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Copper(I) 5-phenylpyrimidine-2-thiolate complexes showing unique optical properties and high visible light-directed catalytic performance[†]

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Solvothermal reactions of 5-phenylpyrimidine-2-thiol (5-phpymtH) with equimolar CuBr afforded one hexanuclear cluster $[Cu_6(\mu_3-5-phpymt)_6]$ (1) along with a tetranuclear by-product $[{(Cu_2Br)(\mu-5-phpymt)_6}]$ phpymtH) $(\mu_3$ -5-phpymt)]₂ (**2**). A two dimensional (2D) polymer $[Cu_4(\mu_5$ -5-phpymt)₂(μ -Br)₂]₀ (**3**) was isolated from the reaction of 5-phpymtH with two equiv. of CuBr. Analogous reactions of 5-phpymtH with one or four equiv. of Cul produced one tetranuclear cluster $[{Cu_2(\mu-5-phpymtH)(\mu-5-phpymt)}(\mu_3-I)]_2$ (4) and one 2D polymer $[Cu_6]_2(\mu_4-I)_2(\mu_4-5-phpymt)_2]_n$ (5). Compound 1 possesses a water-wheel-shaped hexameric structure. Compound 2 has an H-shaped tetrameric structure. Compound 3 possesses a 2D network in which unique 1D $[Cu_8(\mu-Br)_2(\mu_5-5-phpymt)_4]_n$ chains are connected by $\mu-Br^-$ ions. Compound 4 has another tetrameric structure in which two $\{Cu_2(\mu-5-phpymtH)_2(\mu-5-phpymt)\}$ fragments are linked by a pair of μ_3 -1⁻ ions. Compound **5** contains another 2D network in which hexanuclear {Cu₆l₂(μ_4 -l)₂} units are linked by μ_4 -5-phpymt bridges. The 5-phpymt ligand shows four coordination modes: $\mu - \kappa^{1}(S) - \kappa^{1}(N)$ (4), $\mu_{3} - \kappa^{2}(S) - \kappa^{1}(N)$ (1 and 2), $\mu_{4} - \kappa^{1}(N) - \kappa^{2}(S) - \kappa^{1}(N')$ (5) and $\mu_{5} - \kappa^{1}(N) - \kappa^{3}(S) - \kappa^{1}(N')$ (3). Complex 1 shows strong solvatochromic behaviour and displays reversible luminescence switching upon alternate addition of CF₃COOH and Et₃N into its CHCl₃ solution. Complexes **1–5** exhibit a high photocatalytic activity towards the aerobic oxidative hydroxylation of arylboronic acids to phenols under visible light irradiation. Catalyst 5 can be reused in several cycles without any obvious decay of the catalytic efficiency. These results offer an interesting insight into how the CuX/5-phpymtH molar ratios and X^- ions exert great impacts on the coordination modes of the 5-phpymt⁻ ligand, the structures of the final complexes, and the luminescence and catalytic properties.

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Introduction

Phenol derivatives are important synthetic intermediates and widely used in the synthesis of pharmaceuticals, agrochemicals, natural products and polymeric forms.^{1–3} The synthetic routes to phenols include metal-catalysed hydroxylation of aryl halides,^{4–6} and the hydroxylation or oxidative hydroxylation of arylboronic acids using oxidants and/or metal catalysts.^{7–10} From both practical and environmental viewpoints, there is a

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strong need to screen out more acceptable catalytic approaches using visible light-promoted transformation.¹¹⁻¹⁴ Some homogeneous catalysts such as $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine),¹¹ methylene blue (MB),¹² rose bengal (RB),¹³ and eosin Y¹⁴ have been used as visible light-mediated photoredox catalysts to facilitate aerobic oxidative hydroxylation. However, these approaches suffer from inherent problems in the separation and recycling of the catalysts from the products. To date, there are only a few examples of visible light-promoted oxidative hydroxylation of arylboronic acids to phenols by using heterogeneous catalysts.¹⁵⁻¹⁷ Cohen et al. demonstrated that α -UiO-67¹⁸ incorporated with the $[Ru(bpy)_3]^{2+}$ group showed efficient and recyclable catalytic activity for the aerobic oxidation of arylboronic acids under near-UV and visible light irradiation. On the other hand, the majority of transition metal complex photosensitizers are based on expensive, nonearth abundant noble metals including Ru(II), Pt(II), Re(I), Os(II) and Ir(III).^{19–24} Copper(I) complexes used in solar energy technologies are an attractive alternative, because they are less expensive and environmentally more benign.25-27 Homoleptic



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Paper

or heteroleptic Cu(I) photosensitizers with two phenanthroline N^N ligands or one bidentate P^P and one N^N chelate ligand have been known as efficient visible-light photoredox catalysts for alkene azidation,²⁸ benzylic azidation,²⁹ atom transfer radical addition and allylation reactions,^{30,31} hydrogen generation from water,³²⁻³⁴ α-amino C-H bond functionalization,³⁵ cross-dehydrogenative coupling reactions³⁶ and oxidative C-N coupling of anilines with terminal alkynes.³⁷ In addition, copper(I) complexes with N-heterocyclic thiolates possess high stability, visible light absorption, intense luminescence and long fluorescence lifetime,³⁸⁻⁴¹ which may lead to high photocatalytic activity under visible light irradiation. To our knowledge, there are virtually no examples of such copper(1) thiolates that are used as an efficient visible light-driven photoredox catalyst. Recently, we have been interested in the syntheses and properties of metal/pyrimidine-2-thiolate complexes,42,43 and found that they do exhibit high catalytic activity towards organic reactions such as C-C, or C-N bond formation.⁴⁴⁻⁴⁷ In this paper, we delicately choose 5-phenylpyrimidine-2-thiol (5-phpymtH) to react with different equivalents of CuX (X = Br, I) under solvothermal conditions. One hexanuclear cluster $[Cu_6(\mu_3-5-phpymt)_6]$ (1), two tetranuclear clusters $[{(Cu_2Br)(\mu-5-phpymtH)}(\mu_3-5-phpymt)]_2$ (2)and $[{Cu_2(\mu-5-phpymtH)(\mu-5-phpymt)}(\mu_3-I)]_2$ (4), and two 2D polymers $[Cu_4(\mu_5-5-phpymt)_2(\mu-Br)_2]_n$ (3) and $[Cu_6I_2(\mu_4-I)_2(\mu_4-5 [phpymt]_2]_n$ (5) are isolated therefrom. Complex 1 shows strong solvatochromic behavior and reversible luminescence switching upon alternately adding CF₃COOH and Et₃N into its CHCl₃ solution. More interestingly, complexes 1-5 display high photocatalytic activity toward aerobic oxidative hydroxylation of arylboronic acids to generate phenols under irradiation of visible light. The catalytic system modelled by 5 can also be recycled several times without evident decay of its catalysis efficiency. Herein we describe their synthesis, structural characterization, luminescence and photocatalytic properties.

Results and discussion

Synthesis and characterization aspects of 1-5

At the beginning, we carried out the solvothermal reactions of CuBr with equimolar 5-phpymtH in MeCN and DMSO at 120 °C in air. However, we did not isolate any expected Cu(I)5-phpymt complexes. Only an unexpected Cu(II) complex [Cu $(5-\text{phpyms})_2]_n$ (5-phpymsH = 5-phenyl-pyrimidine-2-sulfonic acid) was obtained as blue octahedral crystals in 46% yield (see the ESI[†]). X-ray analysis revealed that it has a 1D chain (extending along the b axis) in which each Cu adopts an octahedral geometry defined by four O and two N from four 5-phpyms ligands, while each 5-phpyms takes а $\mu_3 - \kappa^1(N) - \kappa^1(O) - \kappa^1(O')$ chelating/bridging mode to bind at two Cu atoms (Fig. S1[†]). Such a copper-catalyzed oxidation of pyrimidine-2-thiol is similar to that of pyridine-2-thiol.48 In this reaction, Cu(I) was evidently oxidized into Cu(II) and the SH group of 5-phpymtH was in situ oxidized into a sulfo group, forming a new 5-phpyms⁻ anion. The formation of this Cu(π)

complex suggests that the aforementioned reaction using CuX and 5-phpymtH should be performed under an inert gas atmosphere in order to yield the desired Cu(I)/5-phpymt complexes. Thus we ran the solvothermal reactions of the same components in MeCN and DMF at 120 °C under N2 and obtained one yellow hexanuclear cluster $[Cu_6(\mu_3-5-phpymt)_6]$ (1) (in 58%) yield) coupled with red blocks of a tetranuclear cluster $[{(Cu_2Br)(\mu-5-phpymtH)}(\mu_3-5-phpymt)]_2$ (2) (in 17% yield). Addition of triethylamine (Et_3N) into this reaction only gave 1 with a higher yield (85%). An analogous reaction of CuBr with 5-phpymtH in a 2:1 molar ratio under similar reaction conditions afforded a 2D polymer $[Cu_4(\mu_5-5-phpymt)_2(\mu-Br)_2]_n$ (3) in 67% yield. If the CuBr/5-phpymtH molar ratio was increased to 3:1 or 4:1, the reaction always generated a yellow precipitate that was insoluble in common solvents and uncharacterizable. These results suggested that the molar ratio of the two components did play an important role in the formation of 1-3 (Scheme 1).

When CuI was reacted with equimolar 5-phpymtH in MeCN and DMF at 120 °C, one tetranuclear complex [{Cu₂(µ-5phpymtH)(μ -5-phpymt)}(μ ₃-I)]₂ (4) was isolated in 89% yield (Scheme 1). In the presence of Et₃N, the mixture of 5-phpymtH with CuI also produced 1 in a high yield. An analogous reaction of 5-phpymtH with two equiv. of CuI at 120 °C afforded orange red blocks of $[Cu_6I_2(\mu_4-I)_2(\mu_4-5-phpymt)_2]_n$ (5) in *ca*. 18% yield along with some uncharacterizable yellow powder. The higher CuI/5-phpymtH molar ratios (from 3/1 to 6/1) also gave 5 as the only product and did increase the yield of 5 (up to 82%). Again the molar ratio of the two components dictated the outcomes (4 and 5) of the above two reactions. Notably, the halide (Br⁻ or I⁻) ion seems to exert a significant effect on the formation of 1-5. In 2 and 4, half of the Br⁻ or I⁻ anion in CuX (X = Br, I) is replaced by a 5-phpymt⁻ ligand. The other ligands coordinate to the Cu(I) atom in a 5-phpymtH neutral form. As described later in this article, the bromide in 2 and 3 serves as a terminal (2) or μ -Br (3) ligand while the iodide in 4 and 5 takes a μ_3 -I (4) or μ_4 -I/ κ^1 (I) (5) coordination mode. The differences in halide coordination modes are probably due to the shorter radius of the Br atom than that of the I atom. The different coordination modes of 5-phpymt also contribute to the formation of 1-5. Each 5-phpymt in 2 and 3 binds more Cu(1) atoms than the corresponding one in 4 and 5. For 5phpymt, four coordination modes are observed: $\mu - \kappa^{1}(S) - \kappa^{1}(N)$ (4), $\mu_3 - \kappa^2(S), \kappa^1(N)$ (1 and 2), $\mu_4 - \kappa^1(N), \kappa^2(S) - \kappa^1(N')$ (5) and



Scheme 1 Synthesis of complexes 1-5.

 $\mu_5-\kappa^1(N),\kappa^3(S)-\kappa^1(N')$ (3). Each 5-phpymtH in 2 or 4 exhibits a bridging bidentate $\mu-\kappa^1(S)-\kappa^1(N)$ fashion. Of course, other factors that may have effects on the formation of 1–5, such as reaction temperature and pH value, could not be ruled out.

Compounds 1-5 are stable toward oxygen and moisture. Compounds 1, 2, and 4 are slightly soluble in EtOH, ⁱPrOH, CHCl₃, CH₂Cl₂, DMSO and DMF but insoluble in toluene, hexane, MeOH, Et₂O and H₂O. Compounds 3 and 5 are insoluble in common organic solvents. Their elemental analyses are consistent with their chemical formula. The powder X-ray diffraction (PXRD) patterns for each of them match well with those simulated from their corresponding single crystal data, suggesting its bulk phase homogeneity (Fig. S2-S7[†]). The thermal stability of 1-5 is investigated by thermogravimetric analysis. They are thermally stable up to 240 °C (Fig. S8[†]). Compound 1 continuously decomposes in the range of 300-964 °C and the final residue amounts to Cu₂S. In the range of 246-300 °C, 2 has a weight loss of 13.39% (calcd 13.72%), which corresponds to the loss of bromide. The final residue at 995 °C is equal to CuS. Compound 3 has a weight loss of 9.7% (calcd 10.04%) in the temperature range of 332-358 °C, which agrees well with the total loss of bromide. The final residue is assumed to be Cu_2S . For 4, the weight loss of 20.52% from 254 °C to 322 °C amounts to the loss of all coordinated iodide atoms (calcd 20.16%). The final residue is assumed to be CuS. Compound 5 has a weight loss of 10.2% (calcd 10.04%) (amounting to two iodides) in the range of 326 and 385 °C. A further loss of 30.30% (calcd 30.12%) (amounting to other iodides) appears in the range of 385-703 °C. A final residue of Cu₂S is formed at 966 °C.

Crystal structures of 1.2MeCN

Compound 1.2MeCN crystallizes in the triclinic space group $P\bar{1}$ and its asymmetric unit consists of half of one discrete $[Cu_6(5-phpymt)_6]$ molecule and one MeCN solvent molecule. Six Cu(I) atoms in 1 are connected by six 5-phpymt ligands to form a water-wheel-shaped structure. Such a Cu₆S₆ core structure is similar to those observed in other hexanuclear Cu(I) clusters with derivatives of pyridine-2-thiolate and pyrimidine-2-thiolate.⁴⁹⁻⁵⁴ Each 5-phpymt binds to three Cu(1) atoms in a $\mu_3 - \kappa^1(N) - \kappa^2(S)$ coordination mode. Each Cu(I) is coordinated by two bridging S atoms of two 5-phpymt ligands and one N atom of the third 5-phpymt ligand, forming an approximate trigonal planar coordination environment (Fig. 1). The Cu-µ₃-S bond distances (Table S1[†]) in 1 are comparable to the corresponding ones observed in $[Cu_3(pymt)_3]_n$ (pymt = pyrimidine-2thiolate).55 The Cu-N bond distances are close to those observed in [Cu₆(dmpymt)₆] (dmpymt = 4,6-dimethyl-pyrimidine-2-thiolate).⁵¹ The Cu--Cu distances vary in the range of 2.7758(4)-3.0335(4) Å, which are close to the sum of the van der Waals radii (2.80 Å) of Cu(1) centers, suggesting the existence of weak Cu(I)-Cu(I) interactions.55

Crystal structures of 2

Compound 2 crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit has half an independent molecule of



Fig. 1 View of the molecular structure of 1 with a labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.

 $[{(Cu_2Br)(5-phpymtH)}(5-phpymt)]_2$. It may be viewed as having an H-shaped structure with the crystallographic center of symmetry located on the midpoint of Cu2 and Cu2A (Fig. 2). The 5-phpymtH or 5-phpymt ligand adopts a $\mu - \kappa^{1}(S), \kappa^{1}(N)$ and $\mu - \kappa^2(S), \kappa^1(N)$ mode, respectively. In 2, two {Cu(CuBr)₂(μ -5phpymtH)} fragments are connected by a pair of μ_3 -5-phpymt ligands. Each Cu adopts a trigonal planar geometry, coordinated by one S from one µ-5-phpymtH molecule, one N and one S of one μ_3 -5-phpymt (Cu1 and Cu1A) or by one N from one μ -5-phpymtH, one S of μ_3 -5-phpymt and one Br⁻ (Cu2 and Cu2A). The Cu1-N1 bond length is shorter than the Cu2-N3 distance. The Cu1-S2 and Cu2-S1 bond lengths are shorter than the Cu2-S2A length. The mean Cu-S bond distance in 2 is longer than that of 1. The Cu1-Br1 bond distance is longer than those found in [Cu(SN-Ph)Br] (2.3410(3) Å; SN-Ph = N-(2-pyridinyl)amino-diphenylphosphine sulfide), $[Cu(SN-^{i}Pr)Br]$ (2.327 Å, $SN-^{i}Pr = N-(2-pyridinyl)amino-diisopropyl$ phosphine sulfide)⁵⁶ and [(tpypo)CuBr] (2.344(1) Å; tpypo = tris (2-pyridyl)phosphine oxide),⁵⁷ but shorter than those in $[MoS_4Cu_4(mpy)_5Br_2]$ (2.496(3) Å and 2.643(4) Å; mpy = α -methylpyridine).⁵⁸ The Cu1…Cu2 separation (2.6444(8) Å) is



Fig. 2 View of the molecular structure of **2** with a labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.

shorter than that of **1**, implying relatively stronger Cu(1)–Cu(1) interactions. The Cu1···Cu2A, Cu1···Cu1A and Cu2···Cu2A separations are 3.781 Å, 5.325 Å, 3.770 Å, respectively, which excludes any metal–metal interaction. Notably, the H-bonding interaction between N2 and N4 [N2–H2···N4 with x, 1 + y, z, 2.793 Å] leads to the formation of a 1D chain extended along the a axis (Fig. S9†).

Crystal structures of 3

Compound 3 crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit holds half a discrete [(5-phpymt)₄Cu₈Br₄] unit. The six Cu atoms in 3 are bridged by one pair of bromides and two pairs of 5-phpymt ligands to form a [(5phpymt)₄Cu₆Br₂] fragment (Fig. 3). Such a fragment is interconnected by Cu⁺ ions through one Cu-N bond and one Cu-S bond, generating a 1D chain $[Cu_8(\mu_5-5-phpymt)_4(\mu-Br)_2]_n$ extended along the b axis. This chain is further connected to its equivalent ones via bromides to form a 2D layer extending along the ab plane. Each 5-phpymt in 3 takes a $\mu_5 - \kappa^1(N) - \kappa^3(S) - \kappa^1(N')$ mode to bind five Cu atoms. Cu1 and Cu4 adopt a trigonal planar geometry, coordinated by one N and two S atoms from three 5-phpymt ligands (Cu1) or by one N and one S from two 5-phpymt ligands and one Br (Cu4). Based on the bond angles listed in Table S1,† Cu2 (or Cu3) in 3 may be viewed as having a triangle pyramidal coordination geometry in which N1, S2, and Br2 (or Br1, S1A, and N3I) lie



Fig. 3 (a) View of a portion of the 1D chain of 3 (extending along the *b* axis). (b) View of the 2D network of 3 (extending along the *ab* plane).

on the basal plane while Br1 (or S2) occupies the apical position. The Cu–Br bond lengths in 3 are comparable to those in $[Cu_2Br_2(bpe)_2]_n$ (bpe = 1,2-bis(4-pyridyl)ethane)⁵⁹ and $[Cu_4Br_4(PPh_2py)_2]$ (PPh_2py = 2-(diphenylphosphino)pyridine).⁶⁰ The mean Cu–N bond distance is close to that of 1. In 3, the Cu1–S1 and Cu3–S2 bond distances are much longer than those of the Cu1–S1A, Cu2–S2 and Cu3–S1A bonds. The elongated distance is ascribed to the steric hindrance of the two face-to-face 5-phpymt ligands.

Crystal structures of 4

Compound 4 crystallizes in the monoclinic space group P21/c, and its asymmetric unit contains half a discrete molecule $[Cu_2(\mu-5-phpymtH)(\mu-5-phpymt)(\mu_3-I)]_2$. Two dimeric $\{Cu_2(\mu-5-phpymtH)(\mu-5-ph$ phpymtH)₂(μ -5-phpymt)} units in 4 are connected by two μ_3 -I, forming a tetranuclear structure (Fig. 4). The crystallographic center of symmetry is located on the midpoint of Cu2 and Cu2A atoms. Each 5-phpymtH or 5-phpymt adopts a $\mu - \kappa^{1}(S), \kappa^{1}(N)$ bridging mode to bind two Cu atoms *via* one Cu-N bond and one Cu-S bond. In such a {Cu₂(µ-5phpymtH)₂(μ -5-phpymt)} fragment, two Cu atoms are bridged by one µ-5-phpymtH ligand and one µ-5-phpymt ligand through two Cu-S bonds and two Cu-N bonds. Cu1 or Cu1A atom adopts a trigonal planar geometry, coordinated by one N of one μ -5-phpymtH, one S from μ -5-phpymt and one μ_3 -I, while Cu2 and Cu2A in 4 adopt a distorted tetrahedral coordination geometry, coordinated by one N of µ-5-phpymtH, one S of µ-5-phpymt and two µ3-I atoms. Cu1-N1, Cu1-S2A and Cu1-I1 bond lengths are shorter than those of the corresponding ones of Cu2-N3, Cu2-S1, Cu2-I1 and Cu2-I1A bonds. The shorter bond distances are likely due to the fact that Cu1 has a lower coordination number than Cu2. The Cu2-N3 bond length is slightly longer than that found in $[Cu_3(pymt)_3]_n$.⁵⁵ The Cu-S bond distances are comparable with those in $[Cu_3(pymt)_3]_n$. The Cu1···Cu2A separation (2.5678(12) Å) in 4 is shorter than those in Cu1…Cu1B (2.9539(18) Å), Cu2…Cu2A (2.997(2) Å) and Cu1…Cu2 in 2, implying stronger Cu(I)-Cu(I)



Fig. 4 View of the molecular structure of **4** with a labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.

interactions. A two-dimensional H-bonded network (Fig. S10†) extended *bc* plane is further generated from the intermolecular hydrogen bonding interaction between N2 and N4 [N2–H2…N4 with -x, -1/2 + y, 3/2 - z, 2.083 Å].

Crystal structures of 5

Compound 5 crystallizes in the monoclinic space group C2/m, and its asymmetric unit contains one-fourth of the $[Cu_6I_4(5$ phpymt)₂] unit. 5 consists of a 2D sheet structure (extended along the *ab* plane) in which hexanuclear $\{Cu_6I_2(\mu-I)_2\}$ fragments are interconnected to the adjacent ones by three pairs of μ_4 -5-phpymt ligands (Fig. 5). Each 5-phpymt takes a $\mu_4 - \kappa^1(N) - \kappa^2(S) - \kappa^1(N')$ mode to coordinate to four Cu atoms of three $\{Cu_6I_2(\mu-I)_2\}$ cores. In $\{Cu_6I_2(\mu-I)_2\}$, two Cu atoms are linked by two μ -I⁻ atoms, which are further connected by a pair of {CuI} fragments via four Cu-µ4-I bonds. Cu1, Cu1A, Cu1B and Cu1C are located in the same plane, while the two {CuI} units stand above or below the Cu₄I₂ plane. Each Cu in 5 adopts a trigonal planar geometry, coordinated by one S and one N from two μ_4 -5-phpymt ligands and one μ_4 -I (Cu1) or by one I and two μ_4 -I atoms (Cu2). Cu1- μ_4 -I1 and Cu2- μ_4 -I1 bond lengths are longer than that of the Cu2– μ_3 -I2 bond, but close to those in $\{[Cu(mtz)]_3(CuI)\}_n$ (Hmtz = 3,5-dimethyl-1,2,4-triazole).⁶¹ Cu2-µ₃-I2 and Cu1-N1 bond distances are shorter than those of the corresponding ones in 4. The Cu1-S1A bond distance is close to those in 4. Cu1...Cu2 (2.6508(14) Å),



Fig. 5 (a) View of one $\{Cu_6l_2(\mu-1)_2(\mu-5-phpymt)_6\}$ fragment in 5. (b) View of the 2D network along the *ab* plane. All H atoms are omitted for clarity.

Cu1…Cu1A (2.741(2) Å) and Cu2…Cu2B (2.665(3) Å) separations are slightly longer than that of Cu1…Cu2A in **4**.

Optical properties

Complexes 1–5 exhibit a strong and broad absorption with the maxima values ranging from 240 to 450 nm and a long absorption tail to *ca*. 750 nm (Fig. S11†). The UV-vis spectra of 1 in different solvents are also measured (Fig. S12†). The CH₂Cl₂, CHCl₃, 1,4-dioxane and DMF solutions of 1 exhibit similar absorption bands. The two absorption bands at $\lambda < 290$ nm and at 290 nm-400 nm ($\lambda_{max} = 325$ nm) are likely derived from the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ electron transitions. In addition, 1 in EtOH or ⁱPrOH exhibits two absorption bands centred at $\lambda_{max} = 260$ nm and 390 nm. The red shift in protic solvents is probably due to the weak interaction between 1 and EtOH or ⁱPrOH molecule. The absorption of 1 at $\lambda_{max} = 325$ nm in CHCl₃ is gradually red-shifted with the increased addition of CF₃COOH (Fig. S13†).

The emission spectra of 1-5 are investigated at room temperature. Being excited at 380 nm in the solid state, compound 1 exhibits an efficient emission at 583 nm with 12.96% quantum yield (Fig. S14[†]). Complexes 2-5 do not show luminescence in the solid state. The luminescence properties of 1 are also examined in various solvents. As shown in Fig. 6, the emission spectra reveal very substantial but different solvent effects. Excited at 380 nm, the solution of 1 in aprotic solvents such as CHCl₃, or CH₂Cl₂, toluene, acetone, THF, 1,4-dioxane and DMF emits at a maximum of 815-830 nm. The emissions appear at a much lower energy with a large Stokes shift of about 540 nm. The emission of 1 does not get shifted greatly in aprotic solvents and may be originated from the triplet states of ligand-to-metal charge-transfer (LMCT) and/or metalto-ligand charge-transfer (MLCT) characters, mixed with metal-centered (ds/dp) states^{38,55} while the solution of **1** in a protic solvent (EtOH, ⁱPrOH) emits at a shorter wavelength with a maximum at about 720 nm. The reason for the strong blue-shift of emission maxima is probably due to the weak hydrogen-bonding interactions of S and N atoms from the pyri-



Fig. 6 Emission spectra of 1 (1 \times 10⁻⁵ mol L⁻¹) in various solvents at room temperature (at λ_{ex} = 380 nm).

midyl ring with the protic solvent molecules. At room temperature, the quantum yield of **1** is 23.61% in ⁱPrOH or 18.45% in CH_2Cl_2 . Moreover, the photoluminescence lifetimes of **1** in $CHCl_3$ and in the solid state are measured to be 10.0 and 8.7 µs, respectively.

A dramatic change in the fluorescence emission intensity is observed in the CHCl₃-ⁱPrOH mixture (Fig. S15[†]). The emission maximum of 1 in CHCl₃/ⁱPrOH is blue-shifted from 838 to 727 nm along with the increasing amount of ¹PrOH. Such a blue-shift is gradually accompanied by a remarkable enhancement of the emission intensity when the volume ratio of $CHCl_3/^{i}$ PrOH is changed from 100:0 to 1:2. Upon increasing the ⁱPrOH content from 67% to 80%, the emission intensity gets decreased and the maximum at 818 nm vanishes with the formation of a new emission peak at 763 nm. The emission maximum is blue-shifted from 763 nm to 727 nm and the emission intensity increases gradually when the volume ratio of CHCl₃/ⁱPrOH is changed from 1:4 to 1:14. These results show that the interactions between 1 and ⁱPrOH do exert a great impact on the emission. Afterwards, the emission and the emission intensity remain unchanged when the ⁱPrOH fraction is increased up to higher than 93%. Intriguingly, the luminescence of 1 is also influenced by an acid, which may interact with 1 via stronger intermolecular H-bonding interactions. The addition of CF3COOH leads to the loss of luminescence. This can be ascribed to the protonation of S and/or N atom of the 5-phpymt ligand in this complex. It is uncommon that the hydrogen-bonding interaction leads to the fluorescence quenching (Fig. 7). Moreover, this process is reversible when Et₃N is added in this system and can be shuttled several times with no loss of emission intensity. Clearly, the solution of 1 might be used as a luminescence-based on-off switch upon alternate addition of an acid and a base at room temperature. The ¹H NMR spectrum of **1** reveals some useful information about the interaction of CF₃COOH with 5-phpymt in CDCl₃. The addition of CF₃COOH can lead to a downshift of the proton signal of the pyrimidyl ring from δ 8.81 to 8.95. The



Fig. 7 Emission spectra of $1 (1 \times 10^{-6} \text{ mol L}^{-1})$ in CHCl₃ at room temperature (blue line), CF₃COOH added (red line), and then Et₃N added (black line).

resonance of the proton of CF₃COOH shows a remarkable upfield shift from δ 8.14 to 5.30. After the further addition of Et₃N into the solution, the signal at δ 8.95 ppm comes back to 8.81 ppm (Fig. S16–S19†). These results suggest that the N atoms of 5-phpymt are involved in the hydrogen bonding interaction with CF₃COOH.

Photocatalytic properties

The band gap energy (E_g) of 1–5 was determined by the Kubelka–Munk method⁶² based on the diffuse reflectance spectra (Fig. S20†). The energy band gaps obtained by extrapolation of the linear portion of the absorption edges are 1.97 eV (1 and 2), 2.26 eV (3), 1.60 eV (4) and 2.17 eV (5). The narrow band gaps of these compounds encouraged us to investigate their visible light photocatalytic activity, which can be evaluated by the aerobic oxidative hydroxylation of arylboronic acids into phenol derivatives at room temperature. We chose 5 as a catalyst and phenylboronic acid (6a) as the model substrate to investigate suitable reaction conditions.

As shown in Table 1, incubating a mixture of 6a, Et_3N as a sacrificial reducing agent and 5 as a catalyst in 3 mL H₂O under visible light afforded phenol (7a) in 55% yield after 24 h. When this reaction was carried out in organic solvents

 Table 1
 Optimizing the reaction conditions for the oxidative hydroxylation of phenylboronic acids

	cat., R.T., solvent	ОН -	
6a		7a	8a

				m '	$\operatorname{Yield}^{b}(\%)$	
Entry ^a	mol%)	Solvent	Additive	(h)	7a	8a
1	5 (2)	H_2O	Et ₃ N	24	55	_
2	5 (2)	MeCN	Et_3N	24	36	11
3	5 (2)	EtOH	Et_3N	24	8	20
4	5 (2)	MeOH	Et_3N	24	27	38
5	5 (2)	THF	Et_3N	24	_	35
6	5 (2)	$MeCN/H_2O(1/1)$	Et_3N	24	75	3
7	5 (2)	$MeOH/H_2O(1/1)$	Et_3N	24	44	Trace
8	5 (2)	$EtOH/H_2O(1/1)$	Et_3N	24	36	Trace
9	5 (2)	$MeCN/H_2O(2/1)$	Et_3N	24	50	9
10	5 (2)	$MeCN/H_2O(1/2)$	Et_3N	24	65	Trace
11	5 (2)	$MeCN/H_2O(1/4)$	Et ₃ N	24	62	Trace
12	5 (2)	$MeCN/H_2O(1/10)$	Et_3N	24	63	
13	5 (2)	$MeCN/H_2O(1/1)$	Et_3N	48	95	Trace
14	5 (2)	$MeCN/H_2O(1/1)$	Et_3N	72	95	Trace
15	5 (2)	$MeCN/H_2O(1/1)$	ⁱ Pr ₂ NEt	48	94	Trace
16	5 (1)	$MeCN/H_2O(1/1)$	Et_3N	48	84	Trace
17	5 (5)	$MeCN/H_2O(1/1)$	Et_3N	48	94	2
18	5 (2)	$MeCN/H_2O(1/1)$	_	48		_
19	_	$MeCN/H_2O(1/1)$	Et_3N	48	_	_
20^c	5 (2)	$MeCN/H_2O(1/1)$	Et_3N	48	_	_
21	1 (2)	$MeCN/H_2O(1/1)$	Et_3N	48	87	7
22	2(2)	$MeCN/H_2O(1/1)$	Et_3N	48	91	5
23	3 (2)	$MeCN/H_2O(1/1)$	Et_3N	48	89	4
24	4 (2)	$MeCN/H_2O(1/1)$	Et ₃ N	48	93	1

^{*a*} Reaction conditions: phenylboronic acid (1.0 mmol), solvent (3.0 mL), Et₃N (1.0 equiv.), 45 W fluorescence lamp irradiation (610 nm, 540 nm, 430 nm) and in air. ^{*b*} Yields are based on HPLC results. ^{*c*} Without irradiation.

such as MeCN, EtOH or MeOH, the yield of 7a became lower (36% (MeCN); 8% (EtOH); 27% (MeOH)) (Table 1 entries 2-4) coupled with a byproduct biphenyl (8a) (11%-38%). When the reaction was performed in a H_2O -MeCN (v/v = 1/1) mixture, the yield of 7a was increased significantly within 24 h in air (entry 6). The catalyst showed lower activity in aqueous MeOH or EtOH (entries 7 and 8). The optimal ratio of H₂O and MeCN was determined to be 1:1 (entries 6, 9-11). Almost complete conversion of the phenylboronic acid into phenol was achieved when the reaction time was extended to 48 h in H₂O-MeCN (entry 13). Et₃N was necessary for such aerobic oxidative hydroxylation of arylboronic acid (entry 18). No product was observed in the absence of the catalyst, and 6a remained unreacted (entry 19) in contrast to those run in the dark, where no product was formed, indicating that the formation of phenol from phenylboronic acid was truly induced by visible light irradiation (entry 20). Therefore, suitable conditions for the photosynthesis of phenols from arylboronic acids are summarized as follows: Et₃N as the sacrificial electron donor, MeCN-H₂O (1:1) as a solvent system, and air as an oxidant in the presence of visible light at room temperature for 48 h. With these optimized conditions, the catalytic performances of 1-4 were also investigated. Compound 2 or 4 as a homogeneous catalyst also exhibited excellent activity toward the oxidative hydroxylation of phenylboronic acid to phenol. Complexes 1 and 3 exhibited relatively poor catalytic performance and lower selectivity than that of 5.

The scope of the visible light-induced photoredox catalytic aerobic oxidative hydroxylation of arylboronic acids using 5 as a photocatalyst is examined (Table 2). When arylboronic acids are electron-rich, electron-poor, or sterically bulky, they are all smoothly transformed into the corresponding phenol derivatives in good to excellent yields under the optimized reaction conditions. The m-, p-methyl, m-, p-methoxyphenylboronic acids are converted smoothly to their corresponding phenols in 91%, 96%, 93% and 97% yields, respectively (entries 2-5). Phenylboronic acids with electron-withdrawing substituents like -NO₂, -COCH₃ and -F can proceed conveniently, in 81%, 86%, and 70% yields (entries 10-12), respectively. The steric hindrance of arylboronic acids has influence on the catalytic activity of the transformation from arylboronic acids to phenols. Substrates with higher steric hindrance such as (2-methoxyphenyl)boronic acid, o-tolylboronic acid, (2,6-dimethylphenyl)boronic acid, mesitylboronic acid are also converted into their corresponding phenols in good yields (74%-88%; entries 6-9). Notably, naphthalen-2-ylboronic acid, 1,4phenylenediboronic acid and 1,3-phenylenediboronic acid can also be oxidatively hydroxylated with satisfactory yields (entries 13-15). The substrate scope of this methodology has been extended to the use of arylboronic pinacol esters. The desired products are isolated in 95% and 94% yields under the same reaction conditions (entries 16 and 17).

The reusability of 5 was also examined for the oxidative hydroxylation of phenylboronic acid to phenol. After the first reaction cycle, the catalyst was separated by centrifugation and then washed with H_2O . The isolated catalyst was used for the

 Table 2
 Oxidative hydroxylation of arylboronic acids catalyzed by 5

 under visible light irradiation
 5

Entry ^a	Boronic acid	Product	Yield ^b %
1	B(OH)2	─ —он	95/93% ^c
2	р	рОн	97
3			96
4	-O B(OH) ₂	_оон	93
5	►	ЮН	91
6	0− −В(ОН)₂	сурон	88
7		— он	81
8	→ B(OH)₂	С	75
9			74
10	02N	О₂№−ОН	81
11	9→-€(ОН)2	уон	86
12	F-C-B(OH)2	г∕он	70
13	B(OH)2	Срон	86
14	(HO) ₂ BB(OH) ₂	но{он	75
15	(HO) ₂ B B(OH) ₂	но	74
16		<i>С</i> -он	95
17	~D-\$‡	он	94

^{*a*} Reaction conditions: **6** (0.50 mmol), **5** (2 mol%), Et₃N (1.0 equiv.), acetonitrile/water (1.5 mL/1.5 mL), 45 W fluorescence lamp irradiation (610 nm, 540 nm, 430 nm) for 48 h, in air. ^{*b*} Yield of isolated products. ^{*c*} Under irradiation of a 300 W Xe lamp with a 420 nm cut-off filter (420 nm $\leq \lambda \leq$ 760 nm) for 24 h.

second cycle by adding phenylboronic acid, Et_3N and solvent. As indicated in Fig. 8, no significant loss of catalytic activity was observed after the catalytic system was re-used for five times. After 5 cycles, about 79% of **6a** was converted to **7a**. After the catalytic reaction, solid **5** was collected by filtration,

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Fig. 8 Recycling tests for oxidative hydroxylation of phenylboronic acid using 5 under visible light irradiation.

washed with MeCN and Et_2O , dried in air and then characterized by PXRD. The PXRD patterns were in good agreement with the simulated ones generated from the single crystal data of 5, suggesting that the original framework structure of 5 was retained during the catalysis (Fig. S21†).

Electrons (e⁻) in the valence band (VB) are excited to the conduction band (CB), generating an equal amount of conceivable holes (h⁺) in the VB under the light irradiation. The resulting hole (h^+) can react with H₂O to yield a hydroxyl radical ('OH). The electron (e^-) binds one O_2 molecule to get reduced to O2. To obtain some insight into the potential photocatalytic reaction pathway, the experiments with phenylboronic acid are carried out in the presence of tert-butyl alcohol (TBA) or 1,4-benzoquinone (PBQ) under the optimized catalytic conditions. TBA and PBQ are used as 'OH and O2'scavengers, respectively.63 The addition of TBA has little effect on the oxidative hydroxylation of phenylboronic acid. The catalytic efficiency of the system is found to decrease from 95% to 38% in the presence of PBQ (Scheme 2). Thus the oxidative hydroxylation process with 5 as the catalyst predominantly depends on O2⁻ radicals to attack the arylboronic acid. The possible photocatalytic mechanism¹¹⁻¹⁸ for the above oxidative hydroxylation of arylboronic acids is also proposed (Scheme S1[†]). Under the irradiation of visible light, electrons (e⁻) in the valence band (VB) are excited to the conduction band (CB), and holes (h^+) are left in the VB. The interaction of the hole with Et_3N produces an Et_3N^{*+} radial cation. One electron reduction of O_2 in air generates the superoxide ion $(O_2^{\bullet-})$, which reacts with the boronic acid to form the intermediate I. The radical anion I then abstracts a hydrogen atom from Et_3N^{+} to form intermediate II. The rearrangement of II may yield the intermediate III. The hydrolysis of III gives phenol as the product.



Scheme 2 The oxidative hydroxylation of phenylboronic acids.

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Conclusions

In summary, the solvothermal reactions of CuX (X = Br, I) with 5-phpymtH in different molar ratios under N₂ generated one hexanuclear cluster 1, two tetranuclear clusters 2 and 4, and two 2D coordination polymers 3 and 5. In 1-5, the halide and the molar ratio of the two reactants do have a significant effect on the coordination modes of 5-phpymt, and the structures and properties of the resulting Cu(1)/5-phpymt complexes. Addition of Et₃N into the reaction results in the formation of hexanuclear cluster 1 in a higher yield. When the reaction was carried out in air, the SH group of 5-phpymtH could be oxidized *in situ* into a sulfo group by O_2 from air, forming a 1D Cu(II) polymer $[Cu(5-phpyms)_2]_n$. Reactions of 5-phpymtH with equimolar CuX resulted in the formation of tetra-, or hexanuclear clusters 1, 2 and 4. When 5-phpymtH reacted with two or more equiv. of CuX, 5-phpymt could bind more Cu(1) atoms to yield 2D coordination polymers 3 and 5. In the structures of 1-5, 5-phpymt takes four coordination modes: $\mu - \kappa^{1}(S) - \kappa^{1}(N)$ (4), $\mu_3 - \kappa^1(N), \kappa^2(S)$ (1 and 2), $\mu_4 - \kappa^1(N), \kappa^2(S) - \kappa^1(N')$ (5) and $\mu_5 - \kappa^1(N), \kappa^3(S) - \kappa^1(N')$ (3), while the 5-phpymtH ligand in 2 and 4 only exhibits a bridging bidentate $\mu - \kappa^{1}(S) - \kappa^{1}(N)$ fashion. The solvent-dependent photoluminescence of 1 may allow the development of a luminescent probe that can detect the hydrogen-bond-donating species in aprotic solvents. Compound 1 also works as an acid/base-induced "on-off" luminescence switch material. Compound 5 displays high photocatalytic activity toward the oxidative hydroxylation of various arylboronic acids under visible light irradiation at ambient temperature to produce the corresponding phenols in high yields. Furthermore, this heterogeneous catalyst can be simply recycled and reused without significant loss of activity. Compounds 1 and 5 as two representative examples demonstrate that the Cu(I) complexes of S,N-donor ligands have a large scope of fascinating applications in advanced materials such as photoelectronic devices and photocatalysts. Currently, we are investigating the design and synthesis of other Cu(I) complexes of pyrimidine-2-thiolate ligands that show visible light-promoted and more efficient catalytic activity towards C-C, C-O and C-N bond formation.

Experimental

Materials and methods

General procedure. Ligand 5-phpymtH was prepared according to the literature method.⁶⁴ All other reagents were used as obtained from commercial sources without further purification. The analytical instruments for the characterization of the compounds described in this article are the same as those employed in our previous work unless otherwise mentioned.⁶⁵ The fluorescence spectra were measured on a FLS980 spectrometer.

Synthesis of $[Cu_6(\mu_3-5\text{-phpymt})_6]$ (1·2MeCN) and $[\{(Cu_2Br) (\mu-5\text{-phpymtH})\}(\mu_3-5\text{-phpymt})]_2$ (2). Under N₂, to a pressure bottle (15 mL) were added CuBr (10.8 mg, 0.075 mmol),

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5-phpymtH (14.1 mg, 0.075 mmol), 4 mL of MeCN and 0.2 mL of DMF. The mixture was sealed. The tube was heated in an oven at 120 °C for 48 h and then cooled to room temperature at the rate of 5 °C h⁻¹ to form a large amount of yellow crystals of 1 coupled with red blocks of 2, which were separated mechanically under a microscope. Complex 1: Yield: 11.7 mg (58%). Anal. Calcd (%) for C₆₄H₄₈Cu₆N₁₄S₆: C 48.44, H 3.05, N 12.36. Found: C 48.76, H 3.25, N 11.55. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.81 (s, 2H), 7.52–7.44 (m, 5H). IR (KBr pellet, ν/cm^{-1}): 1629 (w), 1578 (m), 1524 (w), 1445 (w), 1393 (s), 1171 (m), 1035 (w), 768 (m), 693 (m), 509 (w). Complex 2: Yield: 5.3 mg (17%). Anal. Calcd (%) for C₄₀H₃₀Br₂Cu₄N₈S₄: C 41.24, H 2.60, N 9.62. Found: C 41.32, H 2.65, N 9.68. IR (KBr pellet, ν/cm^{-1}): 3047 (w), 1614 (m), 1529 (w), 1489 (w), 1445 (w), 1393 (s), 1369 (s), 1172 (m), 771 (m), 680 (w).

Complex 1 was also prepared as yellow crystals by solvo-thermal reaction of CuBr (10.8 mg, 0.075 mmol), 5-phpymtH (15.1 mg, 0.08 mmol) and one drop of Et_3N in MeCN (2 mL) and DMF (0.2 mL) at 120 °C. Yield: 17.2 mg (86% based on Cu).

Synthesis of $[Cu_4(\mu_5-5-phpymt)_2(\mu-Br)_2]_n$ (3). Compound 3 was prepared as orange crystals in a similar manner to that described for 1, using CuBr (21.6 mg, 0.150 mmol), 5-phpymtH (14.1 mg, 0.075 mmol) as starting materials in MeCN (4 mL) and DMF (0.2 mL). Yield: 19.8 mg (67%). Anal. Calcd (%) for C₂₀H₁₄Br₂Cu₄N₄S₂: C 30.47, H 1.79, N 7.11. Found: C 30.67, H 2.08, N 7.33. IR (KBr pellet, ν/cm^{-1}): 3053 (w), 1631 (m), 1581 (w), 1542 (w), 1492 (w), 1445 (w), 1398 (s), 1172 (m), 760 (m), 694 (m).

Synthesis of $[{Cu_2(\mu-5-phpymtH)(\mu-5-phpymt)}(\mu_3-I)]_2$ (4). Compound 4 was obtained as orange red crystals in an analogous manner to that used for 1, using CuI (14.3 mg, 0.075 mmol), 5-phpymtH (14.1 mg, 0.075 mmol) as starting materials in 4 mL of MeCN and 0.2 mL of DMF. Yield: 21 mg (89%). Anal. Calcd (%) for $C_{40}H_{30}Cu_4I_2N_8S_4$: C 38.16, H 2.40, N 8.90. Found: C 37.63, H 2.45, N 9.13. IR (KBr pellet, ν/cm^{-1}): 3032 (w), 1602 (m), 1622 (s), 1553 (w), 1526 (w), 1507 (w), 1443 (w), 1397 (s), 1385 (s) 1367 (s), 1164 (s), 1151 (m), 754 (m), 762 (m), 693 (m).

Synthesis of $[Cu_6I_2(\mu_4-I)_2(\mu_4-5-phpymt)_2]_n$ (5). Compound 5 was produced as orange red crystals using a similar route to that described for 1, using CuI (57 mg, 0.30 mmol), 5-phpymtH (14.1 mg, 0.075 mmol) as starting materials in MeCN (4 mL) and DMF (0.2 mL). Yield: 39 mg (82%). Anal. Calcd (%) for C₄₀H₂₈Cu₁₂I₈N₈S₄: C 19.01, H 1.12, N 4.43. Found: C 18.88, H 1.32, N 4.36. IR (KBr pellet, ν/cm^{-1}): 3031 (w), 1601 (m), 1551 (w), 1525 (w), 1489 (w), 1367 (s), 1348 (m) 1164 (s), 1151 (m), 762 (m), 693 (m).

X-Ray data collection and structure determination

Single crystals of 1·2MeCN and 2–5 suitable for X-ray analysis were obtained directly from the above preparations. Their crystal data were collected on a Rigaku Mercury CCD X-ray diffractometer (for 4) (3 kV, sealed tube) by using graphite monochromated Mo K α (λ = 0.71073 Å), an Agilent Xcalibur diffractometer (for 2 and 5) or a Bruker APEX-II CCD (for 1 and 3) using an X-ray source Mo K α (λ = 0.71073 Å). Single crystals of 1·2MeCN and 2–5 were mounted on glass fibers with grease at room temperature (4) or cooled under a liquid nitrogen stream at 153 K (1, 3) and 223 K (2, 5). The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver. 1.3, 2001), Bruker APEX2 or CrysAlisPro, Agilent Technologies (CrysAlis171.NET, Version 1.171.36.28) and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

Table 3 Crystal data and structure refinement parameters for 1.2MeCN and 2-5

	1.2MeCN	2	3	4	5
Empirical formula	C64H48Cu6N14S6	C40H30Br2Cu4N8S4	C ₂₀ H ₁₄ Br ₂ Cu ₄ N ₄ S ₂	C40H30Cu4I2N8S4	C40H28Cu12I8N8S4
Formula weight	1586.76	1164.94	788.45	1258.92	2526.62
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	C2/m
a(Å)	8.9345(7)	7.9432(4)	8.3588(6)	9.0698(12)	12.5100(9)
b (Å)	14.2016(10)	9.9838(7)	9.3642(7)	13.4850(16)	9.4515(6)
c (Å)	14.3237(11)	12.8707(9)	14.7668(11)	17.156(2)	12.0472(9)
$\alpha(\circ)$	105.957(2)	79.980(6)	88.688(4)		
$\beta(\hat{\circ})$	104.457(2)	82.732(5)	76.130(4)	103.926(3)	107.004(8)
γ (°)	107.305(2)	81.898(5)	85.922(4)		
$V(Å^3)$	1555.8(2)	989.63(11)	1119.29(14)	2036.6(4)	1362.16(17)
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.694	1.955	2.339	2.053	3.080
Z	1	1	2	2	1
$\mu ({\rm mm}^{-1})$	2.270	4.394	7.523	3.824	9.306
F(000)	800	576	760	1224	1160
Total reflns	89 970	6543	18 795	19 395	3305
Unique reflns	7175	3683	5133	3729	1357
Observed reflns	6147	2984	3441	3033	1073
Variables	407	260	283	268	94
R^{a}	0.0258	0.0402	0.0714	0.0498	0.0371
wR^b	0.0529	0.0765	0.1883	0.0957	0.0703
GOF^{c}	1.034	1.009	1.021	1.099	0.996

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}wR = \{\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}\}^{1/2}. {}^{c}GOF = \{\sum w((F_{o}^{2} - F_{c}^{2})^{2}) / (n-p)\}^{1/2}, where n = number of reflections and p = total number of parameters refined.$

The crystal structures of 1·2MeCN and 2–5 were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXL-97 program.⁶⁶ All non-H atoms were refined anisotropically. The H atoms of N2 from the 5-phpymt molecules in 2 and 4 were located using the Fourier maps with the N–H distance being fixed at 0.82 Å. All other hydrogen atoms were placed in the geometrically idealized positions and constrained to ride on their parent atoms. Pertinent crystal data and collection and refinement parameters for 1·2MeCN and 2–5 are summarized in Table 1, while their selected bond lengths and angles are listed in Table 3.

General procedure for the preparation of phenols from arylboronic acids

In a typical procedure, a test tube equipped with a magnetic stirring bar was charged with phenylboronic acid (0.061 g, 0.5 mmol), 5 (0.0021 g), Et₃N (0.051 g, 0.5 mmol), MeCN (1.5 mL) and H₂O (1.5 mL). The reaction mixture was kept stirring for 48 h under a 45 W fluorescence lamp light, quenched with water after completion and the catalyst was filtered off. The filtrate was extracted three times with ethylacetate (3×5 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether and ethyl acetate as the eluent and the filtrate was concentrated *in vacuo*.

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