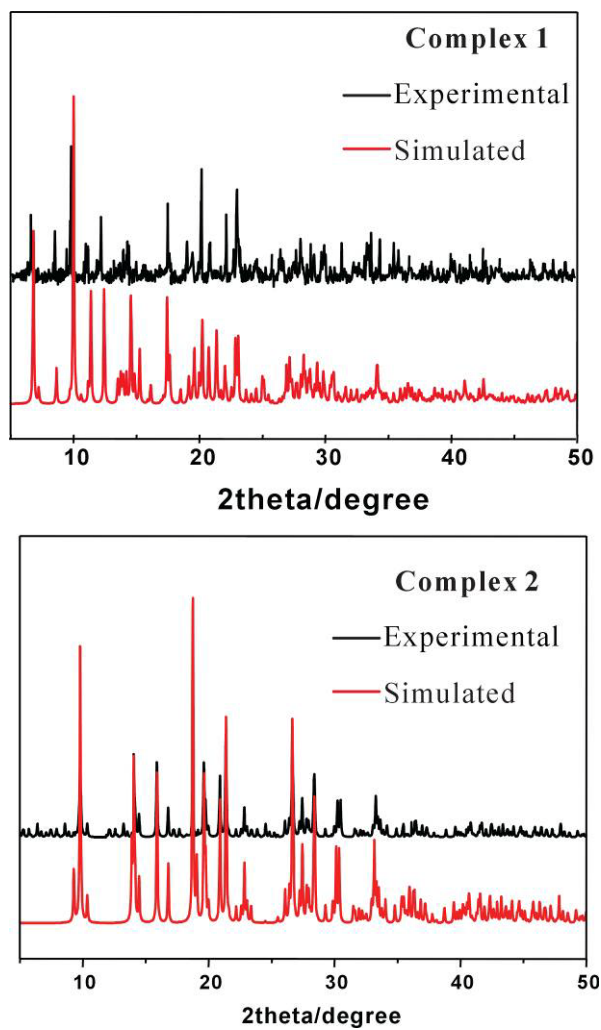
**(5) Table S2: Crystal data for 1 and 2**

Compounds	<b>1</b>	<b>2</b>
Formula	C <sub>30</sub> H <sub>33</sub> Ag <sub>2</sub> N <sub>8</sub> O <sub>7</sub>	C <sub>36</sub> H <sub>41</sub> Ag <sub>2</sub> N <sub>8</sub> O <sub>6</sub>
<i>M<sub>r</sub></i>	833.38	897.51
Crystal system	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>C2</i>
<i>a</i> (Å)	25.317(12)	18.193(8)
<i>b</i> (Å)	9.877(5)	11.273(5)
<i>c</i> (Å)	26.864(12)	8.606(4)
<i>β</i> (deg)	104.382(16)	91.271(8)
<i>Z</i>	8	2
<i>V</i> (Å <sup>3</sup> )	6507(5)	1764.6(13)
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.701	1.689
<i>μ</i> (mm <sup>-1</sup> )	1.263	1.169
<i>F</i> (000)	3352	910
no. of unique reflns	5707	3135
no. of obsd reflns [ <i>I</i> > 2σ( <i>I</i> )]	5032	2900
Parameters	436	242
GOF	1.102	1.155
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>a,b</sup>	<i>R</i> <sub>1</sub> = 0.0671 <i>wR</i> <sub>2</sub> = 0.1640	<i>R</i> <sub>1</sub> = 0.0543 <i>wR</i> <sub>2</sub> = 0.1233
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0755 <i>wR</i> <sub>2</sub> = 0.1698	<i>R</i> <sub>1</sub> = 0.0595 <i>wR</i> <sub>2</sub> = 0.1262
Largest difference peak and hole (e Å <sup>-3</sup> )	2.071 and -0.969	1.046 and - 1.874
<sup>a</sup> <i>R</i> <sub>1</sub> = ∑   <i>F</i> <sub>o</sub>   -   <i>F</i> <sub>c</sub>   /∑  <i>F</i> <sub>o</sub>  . <sup>b</sup> <i>wR</i> <sub>2</sub> = [∑ <i>w</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> - <i>F</i> <sub>c</sub> <sup>2</sup> ) <sup>2</sup> /∑ <i>w</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>2</sup> ] <sup>0.5</sup> .		

(6) Fig. S1: IR spectra of 1 and 2



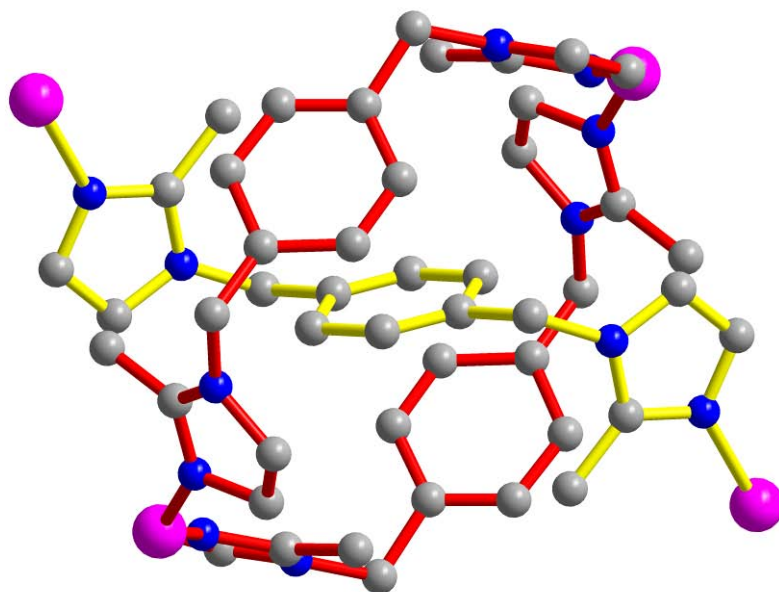
(7) Fig. S2: XRD patterns of 1 and 2



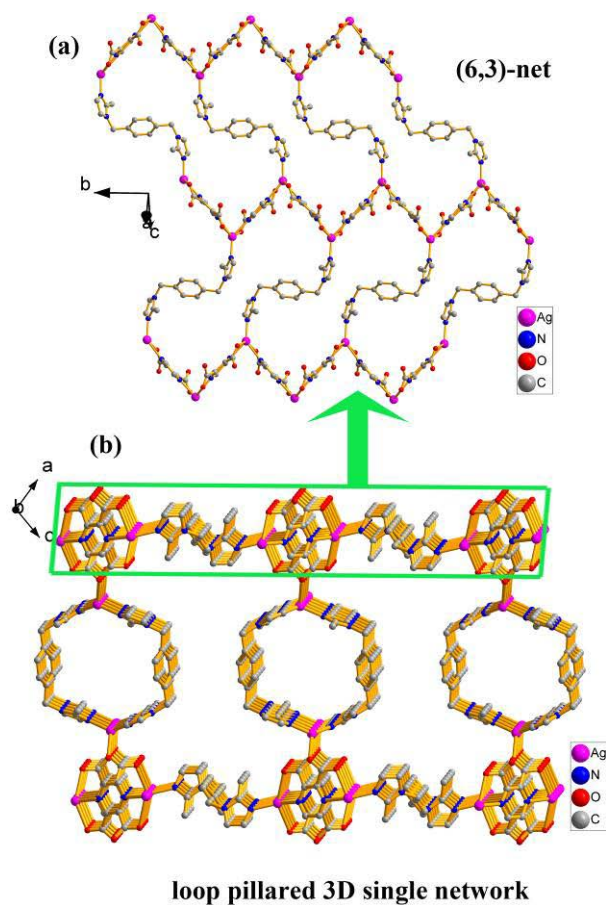


(8) Fig. S3: View of the  $[\text{Ag}_2(\text{bmimb})]$  rod passing through the  $[\text{Ag}_2(\text{bmimb})_2]$

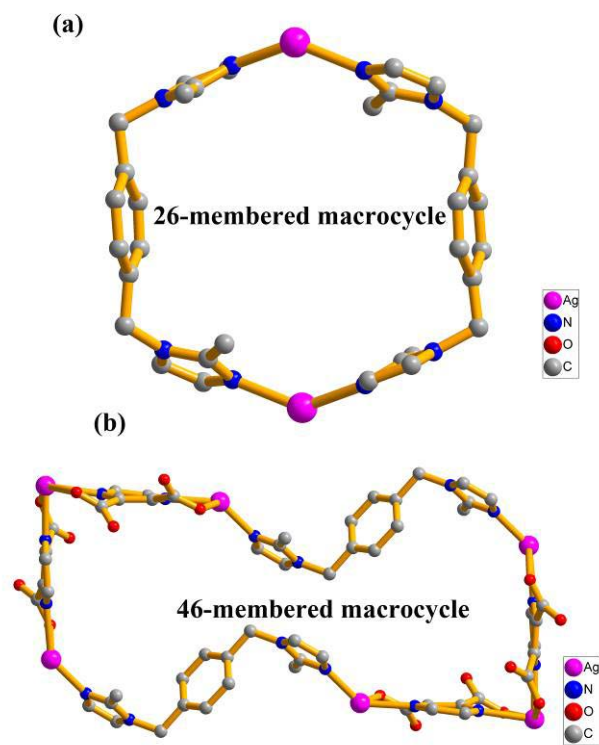
loop.



(9) Fig. S4: View of the 3D single network built from 2D (6,3)-nets and [Ag<sub>2</sub>(bmimb)<sub>2</sub>] loops.

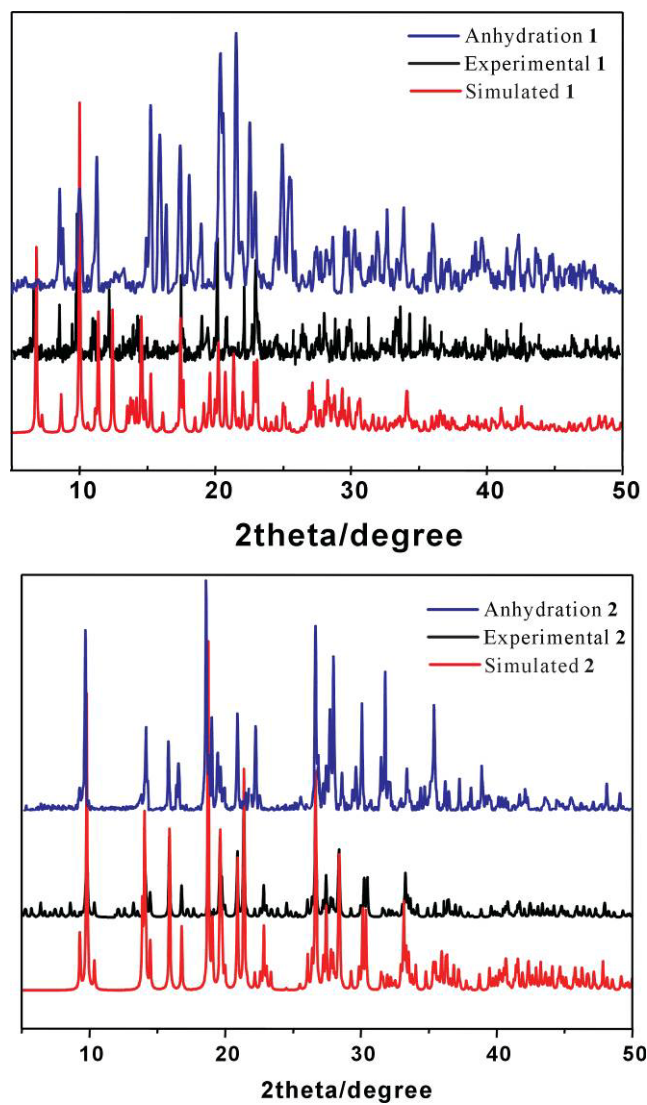


(10) Fig. S5: View of the 26- and 46-membered macrocycles.

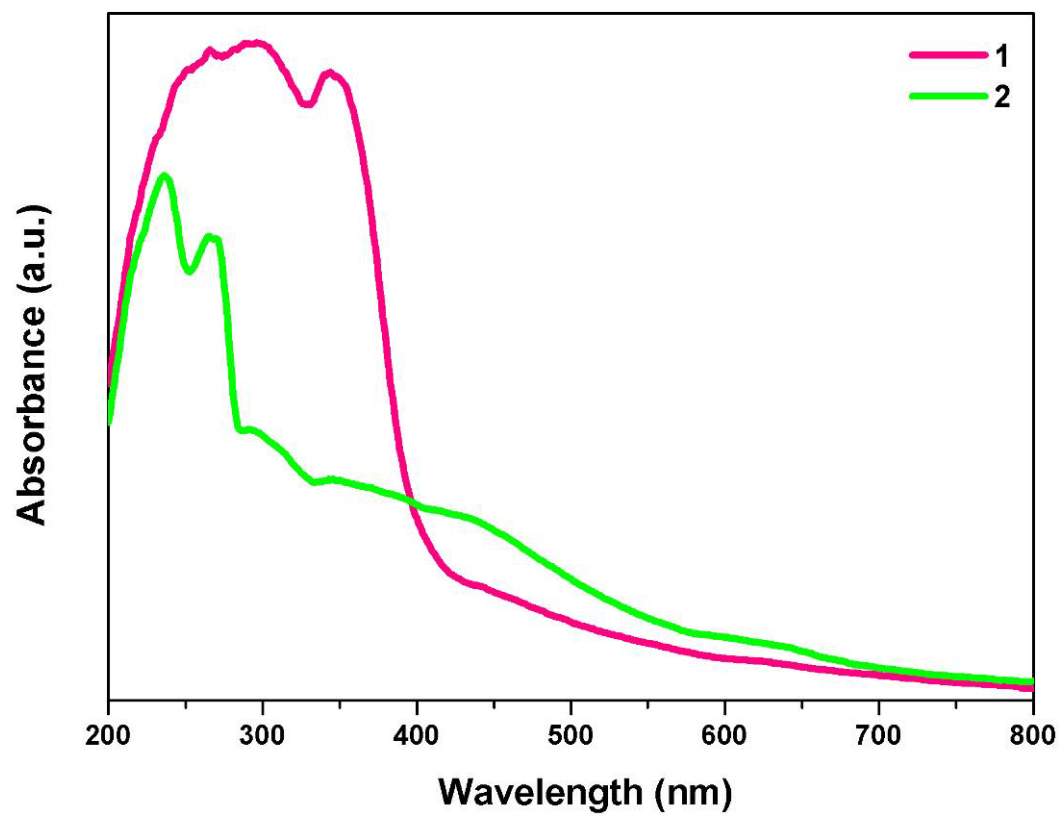


The UV-Vis spectra of complexes 1–4 in solid state.

(11) Fig. S6: Comparison of PXRD of 1 and 2 with dehydrated 1' and 2'.



(12) Fig. S7: The UV-Vis spectra of 1 and 2



(13) Scheme S1: The *anti* and *syn* conformations of bmimb ligand in **1**.

