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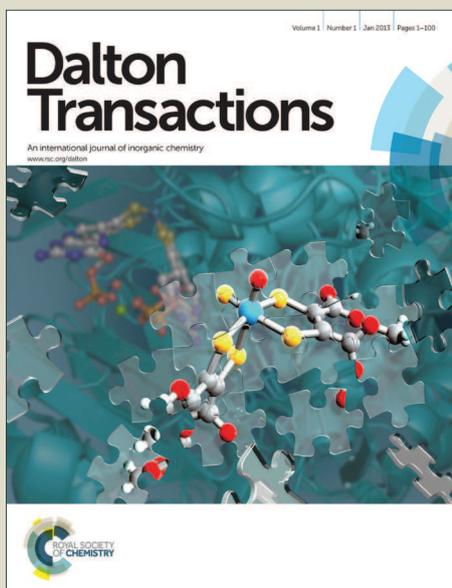
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# Heteroleptic Ir(III) complexes based on 2-(2,4-difluorophenyl)-pyridine and bisthienylethene: structures, luminescence and photochromic properties†

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Two bisthienylethenes 2-(2-hydroxyphenyl)-4,5-bis[2,5-dimethyl(3-thienyl)]-1H-imidazole (L1H) and 2-(2-hydroxyphenyl)-4,5-bis(2,5-dimethyl(3-thienyl))-1-phenyl-imidazole (L2H), which have chelating N,O-donor binding site attached to the photochromic core, have been synthesized using a one-pot condensation reaction, and used to prepare the heteroleptic complexes [Ir(dfppy)<sub>2</sub>(L1)]·2CH<sub>3</sub>OH (**1**) and [Ir(dfppy)<sub>2</sub>(L2)] (**2**) [dfppyH = 2-(2,4-difluorophenyl)-pyridine]. In the crystal structures of all four compounds, two thiophene groups of each bisthienylethene molecule adopt parallel conformation. Neighboring molecules in L1H and **1** are linked into supramolecular chains through hydrogen bonds. Particularly, the packing structure of **1** contains right- and left-handed 2<sub>1</sub> helical chains. In contrast, neighboring molecules in L2H and **2** interact only through Van der Waals interactions. At room temperature, L1H and L2H in CH<sub>2</sub>Cl<sub>2</sub> show fluorescence emission at 442 nm and 469 nm, respectively. Compounds **1** and **2** in CH<sub>2</sub>Cl<sub>2</sub> reveal broad emission bands characteristic of the Ir(III)/dfppy<sup>-</sup> chromophores at 508 nm and 494 nm, respectively, with a mixing of <sup>3</sup>MLCT and <sup>3</sup>LC characters. At room temperature, the photochromism ability of L2H in CH<sub>2</sub>Cl<sub>2</sub> is clearly weaker than that of L1H. Moreover, no photochromism has been observed in **1** and **2**. It is demonstrated that both the substituent group and {Ir(dfppy)<sub>2</sub>}<sup>+</sup> coordination could significantly influence the crystal structures, luminescence and photochromic properties of L1H, L2H, **1** and **2**.

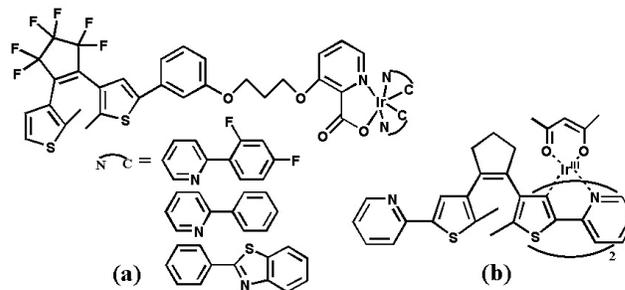
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## Introduction

Considerable attention has been focused on photochromic metal bisthienylethene (BTE) compounds mainly for the following three reasons.<sup>1</sup> (1) The incorporation of a metal ion could modulate the photochromic behavior that originates from the bisthienylethene ligand, giving new types of behaviour.<sup>2</sup> (2) Metal BTE compounds could add metal-based functional behavior to that of the photochromic unit: for example metal centers could provide additional redox, luminescence, optical or magnetic properties to the complexes.<sup>3</sup> (3) As a consequence, the photochromic switching of the bisthienylethene unit could be used as a way to switch the other physical and chemical properties provided by the metal units.<sup>4</sup> So far, several Ir(III)-bisthienylethene compounds have been reported. Park *et al.* synthesized three Ir(III) complexes in which a picolinate ancillary ligand covalently links to a bisthienylethene (BTE) unit (Scheme 1, a).<sup>5</sup> THF solutions of the complexes show strong phosphorescence, but after irradiation with 365 nm light the luminescence becomes weaker due to the structural transition of the BTE unit from the open to the closed form. Using a similar synthetic approach, Guerchai *et al.* obtained Ir(C<sup>^</sup>N-ppy-Me)<sub>2</sub>(N<sup>^</sup>N-bpy-CH=CH-R) (R = BTE unit), showing reversible phosphorescence switching behavior at 77 K.<sup>6</sup> In contrast to these Ir(III) compounds containing noncoordinated BTE units, Tian *et al.* reported compound (Py-BTE)<sub>2</sub>Ir(acac), in which Py-BTE serves as a cyclometalating ligand, using its pyridyl-thiophene moiety to chelate the Ir(III) ion (Scheme 1, b).<sup>7</sup> Upon irradiation

with 313 nm light, its THF solution changed color from pale yellow to green. This process was accompanied by efficient quenching of the phosphorescence emission at 570 nm. These reported Ir(III)-bisthienylethene compounds not only show BTE-based photochromic behavior, but also exhibit the switching of Ir-based luminescence associated with the photochromic structure change.

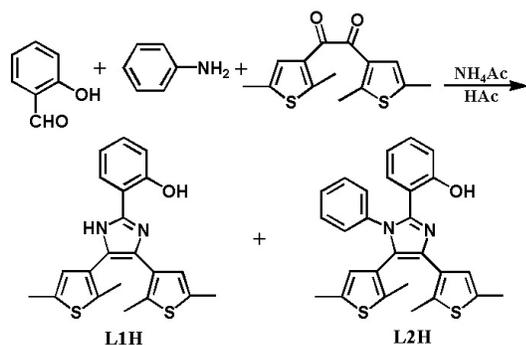
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Scheme 1

It should be noted that no Ir(III)-bisthienylethene compound, in which the ethene bridge unit is involved in coordination, has been reported so far, although this type of compounds could be very important to help understand the influence of Ir(III) coordination on the BTE photochromism. In order to prepare such compounds, we have synthesized bisthienylethenes L1H and L2H (Scheme 2) through a one-pot condensation reaction. In these ligands, the phenol-imidazole moiety provides a site for chelation to an Ir(III) ion. Compared with L1H, L2H contains a

phenyl group attached to the imidazole nitrogen atom. Their reactions with  $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$  dimer afforded the heteroleptic complexes  $[\text{Ir}(\text{dfppy})_2(\text{L1})]\cdot 2\text{CH}_3\text{OH}$  (**1**) and  $[\text{Ir}(\text{dfppy})_2(\text{L2})]$  (**2**) [dfppyH = 2-(2,4-difluorophenyl)-pyridine]. Herein, we report the syntheses, crystal structures, luminescence and photochromic properties of L1H, L2H, **1** and **2**, and we discuss the influences of the coordinated  $\{\text{Ir}(\text{dfppy})_2\}^+$  units on the structures and related physical and chemical properties of the BTE chromophores.



Scheme 2

## Experimental

### Materials and methods

1,2-Bis[2,5-dimethyl(3-thienyl)]ethane-1,2-dione was prepared according to the literature method.<sup>8</sup>  $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$  dimer was prepared following the reported procedure.<sup>9</sup> All other reagents were commercially available and used without further purification. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. The <sup>1</sup>H NMR spectra were recorded at room temperature with a 500 MHz BRUKER AM-500 spectrometer. The powder XRD patterns were recorded on a BRUKER D8 ADVANCE X-ray diffractometer. UV-vis absorption spectra were measured on a Cary 100 spectrophotometer. The luminescence spectra at room temperature were measured on a Perkin Elmer LS55 fluorescence spectrometer, and the luminescence spectra at 77 K on a Jobin-Yvon Fluoromax 4 fluorimeter. The luminescence lifetimes were measured at room temperature, using 508 nm for **1** and 494 nm for **2** to record the decays, on an Edinburgh Min-Tau instrument, with an excitation wavelength of 405 nm from picoquant pulsed diode laser with a pulse width of 100 ps. Photoirradiation was carried out using a 500 W Xe lamp and a monochromator.

### Syntheses of 2-(2-hydroxyphenyl)-4,5-bis[2,5-dimethyl(3-thienyl)]-1H-imidazole (L1H) and 2-(2-hydroxyphenyl)-4,5-bis[2,5-dimethyl(3-thienyl)]-1-phenyl-imidazole (L2H)

Compounds L1H and L2H have been synthesized through the following one-pot condensation reaction. A mixture of 2-hydroxy-benzaldehyde (2 mmol, 0.2440 g), aniline (2 mmol, 0.18 mL) and HOAc (30 mL) was stirred for one hour at room temperature, and then ammonium acetate (14 mmol, 1.081 g) and 1,2-bis[2,5-dimethyl(3-thienyl)]ethane-1,2-dione (2 mmol, 0.5570 g) were successively added. The mixture was refluxed for 16 hours. After evaporation under vacuum, the residue was mixed with H<sub>2</sub>O (20 mL). This mixture was extracted with

CHCl<sub>3</sub> (30 mL × 3). The CHCl<sub>3</sub> solution was dried with MgSO<sub>4</sub>, filtered, and then evaporated, obtaining brown solid. Pure L1H and L2H were obtained after purification with preparative high-performance liquid chromatography using a silica gel column and petroleum ether-ethyl acetate as eluent.

For L1H: 0.2440 g, a yield of 32% based on 2-hydroxy-benzaldehyde. Anal. found (calcd) for C<sub>21</sub>H<sub>20</sub>ON<sub>2</sub>S<sub>2</sub>: C, 66.15 (66.29); H, 5.41 (5.30), N, 7.21 (7.36). IR (KBr, cm<sup>-1</sup>): 3193(s), 2960(w), 2914(m), 2854(w), 1608(m), 1591(m), 1550(w), 1531(w), 1489(s), 1438(s), 1412(m), 1396(m), 1292(w), 1274(s), 1263(s), 1225(w), 1207(w), 1180(w), 1130(s), 1038(w), 939(w), 885(w), 827(s), 793(w), 756(s), 702(w), 669(w), 538(w), 496(m). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN), δ (ppm): 2.14, 2.20, 2.35 and 2.43 (4s, 12H, 4CH<sub>3</sub>), 6.58 and 6.72 (2s, 2H from two thiophene rings), 6.93–7.71 (m, 4H from phenyl group).

For L2H: 0.3130 g, a yield of 34% based on 2-hydroxy-benzaldehyde. Anal. found (calcd) for C<sub>27</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 71.13 (71.02); H, 5.42 (5.30), N, 6.20 (6.13). IR (KBr, cm<sup>-1</sup>): 3057(w), 2914(w), 2852(w), 1599(w), 1582(m), 1541(w), 1495(m), 1479(s), 1445(w), 1404(w), 1383(s), 1300(w), 1279(m), 1256(s), 1142(m), 1126(w), 1070(w), 1030(w), 837(s), 818(m), 798(w), 777(w), 756(s), 746(s), 727(s), 694(s), 675(w), 604(w), 496(w). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 1.94, 2.25, 2.33 and 2.44 (4s, 12H, 4CH<sub>3</sub>), 6.13 and 6.40 (2s, 2H from two thiophene rings), 6.44–7.15 and 7.42 (9 H from two phenyl groups).

### Synthesis of $[\text{Ir}(\text{dfppy})_2(\text{L1})]\cdot 2\text{CH}_3\text{OH}$ (**1**)

The mixture of L1H (0.33 mmol, 0.1256 g),  $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$  (0.15 mmol, 0.1827 g) and Na<sub>2</sub>CO<sub>3</sub> (5 mmol, 0.5300 g) in 2-ethoxyethanol (30 mL) was stirred under argon at 136 °C for one day. After evaporation under vacuum, the resultant brown solid was mixed with water (10 mL). This mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL × 3). The CH<sub>2</sub>Cl<sub>2</sub> solution was dried with MgSO<sub>4</sub>, filtered, and then evaporated. The residue was purified through flash column chromatography using CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (v/v = 1/100) solution, obtaining a yellow solid. This solid was crystallized in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH solution with a yield of 190 mg (62% based on  $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$ ). Anal. found (calcd) for C<sub>45</sub>H<sub>39</sub>O<sub>3</sub>N<sub>4</sub>F<sub>4</sub>S<sub>2</sub>Ir: C, 53.30 (53.19); H, 4.02 (3.87), N, 5.63 (5.51). IR (KBr, cm<sup>-1</sup>): 3443(s), 2920(w), 2856(w), 1603(s), 1572(w), 1557(w), 1478(m), 1450(w), 1435(w), 1402(w), 1292(w), 1267(w), 1246(w), 1160(w), 1100(w), 1042(w), 987(w), 847(w), 828(w), 756(w), 569(w), 528(w). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>), δ (ppm): 1.92–2.24 (12H from 4CH<sub>3</sub>), 4.88–9.18 (18H from two thiophene rings, one phenyl group and two dfppy<sup>-</sup> units).

### Synthesis of $[\text{Ir}(\text{dfppy})_2(\text{L2})]$ (**2**)

Compound **2** was synthesized by the same method as **1**, using L2H instead of L1H. After the purification through flash column chromatography using CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (v/v = 0.5/100) solution, and then the crystallization in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH solution, a yellow solid was obtained with a yield of 188 mg (61 % based on  $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$ ). Anal. found (calcd) for C<sub>49</sub>H<sub>35</sub>ON<sub>4</sub>F<sub>4</sub>S<sub>2</sub>Ir: C, 57.33 (57.24); H, 3.56 (3.43), N, 5.34 (5.45). IR (KBr, cm<sup>-1</sup>): 2916(w), 2855(w), 1599(s), 1570(m), 1554(m), 1472(s), 1431(w), 1400(m), 1323(m), 1288(m), 1267(w), 1246(w), 1157(w), 1130(w), 1113(w), 1095(w), 1072(w), 1041(w), 986(m), 845(w), 831(m), 785(w), 754(s), 727(w), 698(w), 586(w), 567(w), 526(w).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.95 - 2.45 (m, 12 H, 4 CH<sub>3</sub>), 4.78– 7.12 and 7.52 – 9.24 (m, 23 H from two thiophene rings, two phenyl groups and two dfppy<sup>-</sup> units).

### 5 X-ray Crystal Structure Studies

The single crystals of L1H, L2H, **1** and **2** were obtained through the evaporation of their petroleum ether-ethyl acetate solutions for L1H and L2H, and their methanol solutions for **1** and **2**. Single crystals of dimensions 0.20 × 0.08 × 0.06 mm<sup>3</sup> for L1H, 0.22 × 0.20 × 0.18 mm<sup>3</sup> for L2H, 0.10 × 0.08 × 0.06 mm<sup>3</sup> for **1** and 0.25 × 0.20 × 0.20 mm<sup>3</sup> for **2** were used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 173 K for L1H and L2H, and at room temperature (293 K) for **1** and **2**. A hemisphere of data were collected in the  $\theta$  range of 2.41-18.68° for L1H, 2.29-23.89° for L2H, 2.27-24.36° for **1**, and 2.25-21.80° for **2** using a narrow-frame method with scan widths of 0.30° in  $\omega$  and an exposure time of 10 s / frame. Numbers of observed and unique [ $I > 2\sigma(I)$ ] reflections are 10349 and 3344 ( $R_{\text{int}} = 0.1014$ ) for L1H, 19604 and 9357 ( $R_{\text{int}} = 0.0358$ ) for L2H,

24428 and 7465 ( $R_{\text{int}} = 0.0633$ ) for **1**, and 29341 and 9969 ( $R_{\text{int}} = 0.0466$ ) for **2**, respectively. The data were integrated using the Siemens *SAINTE* program,<sup>10</sup> with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Multi-scan absorption corrections were applied. The structures were solved by direct methods and refined on  $F^2$  by full matrix least squares using SHELXTL.<sup>11</sup> All non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were put in calculated positions using a riding model, and were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. The crystallographic data for compounds L1H, L2H, **1** and **2** are listed in Table 1, and selected bond lengths are given in Tables 2-5. CCDC 1023276–1023279 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 1** Crystallographic data and refinement for L1H, L2H, **1** and **2**

	L1H	L2H	<b>1</b>	<b>2</b>
Formula	C <sub>21</sub> H <sub>20</sub> ON <sub>2</sub> S <sub>2</sub>	C <sub>27</sub> H <sub>24</sub> N <sub>2</sub> OS <sub>2</sub>	C <sub>45</sub> H <sub>39</sub> O <sub>3</sub> Na <sub>4</sub> F <sub>4</sub> S <sub>2</sub> Ir	C <sub>49</sub> H <sub>35</sub> ON <sub>4</sub> F <sub>4</sub> S <sub>2</sub> Ir
<i>M</i>	380.51	456.60	1016.12	1028.13
Crystal system	Monoclinic	triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>T</i> /K	173	173	293	293
<i>a</i> /Å	10.083(4)	11.5307(13)	16.885(6)	13.1823(5)
<i>b</i> /Å	15.939(7)	12.7677(14)	11.685(4)	24.5037(10)
<i>c</i> /Å	11.976(5)	18.229(2)	21.931(8)	14.8078(6)
$\alpha$ /°		103.512(2)		
$\beta$ /°	98.764(11)	92.109(2)	95.950(6)	114.8960(10)
$\gamma$ /°		111.527(2)		
<i>V</i> /Å <sup>3</sup>	1902.2(14)	2405.0(5)	4304(3)	4338.7(3)
<i>Z</i>	4	4	4	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.329	1.261	1.568	1.574
<i>F</i> (000)	800	960	2024	2040
Goof on <i>F</i> <sup>2</sup>	1.016	1.008	1.089	1.001
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0627, 0.1044	0.0588, 0.1687	0.0757, 0.2170	0.0466, 0.1289
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (All data) <sup>a</sup>	0.1570, 0.1229	0.1162, 0.2153	0.0923, 0.2423	0.0830, 0.1472
( $\Delta\rho$ ) <sub>max</sub> , ( $\Delta\rho$ ) <sub>min</sub> (e Å <sup>-3</sup> )	0.271, -0.316	0.289, -0.332	2.417, -3.240	1.877, -1.156

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^{3/2}}$$

**Table 2** Selected bond lengths (Å) for L1H

O1-C17	1.354(5)	C14-N2	1.397(4)
C13-N1	1.378(5)	C15-N2	1.307(5)
C15-N1	1.357(4)		

**Table 3** Selected bond lengths (Å) for L2H

O1-C1	1.368(6)	O2-C28	1.319(5)
N1-C7	1.309(5)	N3-C34	1.341(4)
N1-C15	1.381(5)	N3-C41	1.386(4)
N2-C7	1.388(4)	N4-C34	1.366(4)
N2-C14	1.386(5)	N4-C42	1.400(4)

**Table 4** Selected bond lengths (Å) for **1**

Ir1-C1	2.009(9)	N1-C36	1.433(11)
Ir1-C12	1.978(10)	N2-C37	1.345(12)
Ir1-N3	2.026(8)	O1-C39	1.334(13)
Ir1-N4	2.042(8)	N1-C37	1.321(12)
Ir1-O1	2.162(7)	N2-C35	1.387(12)
Ir1-N1	2.181(7)		

**Table 5** Selected bond lengths (Å) for **2**

Ir1-C1	1.993(6)	O1-C39	1.311(7)
Ir1-C12	1.991(6)	N1-C37	1.338(8)
Ir1-N3	2.021(5)	N1-C36	1.388(8)
Ir1-N4	2.039(5)	N2-C37	1.364(8)
Ir1-O1	2.128(4)	N2-C35	1.389(8)
Ir1-N1	2.191(5)		

### 55 Results and discussion

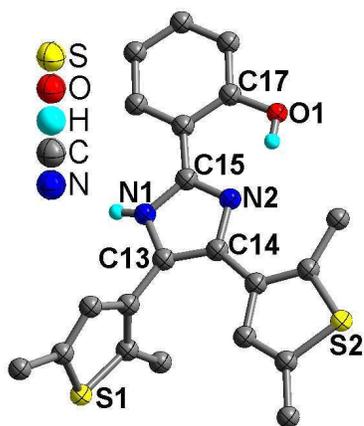
#### Syntheses

Compounds L1H and L2H were both synthesized using the one-pot condensation reaction of 2-hydroxy-benzaldehyde, 1,2-bis[2,5-dimethyl(3-thienyl)]ethane-1,2-dione, aniline, and ammonium acetate (Scheme 2), with a molar ratio of 1:1:1:7 in refluxing acetic acid. It was found that the molar ratio of

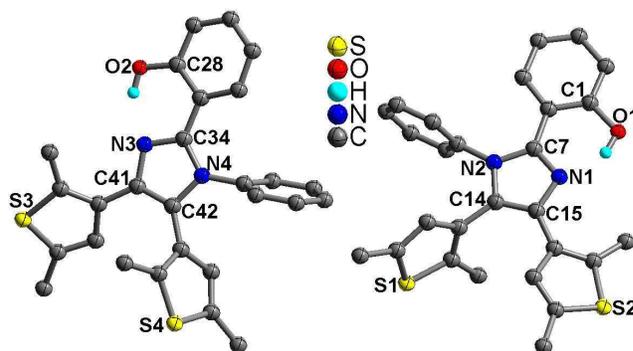
ammonium acetate/aniline had a great influence on the yields of L1H and L2H. When this molar ratio was increased from 1:1 to 7:1, the yield increased from 13% to 32% for L1H, and from 19% to 34% for L2H. A higher ratio did not further improve the yield of either compound. Compounds **1** and **2** were prepared by refluxing the mixture of  $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$  dimer, the appropriate bithienylethene ligand (L1H or L2H), and  $\text{Na}_2\text{CO}_3$  as a base in refluxing 2-ethoxyethanol. Both the presence of  $\text{Na}_2\text{CO}_3$ , and a high reaction temperature (136 °C), were found to be required for the formation of the complex in each case.

### Crystal structures of L1H and L2H

Compounds L1H and L2H crystallize in the monoclinic space group  $P2_1/c$  and the triclinic space group  $P\bar{1}$ , respectively. As shown in Fig. 1 and 2, the asymmetric unit of L1H contains one molecule, whereas for L2H there are two independent molecules in the asymmetric unit. The two thiophene groups of each molecule in the two compounds adopt a non-photoactive parallel conformation. In L1H, the dihedral angle between the imidazole and phenolate rings is  $3.2(1)^\circ$ , which is clearly smaller than these in L2H [ $8.0(1)^\circ$  and  $10.3(1)^\circ$  for the two independent molecules in Fig. 2]. This could be due to the steric hindrance of the phenyl group attached to imidazole nitrogen atom in L2H. Both L1H and L2H show intra-molecular  $\text{OH}\cdots\text{N}$  hydrogen bonds formed between phenol and imidazole moieties [ $\text{O1}\cdots\text{N2} = 2.541(1)$  Å in L1H, and  $\text{O1}\cdots\text{N1} = 2.542(1)$  Å and  $\text{O2}\cdots\text{N3} = 2.563(1)$  Å in L2H]. Neighboring molecules in L1H are connected through hydrogen bond interactions [ $\text{N1}\cdots\text{O1}^a = 2.812(1)$  Å, symmetry code  $a = x, -y + 1/2, z - 1/2$ ], forming a supramolecular chain structure (Fig. S7). In contrast, neighboring molecules in L2H interact only through Van der Waals interactions (Fig. S8).



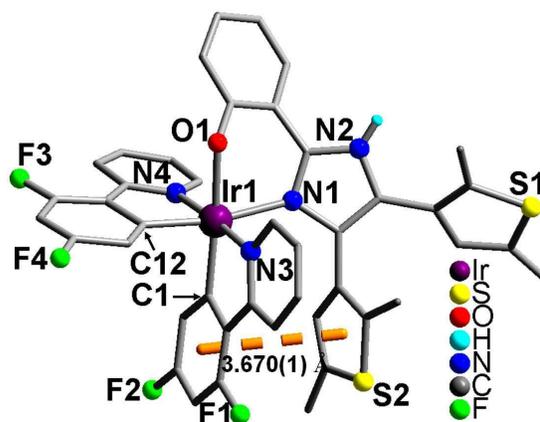
**Fig. 1** Molecular structure of L1H. All H atoms attached to carbon atoms are omitted for clarity.



**Fig. 2** Molecular structure of L2H. All H atoms attached to carbon atoms are omitted for clarity.

### Crystal structures of **1** and **2**

The crystal structures of **1** and **2** are shown in Fig. 3 and 4, respectively. The Ir(III) ion in each compound shows a distorted octahedral coordination geometry. Four of the six coordination sites are occupied by two pyridine nitrogen atoms (N3, N4) and two carbon atoms (C1, C12) from two nonequivalent cyclometallated  $\text{dfppy}^-$  ligands. The remaining two coordination sites are occupied by phenolate oxygen O1 and imidazole nitrogen N1 from the anionic ligand  $[\text{L1}]^-$  or  $[\text{L2}]^-$  respectively. In these compounds, the  $\text{Ir}-\text{C}(\text{N})_{\text{dfppy}}$  distances [ $1.978(10)$ – $2.042(8)$  Å in **1**, and  $1.991(6)$ – $2.039(5)$  Å in **2**] are comparable to those in the precursor compound  $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$  [ $1.989(6)$ – $2.053(3)$  Å].<sup>12</sup> Compared with these  $\text{Ir}-\text{C}(\text{N})_{\text{dfppy}}$  bonds, the  $\text{Ir}-\text{N}(\text{O})_{[\text{L1}]^-/[\text{L2}]^-}$  bonds are significantly longer with a distance range of  $2.128(4)$ – $2.191(5)$  Å, which could be due to the fact that O1 and N1 atoms in  $[\text{L1}]^-/[\text{L2}]^-$  ligands are *trans* to corresponding  $\sigma$ -bound C1 and C12 atoms in the  $\text{dfppy}^-$  ligands.<sup>13</sup>



**Fig. 3** Molecular structure of **1**. Lattice  $\text{CH}_3\text{OH}$  molecules and all H atoms are omitted for clarity.

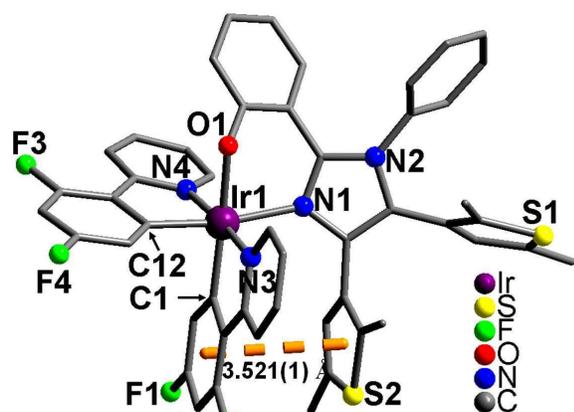


Fig. 4 Molecular structure of **2**. All H atoms are omitted for clarity.

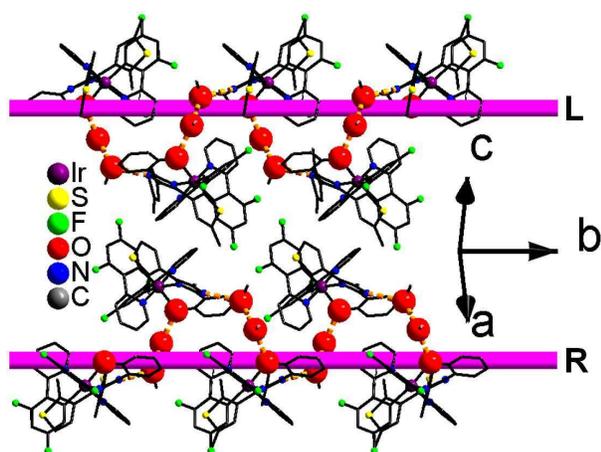


Fig. 5 Packing structure of **1** containing right- and left-handed helical chains (denoted as R and L, respectively). Red balls are O atoms from CH<sub>3</sub>OH molecules or phenolate groups.

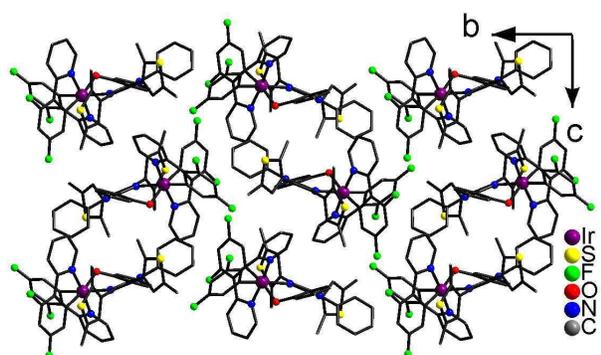


Fig. 6 Packing structure of **2**.

In the molecular structures of **1** and **2**, two dfppy<sup>-</sup> ligands are arranged with the pyridine nitrogen atoms N3 and N4 lying in a *trans* position, which is consistent with the arrangement in [Ir(dfppy)<sub>2</sub>Cl]<sub>2</sub>.<sup>12</sup> Both [L1]<sup>-</sup> and [L2]<sup>-</sup> ligands adopt parallel conformation as observed in the free ligands. But the dihedral angles between the imidazole and phenolate rings in **1** and **2** [38.9(1)° and 39.4(1)°, respectively] are significantly larger than these in free ligands [3.2(1)° in L1H, 8.0(1)° and 10.3(1)° in L2H],

which is assigned to the coordination of phenol-imidazole moiety to Ir(III) ion, with this twist necessary to attain a six-membered chelate ring with sensible bond distances. Both compounds show intra-molecular aromatic stacking interactions between the thiophene ring and the phenyl ring from a dfppy<sup>-</sup> ligand (Fig. 3 and 4), showing centroid-centroid distance of 3.670(1) Å in **1** and 3.521(1) Å in **2**.<sup>14</sup>

In the packing structure of **1** (Fig. 5, S9), neighboring molecules are linked through hydrogen bonds, forming right- or left-handed <sub>2</sub> helical chains along the *b* axis. These hydrogen bonds include O1...O2 = 2.633(1) Å, O3...O2<sup>a</sup> = 2.680(1) Å and N2...O3<sup>b</sup> = 2.815(1) Å (symmetry codes a = -x + 3/2, y - 1/2, -z + 1/2; b = x, y + 1, z), which are formed among phenolate oxygen O1, oxygen atoms O2 and O3 from methanol molecules, and imidazole nitrogen N2. In contrast, neighboring molecules in **2** are stacked only through Van der Waals interactions (Fig. 6).

### Electronic absorption spectra

The UV-vis spectra of L1H, L2H, **1** and **2** were measured in CH<sub>2</sub>Cl<sub>2</sub> at room temperature (Fig. 7, Table S1). L1H shows three absorption maxima at 233, 286 and 325 nm. Compared to L1H, the absorption bands of L2H (228, 280 and 323 nm) exhibit a slight blue shift. Compounds **1** and **2** reveal weak absorptions in the range of 370-475 nm, as well as strong absorptions in the range of 220-370 nm, which are significantly different from those of L1H and L2H. As shown in Fig. 7 and Table S1, the absorption bands in **1** (232, 250 and 287 nm), and in **2** (232, 250, 292 and 328 nm) can be assigned to spin-allowed ligand-centered (<sup>1</sup>LC) transitions (dfppy<sup>-</sup>, [L1]<sup>-</sup> and [L2]<sup>-</sup> ligands). The poorly-defined lower-energy region of absorption around 375 nm in both compounds is likely to be a combination of spin-allowed metal-to-ligand charge transfer (<sup>1</sup>MLCT) and ligand-centered (<sup>1</sup>LC) transitions, because of the high extinction coefficient ( $\epsilon = 1.32 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for **1** and  $\epsilon = 1.28 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for **2**).<sup>6,13,15</sup> The weaker bands around 450 nm are mainly attributed to spin-forbidden <sup>3</sup>MLCT absorptions.<sup>16</sup>

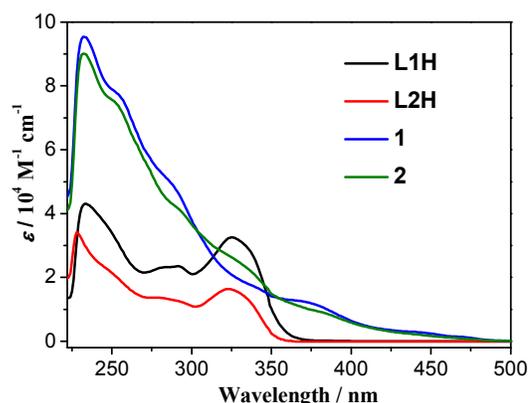


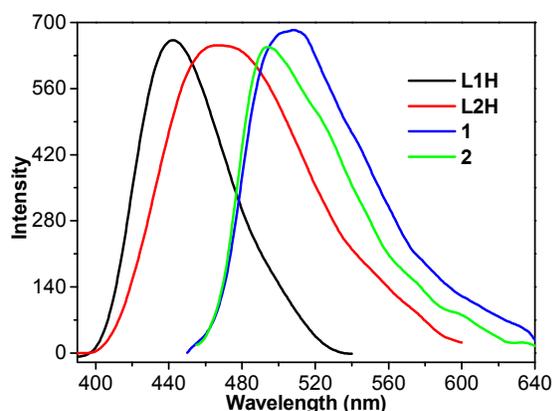
Fig. 7 UV-vis spectra of L1H, L2H, **1** and **2** in CH<sub>2</sub>Cl<sub>2</sub>.

### Luminescence properties

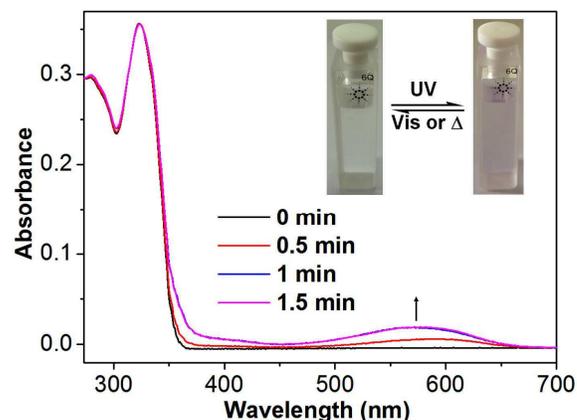
The luminescence spectra of L1H, L2H, **1** and **2** in CH<sub>2</sub>Cl<sub>2</sub> solution were measured at room temperature, using excitation light at 330 nm for L1H, 320 nm for L2H, and 405 nm for **1** and **2** (Fig. 8). The emission of L1H (442 nm) occurs at a shorter

wavelength than for L2H (469 nm), which could be due to a greater degree of conjugation in L2H where a phenyl group is attached to the imidazole nitrogen atom. Compared to L1H and L2H, compounds **1** and **2** reveal significantly red-shifted emission, with broad bands at 508 and 494 nm, respectively. These broad and relatively featureless emissions are characteristic of predominant  $^3\text{MLCT}$  character,<sup>17</sup> which is confirmed by their luminescence spectra measured at 77 K (Fig. S10). At liquid nitrogen temperature, each compound shows two emission bands, 471 nm and 506 nm for **1**, and 469 nm and 504 nm for **2**, exhibiting a clear blue shift with respect to the emissions at room temperature. This rigidochromism is also characteristic of a CT character for the luminescence. The emission lifetimes of **1** and **2** were measured in  $\text{CH}_2\text{Cl}_2$  solution at room temperature. In each case, the decay could be fitted to two exponential components, with  $\tau_1 = 172$  ns (6.1% contribution) and  $\tau_2 = 53$  ns (93.9% contribution) for **1**, and  $\tau_1 = 163$  ns (7.6% contribution) and  $\tau_2 = 48$  ns for **2** (92.4% contribution) (Fig. S11, S12). Such dual-exponential decay for relatively simple mononuclear Ir(III) complexes has been observed before and attributed to aggregation in solution.<sup>18a</sup>

The luminescence spectra of **1** and **2** were further measured at room temperature in solvents with different polarity, including toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  (Fig. S13, S14). Upon increasing solvent polarity from toluene to  $\text{CH}_2\text{Cl}_2$  to  $\text{CH}_3\text{CN}$ , the emission band maximum of **1** shifted from 495, 508, to 519 nm. In contrast, the emission band maximum of **2** exhibited a significantly smaller shift, from 493 nm in toluene, to 494 nm in  $\text{CH}_2\text{Cl}_2$ , to 502 nm in  $\text{CH}_3\text{CN}$ . The greater solvent-dependence of **1** may arise because the NH group on the imidazole ring can interact more strongly with solvent molecules by hydrogen bond interactions. This is similar to the behavior shown by  $[\text{Ru}(\text{bipy})(\text{CN})_4]^{2-}$  in which  $\text{CN}\cdots$ solvent hydrogen bond interactions affect the luminescence.<sup>18b</sup> The luminescence spectra of **1** and **2** in solvents with different polarity indicate that the emissive excited states in **1** and **2** have  $^3\text{LC}$  character as well as predominant  $^3\text{MLCT}$ .<sup>17</sup> In addition, the luminescence intensities of **1** and **2** in  $\text{CH}_2\text{Cl}_2$  are relatively higher than those in toluene and in  $\text{CH}_3\text{CN}$  under the same experiment condition.



**Fig. 8** Luminescence spectra of L1H, L2H, **1** and **2** in  $\text{CH}_2\text{Cl}_2$  ( $c = 3.0 \times 10^{-5}$  M).



**Fig. 9** Absorption-spectra changes of L2H in  $\text{CH}_2\text{Cl}_2$  solution ( $c = 2.5 \times 10^{-5}$  M) upon UV irradiation ( $\lambda = 323$  nm) for 0 – 1.5 minutes.

### Photochromism

Previously, we reported the photochromic behavior of L1H.<sup>3b</sup> Upon irradiation with 321 nm light, its  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{CN}$  solution changed color from colorless to pink. The UV irradiation resulted in the complete structural transition from open to closed form, which was confirmed by its  $^1\text{H}$  NMR spectra before and after UV irradiation (Fig. S1, S15 and S16). For L2H, its  $\text{CH}_2\text{Cl}_2$  solution exhibits a strong absorption band at 323 nm (Fig. 9). Upon irradiation with 323 nm light, an additional broad band around 575 nm was formed. In this process, the solution gradually changed color from colorless to light purple (Fig. 9, inset). Subsequently, upon irradiation of such purple solution with 575 nm light or keeping the solution in the dark at room temperature, the light purple color gradually faded, recovering the original absorption spectrum (Fig. S17). We further measured the  $^1\text{H}$  NMR spectra of L2H before and after irradiation with 323 nm light (Fig. S2, S18, S19). Before UV irradiation, signals at 6.40 and 2.44 ppm can be observed, which are respectively from a hydrogen atom on thiophene ring and a methyl group attached to thiophene ring. These two peaks disappeared after UV irradiation, while two additional signals at 6.42 and 2.42 ppm were formed. These slight changes suggest that L2H has a lower conversion yield from open to closed form compared to L1H. In other words, the photochromism ability of L2H is significantly weaker than that of L1H. This indicates that the phenyl group attached to the imidazole nitrogen atom in L2H suppresses its photochromic behavior.

In contrast to L1H and L2H, neither **1** nor **2** shows photochromic behavior in solution, under the irradiations with 323 nm and 375 nm lights. A similar suppression of photochromic activity has also been observed in metal BTE complexes containing Pt(II),<sup>2a</sup> Ru(II),<sup>19</sup> and Fe(III) ions.<sup>20</sup> Considering the photochromic behavior of the Co(II) complex based on L1H in  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{CN}$  solution, *i.e.* an irradiation with 350 nm light resulting in the color change from near colorless to purple blue,<sup>3b</sup> the lack of photochromism in **1** and **2** could be due to the coordination of the imidazole bridge to  $\{\text{Ir}(\text{dfppy})_2\}^+$  unit. Given the presence of direct electronic coupling between  $[\text{L1}]^+ / [\text{L2}]^+$  and  $\{\text{Ir}(\text{dfppy})_2\}^+$  unit, the UV excitation energy is transferred to the Ir(III) center and used to generate luminescence,

thus resulting in completely absent photocyclization process of [L1]<sup>-</sup> and [L2]<sup>-</sup> molecules in **1** and **2**. In addition, the other possible reason is that the coordination of [L1]<sup>-</sup>/[L2]<sup>-</sup> molecule to {Ir(dfppy)<sub>2</sub>}<sup>+</sup> unit leads to insufficient space for the dimethylthiophene rings to rotate and form a photoactive antiparallel conformation.

## Conclusions

The bisthienylethenes L1H and L2H have been synthesized through a one-pot condensation reaction. Their reactions with [Ir(dfppy)<sub>2</sub>Cl]<sub>2</sub> dimer generated the compounds [Ir(dfppy)<sub>2</sub>(L1)]·2CH<sub>3</sub>OH (**1**) and [Ir(dfppy)<sub>2</sub>(L2)] (**2**). Each Ir(III) ion in **1** and **2**, adopts a distorted octahedral coordination geometry, and is chelated by two dfppy<sup>-</sup> ligands, and one bisthienylethene ligand. Neighboring molecules in **1** are linked into right- or left-handed helical chains through hydrogen bonds. In contrast, only Van der Waals interactions were observed in the packing structure of **2**. At room temperature, the luminescence spectra of L1H, L2H, **1** and **2** were measured in CH<sub>2</sub>Cl<sub>2</sub>. L1H and L2H show fluorescence emission at 442 nm and 469 nm, respectively. Compounds **1** and **2** reveal broad emission band at 508 nm and 494 nm, respectively, with a mixing of <sup>3</sup>MLCT and <sup>3</sup>LC characters. Compound L2H exhibits weak photochromism, which is significantly different from the complete structural transition from open form to closed form in L1H. In addition, no photochromism was observed in **1** and **2**, mainly due to two factors. The one is the presence of the {Ir(dfppy)<sub>2</sub>}<sup>+</sup> unit which accepts the excitation energy, resulting in Ir-based luminescence instead of ligand-centered photochromism. The other one is that **1** and **2** have no sufficient space for the dimethylthiophene rings to rotate and form a photoactive antiparallel conformation. Our experiments demonstrate that both the substituent group and {Ir(dfppy)<sub>2</sub>}<sup>+</sup> coordination significantly influence the crystal structures, luminescence properties and photochromic behaviors of L1H, L2H, **1** and **2**.

## Acknowledgements

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## Notes

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†Electronic Supplementary Information (ESI) available: X-ray crystallographic files in CIF format, UV-vis absorption and luminescence data, some figures including <sup>1</sup>H NMR spectra, XRD patterns, structures, luminescence spectra, and UV-vis

spectra.

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**Abstract**

Two bisthienylethenes 2-(2-hydroxyphenyl)-4,5-bis[2,5-dimethyl(3-thienyl)]-1H-imidazole (L1H) and 2-(2-hydroxyphenyl)-4,5-bis(2,5-dimethyl(3-thienyl))-1-phenylimidazole (L2H), which have chelating N,O-donor binding site attached to the photochromic core, have been synthesized using a one-pot condensation reaction, and used to prepare the heteroleptic complexes  $[\text{Ir}(\text{dfppy})_2(\text{L1})]\cdot 2\text{CH}_3\text{OH}$  (**1**) and  $[\text{Ir}(\text{dfppy})_2(\text{L2})]$  (**2**) [dfppyH = 2-(2,4-difluorophenyl)-pyridine]. In the crystal structures of all four compounds, two thiophene groups of each bisthienylethene molecule adopt parallel conformation. Neighboring molecules in L1H and **1** are linked into supramolecular chains through hydrogen bonds. Particularly, the packing structure of **1** contains right- and left-handed  $2_1$  helical chains. In contrast, neighboring molecules in L2H and **2** interact only through Van der Waals interactions. At room temperature, L1H and L2H in  $\text{CH}_2\text{Cl}_2$  show fluorescence emission at 442 nm and 469 nm, respectively. Compounds **1** and **2** in  $\text{CH}_2\text{Cl}_2$  reveal broad emission bands characteristic of the Ir(III)/dfppy chromophores at 508 nm and 494 nm, respectively, with a mixing of  $^3\text{MLCT}$  and  $^3\text{LC}$  characters. At room temperature, the photochromism ability of L2H in  $\text{CH}_2\text{Cl}_2$  is clearly weaker than that of L1H. Moreover, no photochromism has been observed in **1** and **2**. It is demonstrated that both the substituent group and  $\{\text{Ir}(\text{dfppy})_2\}^+$  coordination could significantly influence the crystal structures, luminescence and photochromic properties of L1H, L2H, **1** and **2**.