Inorganic Chemistry Communications 14 (2011) 1894–1897

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Phosphorescent copper(I) complexes bearing 2-(2-benzimidazolyl)-6-methylpyridine and phosphine mixed ligands

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ARTICLE INFO

Article history:
Received 30 June 2011
Accepted 7 September 2011
Available online 14 September 2011

Keywords:
Copper(I)
Mixed-ligand
Photoluminescence
2-(2-Benzimidazolyl)-6-methylpyridine

ABSTRACT

Two 2-(2-benzimidazolyl)-6-methylpyridine (Hbmp) copper(I) complexes bearing PPh_3 and 1,4-bis(diphenylphosphino)butane (dppb), namely, $[Cu(Hbmp)(PPh_3)_2](ClO_4)$ (**1**) and $[Cu(Hbmp)(dppb)](ClO_4)$ (**2**), have been synthesized. X-ray diffraction analysis reveals that the most significant influence of the phosphine ligands on the structures is on the P–Cu–P bond angle. Both two Cu(I) complexes exhibit a weak low-energy absorption at 360–450 nm, ascribed to the Cu(I) to Hbmp metal-to-ligand charge-transfer (MLCT) transition, perhaps mixed with some ILCT character inside Hbmp. The room-temperature luminescences are observed for **1** and **2**, both in solution and in the solid state, which originate from the MLCT excited states and vary markedly with the phosphine ligands.

There has been considerable interest in luminescent transition-metal complexes of multi-nitrogen heterocyclic ligands [1–3]. Copper(I) complexes are of interest in this context due to their attractive photophysical properties with possible applications in solar energy conversion, electroluminescent devices, luminescence-based sensors, and biological labeling [4–7]. In Cu(I) systems, the selection of N-heterocyclic chelating ligand is the key because it can modulate the emissive properties from the metal-to-ligand charge-transfer (MLCT) excited state [8–11]. In addition, the phosphine auxiliary ligands play a positive role in stabilizing the Cu(I) center, albeit not involved in the MLCT transition, and exert important effects on the photophysical properties of Cu(I) complexes [12–14].

Recently, we have initiated research on photoactive copper(I) complexes with N-heterocyclic chelate bridging ligands [11,15,16]. It is demonstrated that both N-heterocyclic chelate and the ancillary ligand such as halide and phosphine have great effects on the formation and photophysical properties of Cu(I) complexes. Additionally, to the best of our knowledge, the structures of Cu(I) complexes with 1,4-bis(diphenylphosphino)butane (dppb) as a bidentate chelating ligand have not been reported hitherto. Herein, we describe the syntheses, crystal structures, and photophysical properties of two new Cu(I) complexes bearing 2-(2-benzimidazolyl)-6-methylpyridine (Hbmp) and the two different phosphine ligands, *i.e.* $[Cu(Hbmp)(PPh_3)_2](ClO_4)$ (**1**) and $[Cu(Hbmp)(dppb)](ClO_4)$ (**2**). It is demonstrated that complexes **1** and **2** are emissive at ambient temperature in both solution and the solid state, and both the phosphine auxiliary ligand and the P–Cu–P bond angle have an important impact on the photophysical properties of cuprous complexes.

Mononuclear Cu(I) complexes possessing Hbmp and phosphine mixed ligands could be prepared via two simple approaches (Scheme 1) [17]. The PPh_3 complex $[Cu(Hbmp)(PPh_3)_2](ClO_4)$ (**1**) was firstly afforded by the treatment of $Cu(ClO_4)_2 \cdot 6H_2O$ with 4 equivalents of PPh_3, where PPh_3 not only served as a monodentate ligand but also as a reducing reagent, followed by slow addition of 1 equiv of Hbmp. However, in view of the bidentate nature of dppb, a synthetic method different to **1** was executed to prepare the dppb complex $[Cu(Hbmp)(dppb)](ClO_4)$ (**2**), in which copper powder acts as the reducing agent of Cu(II). Complexes **1** and **2** display a light-yellow color and are air-stable in both solution and the solid state, and both were well-defined by NMR, IR, elemental, and X-ray diffraction analyses. In the ^1H NMR spectra of **1** and **2**, the N–H signals of the imidazole rings and the C–H signals from the methyl groups were observed at around 12 and 2 ppm, respectively, besides the aromatic proton signals (δ 6.95–8.44 ppm). In the ^{31}P NMR spectra, complex **1** displays one singlet ^{31}P chemical shift at δ 0.91 ppm, which is in agreement with those recorded in other related Cu(I) PPh_3 complexes [13,18,19], while one singlet peak is also observed at δ −11.20 ppm in **2**, comparable to those of previously reported Cu(I) dppb complexes [20,21].

Single-crystal X-ray diffraction studies of **1** and **2** have been carried out to reveal their structural features [22]. As depicted in Figs. 1 and 2, each four-coordinated Cu(I) atom is bound to two nitrogen atoms of Hbmp and two P donors to constitute a distorted tetrahedral geometry, and the ClO_4^- anion is linked by hydrogen bond with the NH group of the benzimidazolyl ring. The Cu–$N_{pyridyl}$ distances for the pyridyl rings (av.

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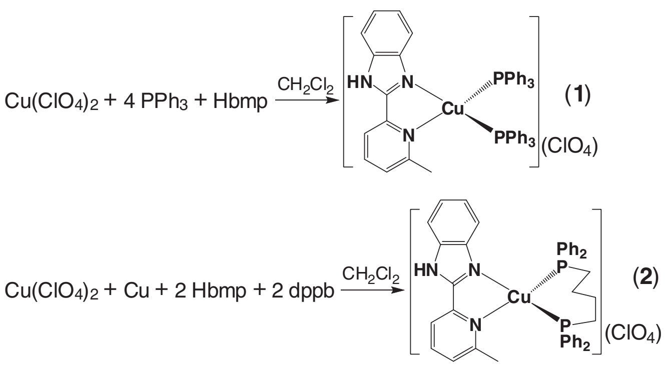
doi:10.1016/j.inoche.2011.09.005



Scheme 1. Synthetic route of complexes **1** and **2**.

2.152 Å) are obviously longer than the Cu–N$_{\text{imidazolyl}}$ distances of the imidazolyl rings (av. 2.079 Å), showing a stronger bonding with the imidazolyl nitrogen, consistent with the related Cu(I) complexes featuring the 2-(2′-quinolyl)benzimidazolyl and 2-(2′-pyridyl)benzimidazolyl fragments [18,19]. The Cu–N and Cu–P distances in **1** and **2** are compatible to those observed in other related Cu(I) complexes [13,18,19,23]. The N–Cu–N bite angles are similar with small variation for **1** (79.44(13)°) and **2** (80.20(11)°). In contrast, however, the P–Cu–P bond angles vary notably from 123.70(5)° of **1** to 111.49(4)° of **2**, and analogous structural phenomenon was also observed in other Cu(I) phosphine complexes containing the 2-(2′-quinolyl)benzimidazolyl and 2-(2′-pyridyl)benzimidazolyl units [13,19]. The P–Cu–P bite angle (123.70(5)°) of **1** resembles those found in Cu(I) PPh_3 complexes [Cu(Hqbm)(PPh_3)](BF_4) (124.24(3)°) [19] and [Cu(pbb)(PPh_3)](BF_4) (124.12(6)°) [13], while the P–Cu–P bond angle (111.49(4)°) of the dppb complex **2** approximates to those of Cu(I) complexes bearing bis[(2-diphenylphosphino)phenyl]ether (DPEphos), [Cu(Hqbm)(DPEphos)](BF_4) (112.40(4)°) [19] and [Cu(pbb)(DPEphos)](BF_4) (113.35(3)°) [13], which is obviously larger than those documented in other reported metal complexes with the chelating dppb [24,25]. In **1**, it is noted that the phenyl rings of the Hbmp ligands from two adjacent molecules are basically parallel and show a favorable pairwise π–π stacking (Fig. 3). The inter-phenyl separation is approximately 3.59 Å, implying the presence of a weak π–π interaction between the intermolecular Hbmp ligands [26]. However, similar π–π stacking is not observed in the crystal lattice of **2**.

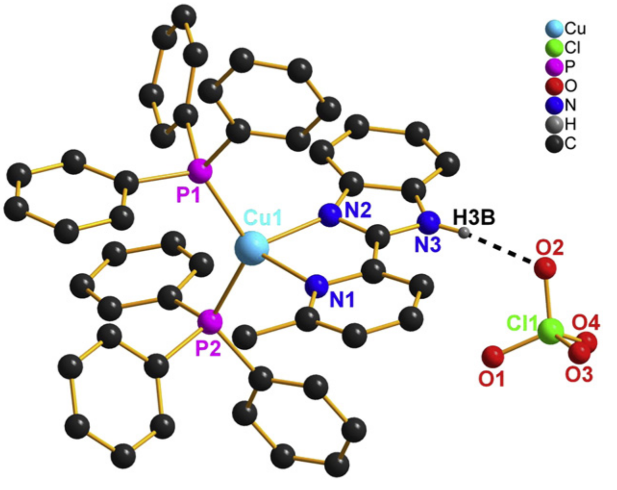


Fig. 1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms except H3B are omitted for clarity. Selected bond distances (Å) and angles (°): Cu1–N1 2.156(3), Cu1–N2 2.078(3), Cu1–P1 2.2614(12), Cu1–P2 2.2631(13), H3B···O2 1.99, N1–Cu1–N2 79.44(13), N1–Cu1–P1 109.16(9), N1–Cu1–P2 114.22(9), N2–Cu1–P1 113.38(10), N2–Cu1–P2 108.43(10), P1–Cu1–P2 123.70(5), N3–H3B···O2 162.0.

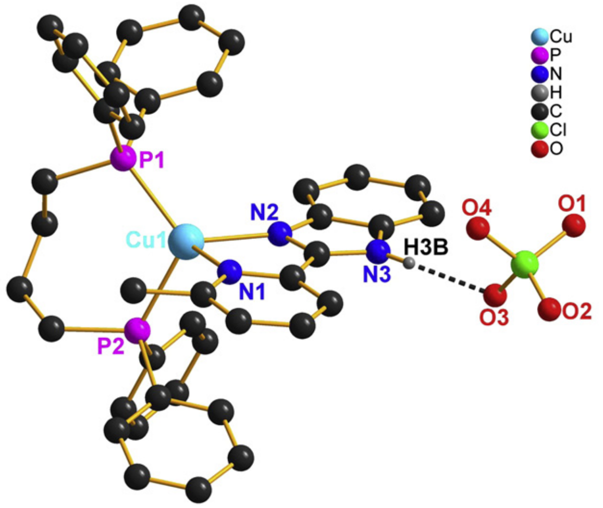


Fig. 2. Molecular structure of **2** with atom-labeling scheme. Hydrogen atoms except H3B are omitted for clarity. Selected bond distances (Å) and angles (°): Cu1–N1 2.148(3), Cu1–N2 2.080(3), Cu1–P1 2.2446(12), Cu1–P2 2.2851(13), H3B···O3 2.03, N1–Cu1–N2 80.20(11), N1–Cu1–P1 124.35(8), N1–Cu1–P2 102.26(8), N2–Cu1–P1 119.35(8), N2–Cu1–P2 115.31(8), P1–Cu1–P2 111.49(4), N3–H3B···O3 160.0.

The UV–vis absorption spectra of Hbmp and its complexes **1** and **2** in CH_2Cl_2 at ambient temperature are depicted in Fig. 4. Hbmp shows two absorptions at $\lambda_{max} \approx 314$ and 327 nm, attributable to the $^1\pi\pi^*$ transitions inside Hbmp. Complexes **1** and **2** exhibit multiple absorption peaks ($\varepsilon > 10^4\ M^{-1}\ cm^{-1}$) in the 240–350 nm region, most likely coming from Hbmp and PPh_3 or dppb. Further support is provided by a close match of the absorption spectra in high-energy region (≤350 nm) of Hbmp and complexes **1** and **2**. The red shift of the π–π* absorptions of **1** and **2** is consistent with better conjugation of the coordinated Hbmp relative to free Hbmp, resulting in a smaller π–π* energy gap. In addition to the high-energy absorptions, complex **1** has a comparatively weak low-energy absorption tail ($\varepsilon < 7.5 \times 10^3\ M^{-1}\ cm^{-1}$) at 360–450 nm, while a weak low-energy absorption with maximum at 378 nm is also observed in **2**. These weak low-energy absorptions are identified as the metal-to-ligand charge-transfer (MLCT) transition from the d_π orbital of Cu(I) center to the unoccupied π* orbital of Hbmp, probably mixed with some intraligand charge-transfer (ILCT) character inside Hbmp.

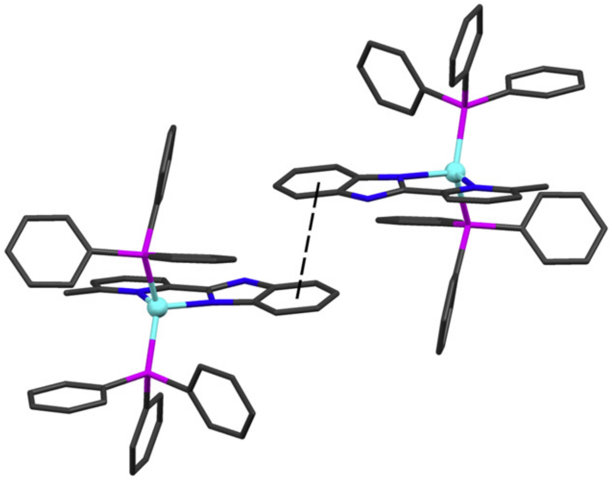


Fig. 3. Side view depicting the pairwise stacking of Hbmp ligands between neighboring cations of **1** in the crystal lattices.

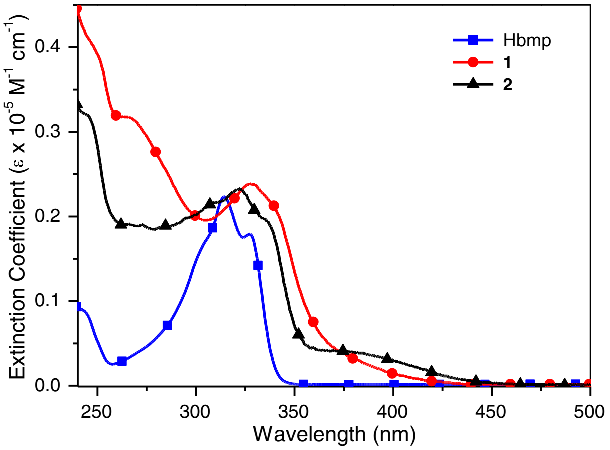


Fig. 4. UV–vis absorption spectra of Hbmp (—■—), **1** (—●—), and **2** (—▲—) in diluted dichloromethane solution at room temperature.

The photoluminescence properties of Hbmp and complexes **1** and **2** are investigated at ambient temperature (Fig. 5). The free ligand Hbmp emits a purple color with $\lambda_{max} \approx 361$ and 373 nm in CH_2Cl_2 and in the solid state, respectively, attributed to the fluorescence emission stemming from ligand-centered $\pi \rightarrow \pi^*$ transition. The solid-state emission of Hbmp has a small red-shift of 12 nm relative to its solution emission, which comes from the inter-Hbmp π–π stacking in the solid state, leading to a decrease of the π–π^* energy gap. Complexes **1** and **2** exhibit a broad emission profile with λ_{max} at 562 and 602 nm in degassed CH_2Cl_2 at room temperature, respectively. From previous work [4,13,18,19], the highest occupied molecular orbitals (HOMO) of **1** and **2** are principally centered on Cu(I), perhaps including some contributions from the phosphine and Hbmp ligands, while their lowest unoccupied molecular orbitals (LUMO) are believed to be primarily localized on Hbmp. Thus the lowest-lying emissive excited states of **1** and **2** are best regarded as the ^{3}MLCT character from $d(Cu) \rightarrow \pi^*(Hbmp)$. The emission of **2** (602 nm) is more red-shifted than that of **1** (562 nm), and such a 40 nm red-shift can be related to the replacement of PPh_3 via a stronger electron-donating dppb, raising the HOMO level, less influencing the LUMO energy, and hence leading to a decrease of the HOMO–LUMO gap. It is reported that a wider P–Cu–P bond angle can decrease the $d\sigma^*$ interactions and enhance the required energy of the MLCT excitation [12]. The emission energies of **1** and **2** follow the sequence of **1** (562 nm)>**2** (602 nm), which is the same order as the P–Cu–P bond angles (123.70(5)° for **1** and 111.49(4)° for **2**), consistent with the observations documented in related Cu(I) phosphine complexes [13,19,27]. Hence, it is believed that the P–Cu–P angle might also play a role in the photoluminescences of **1** and **2**. In sharp contrast to Cu(I) phosphine complexes of N-arylating 2-(2′-pyridylbenzimidazolyl)benzene being non-emissive in the solid state at ambient temperature [13], complexes **1** and **2** display a solid-state emission at ambient temperature with maxima at 514 and 521 nm, respectively. It is possible that the arylation of the NH group has some negative effects on the emissive excited state. The solid-state emissions of **1** and **2** have a blue-shifting of 48–81 nm with respect to their solution emissions, which are most likely from the rigidity of solid-state medium impeding the distortion of the excited-state geometries, and virtually such luminescence rigidochromism is also observed in Ru(II) [28], Ir(III) [29], and Cu(I) systems [9,30]. It is notable that the blue-shift (48 nm) of the solid-state emission of **1** versus its solution emission is much smaller than that (81 nm) of **2**, perhaps due to the inter-Hbmp π–π stacking of **1** (Fig. 3), not found in **2**, lowering the LUMO level, and thus decreasing the HOMO–LUMO gap of **1** in the solid state.

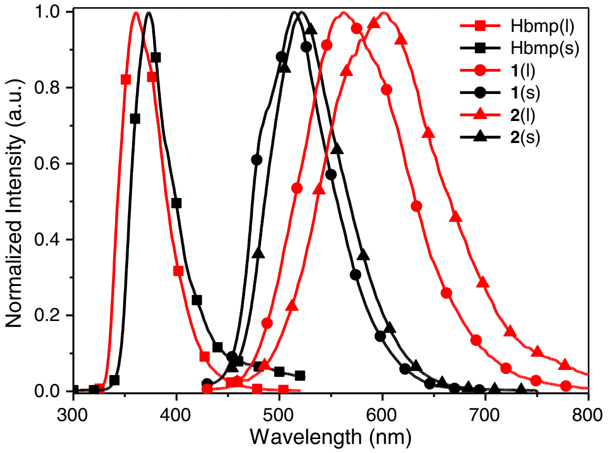


Fig. 5. Emission spectra of Hbmp (■), **1** (●), and **2** (▲) recorded in a diluted CH_2Cl_2 solution (red lines) and in the solid state (black lines) at ambient temperature.

In summary, two new phosphorescent Cu(I)–Hbmp complexes $[Cu(Hbmp)(PPh_3)_2](ClO_4)$ (**1**) and $[Cu(Hbmp)(dppb)](ClO_4)$ (**2**) have been prepared. It is demonstrated that the phosphine auxiliary ligand plays a role in regulating the P–Cu–P bond angle, and both have significant effects on the photophysical properties of Cu(I) complexes. It is suggested that the arylation of the imidazolyl-NH group might has some important impacts on the luminescence properties of cuprous complexes. Further investigation on Cu(I) complexes of NH-functionalized Hbmp is underway.

Acknowledgments

The authors thank the National Natural Science Foundation of China (Nos. 21163009, 21001057), the Key Project of Chinese Ministry of Education (No. 211088), the Natural Science Foundations of Fujian Province (No. 2008F3117) and Jiangxi Province (No. 2009GQH0038), the Science Foundation of Education Bureau of Jiangxi Province (No. GJJ10151), and the Science Foundation of State Key Laboratory of Structural Chemistry (No. 20110015) for the financial support.

Appendix A. Supplementary data

CCDC 829377 and 806918 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.005.

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[17] *Synthesis*. For **1**, a mixture of PPh_3 (123.0 mg, 0.469 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (43.5 mg, 0.117 mmol) was stirred in CH_2Cl_2 (25 mL) at RT for 8 h. To this resultant colorless solution was added dropwise with stirring a solution of Hbmp (24.5 mg, 0.117 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for another 3 h and the solvent was evaporated. Light-yellow crystals of **1** (Yield: 73%) were afforded by slow diffusion of petroleum ether into a 1:3 mixture of CH_2Cl_2 and 1,2-dichloroethane. Anal. Calcd. for $C_{49}H_{41}ClCuN_3O_4P_2$: C, 65.62; H, 4.61; N, 4.69. Found: C, 65.32; H, 4.23; N, 4.47%. Selected IR (KBr, cm^{-1}): 1095 (s, ClO_4). ^1H NMR (400 MHz, $CDCl_3$): δ 12.39 (s, 1H), 8.39 (d, 1H, $J=7.6$ Hz), 7.37–7.32 (m, 6H), 7.26–7.22 (m, 3H), 7.19–7.00 (m, 25H), 6.99 (t, 1H, $J=7.6$ Hz), 6.73 (d, 1H, $J=8.4$ Hz), 2.28 (s, 3H). For **2**, a mixture containing $Cu(ClO_4)_2 \cdot 6H_2O$ (64.2 mg, 0.173 mmol), activated copper powder (55.8 mg, 0.878 mmol) and Hbmp (72.4 mg, 0.346 mmol) was stirred for 30 min in dried acetonitrile (30 mL) under N_2 at RT, to which dppb (147.6 mg, 0.346 mmol) were added and stirred for another 1 h. The resulting light-yellow solution was filtered to remove unreacted Cu, the filtrate was evaporated. Light-yellow crystals of **2** (Yield: 62%) were obtained by slow diffusion of hexane into the CH_2Cl_2 solution. Anal. Calcd. for $C_{41}H_{39}ClCuN_3O_4P_2$: C, 61.65; H, 4.92; N, 5.26. Found: C, 61.32; H, 4.75; N, 5.04%. Selected IR (KBr, cm^{-1}): 1060 (s, ClO_4). ^1H NMR (400 MHz, $CDCl_3$): δ 12.56 (s, 1H), 8.42 (d, 1H, $J=7.6$ Hz), 7.99 (d, 1H, $J=8.0$ Hz), 7.83 (t, 1H, $J=7.6$ Hz), 7.69 (t, 1H, $J=8.0$ Hz), 7.51–7.44 (m, 2H), 7.37 (t, 1H, $J=7.6$ Hz), 7.26–7.22 (m, 13H), 7.20–7.11 (m, 6H), 6.98 (t, 1H, $J=7.6$ Hz), 2.58 (s, 4H), 2.14 (s, 4H), 1.91 (s, 3H).

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[22] Crystal data for **1** (CCDC 829377): $C_{49}H_{41}ClCuN_3O_4P_2$; $Mr=896.79$; triclinic; $P\,1$; $a=11.132(3)$, $b=13.443(3)$, $c=15.803(4)$ Å; $\alpha=90.533(3)$, $\beta=107.428(3)$, $\gamma=94.088(3)°$; $V=2249.4(10)$ Å^3; $Z=2$; $D_c=1.324\ g\ cm^{-3}$; $\mu=0.663\ mm^{-1}$; $S=1.095$; Final R indices $[I>2\sigma(I)]$ $R_1=0.0521$, $wR_2=0.1400$; R indices (all data) $R_1=0.0710$, $wR_2=0.1495$. Crystal data for **2** (CCDC 806918): $C_{41}H_{39}ClCuN_3O_4P_2$; $Mr=798.68$; monoclinic; $P2_1/c$; $a=14.871(7)$, $b=17.892(8)$, $c=14.936(7)$ Å; $\beta=101.173(6)°$; $V=3885(3)$ Å^3; $Z=4$; $D_c=1.366\ g\ cm^{-3}$; $\mu=0.758\ mm^{-1}$; $S=0.991$; Final R indices $[I>2\sigma(I)]$ $R_1=0.0519$, $wR_2=0.1075$; R indices (all data) $R_1=0.1211$, $wR_2=0.1331$.

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