

DOI:10.1002/ejic.201500069

Synthesis of Two Coordination Polymer Photocatalysts and Significant Enhancement of Their Catalytic Photodegradation Activity by Doping with Co²⁺ Ions

Duan-Xiu Li,^[a,b] Zhi-Gang Ren,^{*[a]} David J. Young,^[c] and Jian-Ping Lang^{*[a,b]}

Keywords: Coordination polymers / Photocatalysis / Zinc / Cobalt / Doping / N ligands / Carboxylate ligands

The coordination polymers (CPs) $[Zn_2(tipm)(1,3-BDC)_2]$ (1) and $[Co_2(tipm)(1,3-BDC)_2]\cdot 0.5CH_3CN$ (2 $\cdot 0.5CH_3CN$) were synthesized by the reactions of $Zn(NO_3)_2$ or $Co(NO_3)_2$ with tetrakis[4-(1-imidazolyl)phenyl]methane (tipm) and benzene-1,3-dicarboxylic acid (1,3-H₂BDC) under solvothermal conditions. Compounds 1 and 2 are isostructural and possess complicated three-dimensional frameworks with the Schläfli

Introduction

Photocatalysis is an environmentally friendly method for destroying organic dyes and other industrial pollutants.^[1,2] Suitable coordination polymers (CPs) can exhibit excellent photocatalytic efficiencies and stabilities.^[3,4] Photocatalytic efficiency can be improved by doping specific transition metal ions into CP frameworks.^[5] Liu reported that the photocatalytic activity of $[Zn(cca)(4,4'-bipy)]_n$ (cca = 4carboxycinnamate dianion, 4,4'-bipy = 4,4'-bipyridine) towards the decomposition of rhodamine B (RhB) was enhanced by doping with Fe³⁺, Cr³⁺, Ru³⁺, Co²⁺ or Ni²⁺ ions through a simple ion-exchange process.^[5c] This phenomenon may be explained by the narrower band gaps (E_g) of the doped CPs. Multidentate N-donor ligands, multicarboxylates and their admixtures are powerful building blocks for the construction of CPs.^[6] Among the various multidentate N-containing ligands, multipyridyl, multiimidazolyl, and multipyrazolyl ligands as well as their derivatives are commonly used, particularly bidentate examples.^[6e-6h,7] Triand tetradentate ligands are harder to prepare and harder

http://lmdc.suda.edu.cn/index.asp

[c] School of Science, Monash University Malaysia, Jalan Lagoon Selatan,

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201500069.

symbol $(4\cdot7^2)(6^2\cdot7^3\cdot12)(4\cdot6^2\cdot7^3)$. Cobalt ions were incorporated into the Zn-based CP framework 1 during solvothermal crystallization to yield $[Zn_{(2-2x)}Co_{2x}(tipm)(1,3-BDC)_2]\cdot bH_2O$ (x = 2.4 %, b = 0 for 1a, x = 23 %, b = 1 for 2a·H₂O). Doped CPs 1a and 2a·H₂O exhibited greater catalytic photodegradation of the dye rhodamine B (RhB) than the undoped complexes 1 and 2 and many literature examples.

to control in designed CP syntheses.^[8] The rigid ligand 3,3',5,5'-tetra(1*H*-imidazol-1-yl)-1,1'-biphenyl (L) and the auxiliary 1,3,5-tri(4-carboxyphenyl)benzene (H₃BTB) have been combined with ZnSO₄·7H₂O to yield the two-dimensional network [Zn(L)_{0.5}(CO₃)]·H₂O.^[8e] Rigid ligands with longer branched chains were used in this case to prevent the formation of chelate compounds.

In our previous studies, we have constructed CPs with imidazole ligands as the building blocks and investigated their photocatalytic activity.^[9] In this work, we designed and synthesized the rigid tetraimidazolyl-based ligand tetrakis[4-(1-imidazolyl)phenyl]methane (tipm). This fourconnected ligand can be topologically represented as a tetrahedral node and has not, to the best of our knowledge, been used hitherto to construct CPs. This ligand was chosen because (1) four imidazole N atoms of the tipm ligand can act as four potential coordination nodes and (2) the four phenyl groups can lengthen the distance to the quaternary carbon atom (Ccentre) to meet the requirements of the coordination geometries. We have successfully synthesized the tipm ligand in high yield through microwave heating. The solvothermal reactions of tipm and 1,3-benzenedicarboxylic acid (1,3-H₂BDC) with Zn(NO₃)₂ or Co(NO₃)₂ gave rise to the coordination polymers $[Zn_2(tipm)(1,3-BDC)_2]$ (1) and [Co₂(tipm)(1,3-BDC)₂]·0.5CH₃CN (2·0.5CH₃CN). Coordination polymers 1 and 2 are isostructural and possess complicated 3D frameworks with the Schläfli symbol $(4\cdot7^2)(6^2\cdot7^3\cdot12)(4\cdot6^2\cdot7^3)$. The doping of different amounts of Co²⁺ ions into 1 during the solvothermal crystallization yielded the doped isostructural CPs $[Zn_{(2-2x)}Co_{2x}]$ $(tipm)(1,3-BDC)_2]\cdot bH_2O$ (x = 2.4%, b = 0 for 1a, x = 23%, b = 1 for 2a·H₂O). The photocatalytic activities of these

 [[]a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China E-mail: jplang@suda.edu.cn

[[]b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

⁴⁷⁵⁰⁰ Bandar Sunway, Selangor Darul Ehsan, Malaysia



undoped and doped products were investigated with the degradation of RhB as a model reaction, and the results indicated that the doped CPs **1a** and **2a** exhibited higher photocatalytic activities than the undoped **1** and **2** and many literature examples.

Results and Discussion

The ligand tipm was synthesized by a microwave-assisted solid-state Ullmann coupling reaction between tetrakis(4bromophenyl)methane and imidazole. The traditional solution reaction requires reflux in dimethyl sulfoxide (DMSO) for 2 d.^[10a] The convenient method reported herein is complete in 90 s and uses less organic solvent. Excess imidazole was used to compensate for the possible sublimation of this reagent. The ligand tipm is stable in air and soluble in common solvents such as MeOH, EtOH, CH₂Cl₂, CHCl₃, N,Ndimethylformamide (DMF) and DMSO but insoluble in H₂O. In the ¹H NMR spectrum of tipm in CDCl₃ at 298 K (Figure S1), three singlets at $\delta = 7.87$, 7.29 and 7.21 ppm could be assigned to be the proton signals of the imidazole groups, and one singlet at $\delta = 7.38$ ppm was assigned to be the proton signal of the phenyl group. The ¹³C NMR spectrum of tipm in CDCl₃ at 298 K exhibited signals for seven different carbon atoms of the imidazole and phenyl rings at $\delta = 117.9 - 144.7$ ppm and that of the quaternary carbon atom (C_{centre}) at δ = 63.7 ppm (Figure S2). The hydrothermal reactions of $Zn(NO_3)_2$ or $Co(NO_3)_2$ with tipm and 1,3-H₂BDC (molar ratio 2:1:2) in H₂O/CH₃CN (4:1 v/v) at 150 °C for 1 d afforded yellow blocks of 1 (62% yield) or blue blocks of 2 (54% yield). When zinc(II) and cobalt(II) nitrates were added at the Zn^{II}/Co^{II}/tipm/1,3-H₂BDC ratios of 2:2:1:2 and 1:2:1:2, 1a and 2a could be separated with the Zn/Co ratios of 97.6:2.4 (1a) and 77:23 (2a), respectively. Increasing the percentage of Co from 1 to 1a, 2a and 2 changed the colours of these compounds from yellow (1) to orange (1a), red (2a) and blue (2; Figure S3). Complexes 1, 2, 1a and 2a are stable in air and insoluble in common solvents such as H₂O, CHCl₃, CH₃CN, DMF and DMSO. Their elemental analyses were consistent with their chemical formulas. The Zn/Co ratios in 1a and 2a were determined by atomic absorption spectroscopy (AAS) analyses. The observed powder XRD (PXRD) patterns for each compound correlated well with the simulated ones generated from their single-crystal X-ray diffraction data (Figure S4). The IR spectra of 1, 2, 1a and 2a exhibited strong absorption bands in the ranges $\tilde{v} = 1524-1614$ and 1313-1374 cm⁻¹, which indicated that they all contain coordinated carboxylic groups. The strong peaks at $\tilde{v} \approx 1068$ and 655 cm⁻¹ confirm the existence of imidazolyl groups in these complexes.

The coordination polymers 1, $2 \cdot 0.5 \text{CH}_3 \text{CN}$, 1a and $2a \cdot \text{H}_2 \text{O}$ crystallize in the monoclinic space group C/2c. The asymmetric units contain two crystallographically unique M^{II} ions, one tipm ligand, two 1,3-BDC ligands and CH₃CN ($2 \cdot 0.5 \text{CH}_3 \text{CN}$) or H₂O ($2a \cdot \text{H}_2 \text{O}$) solvent molecules. The 3D supramolecular architectures of 1, 2, 1a and 2a are

similar except for the central metal atoms. Thus, only the structure of 1 (Figure 1, Table 1) is described in detail. Each Zn atom in 1 is tetrahedrally coordinated by two N atoms from two different tipm ligands and two O atoms from two different 1,3-BDC ligands. The average Zn-N [2.001(6) Å] and Zn–O bond lengths [1.961(5) Å] in 1 are shorter than in [Zn₂(tib)₂(HBDC-OH)₂(BDC-OH)]·2H₂O those [2.017(2) and 1.972(2) Å, respectively; tib = 1,3,5-tris(1-1)imidazolyl)benzene].^[11] The orientations of the 1,3-BDC molecules connecting Zn1 and Zn2 are different (Figure 1, a and b); thus, the coordination sphere of Zn1 differs somewhat from that of Zn2. The two 1,3-BDC ligands around Zn1 are trans with an O1–Zn1–O3A angle of 98.5(2)° and connect two neighbouring Zn1 atoms to form a 1D $[Zn_2(1,3-BDC)_2]_n$ chain extending along the b axis (Figure 1, c). By comparison, the 1,3-BDC molecules bonded to Zn2 are cis with an O5–Zn2–O7C angle of 119.3(3)° and lead to the formation of a cyclic dinuclear $[Zn_2(1,3-BDC)_2]$ unit (Figure 1, d). The 1D $[Zn_2(1,3-BDC)_2]_n$ chain connects to adjacent chains through tipm ligands to form a 2D $[Zn_2(tipm)_2(1,3-BDC)_2]$ layer (Figure 1, e), which is further interpenetrated with an adjacent layer along the bc plane (Figure 1, f). An important structural feature of these complexes is that each of them possesses an array (Figure S5) formed from weak edge-to-face π - π stacking interactions. The distances between the imidazole proton and the phenyl ring centroid are ca. 3.2406(4) Å (1), 3.1508(4) Å (2), 3.1769(7) Å (1a) and 3.1590(1) Å (2a), and these interactions play a significant role in the stabilization of the corresponding framework. This interpenetrated double 2D layer is connected by the aforementioned $[Zn_2(1,3-BDC)_2]$ units to form a 3D framework (Figure 1, h). If each Zn1 centre, each Zn2 centre and each tipm ligand are regarded as a four-connecting node, a three-connecting node and a fourconnecting node, respectively, the whole net can be simplified as a 3D (3,4,4)-connected net. Compounds 1 and 2 are isostructural and possess complicated 3D frameworks with the Schläfli symbol $(4 \cdot 7^2)(6^2 \cdot 7^3 \cdot 12)(4 \cdot 6^2 \cdot 7^3)$ (Figure 1, i). The solvent-accessible void volumes calculated with PLA-TON24 are 25.1% for 1, 25.6% for 2, 25.1% for 1a and 24.1% for 2a.

The framework stabilities of 1, 2, 1a and 2a were investigated by thermogravimetric analysis (TGA) under an ambient atmosphere (Figure S6). The first weight losses (1.86% for 2 and 1.57% for 2a; calculated: 1.95% for 2 and 1.70% for 2a) from 20 to 150 °C correspond to the loss of the acetonitrile molecules or water solvate. For all samples, the main weight loss was produced in the temperature range 350–600 °C and can be attributed to the decomposition of the organic linkers. The residual weights (16.03% for 1, 14.76% for 2, 15.02% for 1a and 16.21% for 2a) were calculated, and the residual species were assumed to be ZnO for 1 (calcd. 15.60%), CoO for 2 (calcd. 14.25%), ZnO/CoO for 1a (calcd. 15.60%) and ZnO/Co₂O₃ for 2a (calcd. 15.44%).

The band gap energy (E_g) of a photocatalyst is a factor in its photocatalytic efficiency.^[12] The optical diffuse reflectance spectra of crystalline solids 1, 2, 1a and 2a (Figure S7) were recorded at room temperature, and the absorption

1982











(d)





(f)



Figure 1. (a) View of the coordination environment of the Zn1 centre in 1 with a labeling scheme. (b) View of the coordination environment of the Zn2 centre in 1 with a labeling scheme. (c) View of the 1D $[Zn_2(1,3-BDC)_2]_n$ chain based on the Zn1 centre. (d) View of the cyclic dinuclear $[Zn_2(1,3-BDC)_2]$ unit based on the Zn2 centre. (e) View of the 2D $[Zn_2(tipm)_2(1,3-BDC)_2]$ network along the *a* axis. (f) View of the 2D $[Zn_2(tipm)_2(1,3-BDC)_2]$ double layers along the *c* axis. The tipm ligands in the two interpenetrated layers are plotted with blue and yellow lines, respectively. (g) View of the 3D net along the *c* axis. (h) Schematic view of the topological net of 1. The cyan and blue spheres represent Zn centres and tipm ligands, respectively. The thin and thick red lines represent the single carboxylate bridge in the 1D $[Zn_2(1,3-BDC)_2]_n$ chain and the double carboxylate bridge in the $[Zn_2(1,3-BDC)_2]$ unit, respectively. Symmetry codes: A: x, -y, z + 1/2; B: -x + 1, y - 1, -z + 3/2; C: -x + 1/2, -y + 1/2, -z + 2; D: -x + 1/2, -y + 1/2, -z + 1; all H atoms are omitted for clarity.



Table 1. Selected bond lengths [Å] and angles [°] for 1 and 2.^[a]

7 (1) 0 (2.1)	
Zn(1) - O(3A)	1.996(5)
Zn(1)-N(5B)	2.003(6)
Zn(2)–O(7C)	1.939(5)
Zn(2)–N(7D)	1.987(6)
O(1)-Zn(1)-N(1)	111.3(2)
O(1)-Zn(1)-N(5B)	103.2(2)
N(1)-Zn(1)-N(5B)	129.2(3)
O(5)-Zn(2)-N(7D)	119.3(3)
O(5)-Zn(2)-N(3)	110.2(3)
N(7D)-Zn(2)-N(3)	106.3(2)
Co(1)–O(3A)	1.999(3)
Co(1)-N(3B)	2.014(4)
Co(2)–O(7C)	1.954(4)
Co(2)–N(7D)	2.007(3)
O(1) - Co(1) - N(3)	107.79(14)
O(1)-Co(1)-N(1)	103.25(14)
N(3)-Co(1)-N(1)	130.42(16)
O(5)–Co (2)–N(7D)	121.58(16)
O(5)–Co(2)–N(5)	111.99(15)
N(7D)-Co(2)-N(5)	105.53(13)
	$\begin{array}{c} Zn(1)-O~(3A)\\ Zn(1)-N(5B)\\ Zn(2)-O(7C)\\ Zn(2)-N(7D)\\ O(1)-Zn(1)-N(1)\\ O(1)-Zn(1)-N(5B)\\ N(1)-Zn(1)-N(5B)\\ O(5)-Zn(2)-N(7D)\\ O(5)-Zn(2)-N(3)\\ N(7D)-Zn(2)-N(3)\\ N(7D)-Zn(2)-N(3)\\ \hline \\ Co(1)-O(3A)\\ Co(1)-N(3B)\\ Co(2)-O(7C)\\ Co(2)-N(7D)\\ O(1)-Co(1)-N(3)\\ O(1)-Co(1)-N(3)\\ O(1)-Co(1)-N(1)\\ N(3)-Co(1)-N(1)\\ N(3)-Co(1)-N(1)\\ O(5)-Co(2)-N(7D)\\ O(5)-Co(2)-N(5)\\ N(7D)-Co(2)-N(5)\\ \end{array}$

[a] Symmetry codes for 1: A: x, -y, z + 1/2; B: -x + 1, y - 1, -z + 3/2; C: -x + 1/2, -y + 1/2, -z + 2; D: -x + 1/2, -y + 1/2, -z + 1; symmetry codes for 2: A: x, -y, z + 1/2; B: -x + 1, y - 1, -z + 3/2; C: -x + 1/2, -y + 1/2, -z + 2; D: -x + 1/2, -y + 1/2, -z + 1.

(a/S) data were calculated from the reflectance by using the Kubelka–Munk (K–M) function:^[13]

 $a/S = \frac{(1-R)^2}{2R}$

a is the absorption, *S* is the scattering coefficient, and *R* is the reflectance at a given energy. The band gap energies (E_{onset}) obtained by extrapolation of the linear portion of the absorption edges were estimated to be 2.25 (1), 1.38 (2), 1.80V (1a) and 1.77 eV (2a), which are in the semiconductor range (Figure 2).



Figure 2. K-M functions versus energy [eV] for 1, 2, 1a and 2a.

The photocatalytic activities of the undoped CPs 1 and 2 and the doped CPs 1a and 2a were evaluated by measuring the degradation of RhB in aqueous solution by absorp-

tion spectroscopy. The λ_{max} at 554 nm for RhB (Figure S8) decreased with the irradiation time and particularly in the presence of 1, 2, 1a and 2a. RhB decomposed very slowly without any catalyst under the same conditions (Figure S9). Plots of $\log(c_t/c_0)$ versus irradiation time are given in Figure 3. When the reaction solutions were mixed with equimolar catalyst and irradiated by UV light, each substrate was almost completely decomposed within 4 h (for 1 at 4 h, 95%; for 2 at 3 h, 97%; for 1a at 2.5 h, 94%; and for 2a at 2 h, 90%). A comparison of the photodegradation parameters for reactions catalyzed by 1, 2, 1a, 2a and some known catalysts is presented in Table 2. The times required for almost complete degradation of RhB in the presence of 1a and 2a were comparable to those of Fe₃O₄@SiO₂@TiO₂/ graphene oxide $(2 \text{ h}, 92\%)^{[14a]}$ and Ag/Pt@TiO₂ (2.5 h, 99%)^[14b] and significantly shorter than those (9 h) required with the photocatalysts (3-H₂pya)[(3-Hpya)₂Ag]- $[AgAlMo_6H_6O_{24}]$ ·3H₂O [pyrolysis, 3-Hpya = 3-(3-pyridyl)acrylic acid], HNa₂[(3-pya)(3-Hpya)Ag]₂[AlMo₆H₆O₂₄]· 8H₂O (pyrolysis) and [(3-Hpya)₂Ag][(H₂O)₂Ag]₂[Al-Mo₆H₆O₂₄]·2H₂O (pyrolysis).^[14c] The degree of degradation after 4 h for reactions catalyzed by $[La(HL)(L)(H_2O)_6 \{La(H_2L)_{0.5}(\alpha - PW_{11}O_{39}H)La(H_2O)_4\}]_2 \cdot 8H_2O, [Ce(HL)(L) (H_2O)_6\{Ce(H_2L)_{0.5}(\alpha-PW_{11}O_{39}H)Ce(H_2O)_4\}]_2\cdot 12H_2O$ and $[Pr(HL)(L)(H_2O)_6\{Pr(H_2L)_{0.5}(\alpha - PW_{11}O_{39}H)Pr(H_2O)_4\}]_2 \cdot$ $8H_2O$ ($H_2L = 2,5$ -pyridinedicarboxylic acid) were 60, 56 and 45%, respectively.^[14d] These results indicate that the doped CPs 1a and 2a are superior photocatalysts than the undoped CPs 1 and 2 and that all four CPs are comparable or better than previously reported photocatalysts, for which comparison is possible. Moreover, 2a could be recovered from the catalytic system by centrifugation and reused for a fresh photodegradation. This catalyst showed no significant decrease in efficiency even after five cycles (Figure S10). The PXRD patterns of the recycled catalyst were almost identical to those of the freshly made material; therefore, its original structural framework was retained during the photocatalytic degradation process (Figure S11). After the



Figure 3. Photocatalytic degradation rate of RhB as a function of irradiation time in the presence of catalysts 1 (green), 2 (blue), 1a (yellow) and 2a (pink). A control experiment without any catalyst (black) was run under the same conditions.



Table 2.	Comparison	of the efficienc	y of the c	catalytic 1	ohotodegradation	of RhB w	vith different	catalysts
			2	~ ~ ~	<u> </u>			~

Catalyst	Reaction time [h]	Photocatalytic efficiency [%]	Ref.
1	4	95	this work
2	3	97	this work
1a	2.5	94	this work
2a	2	90	this work
Fe ₃ O ₄ @SiO ₂ @TiO ₂ /GO	2	92	[14a]
Ag/Pt@TiO ₂	2.5	99	[14b]
(3-H ₂ pya)[(3-Hpya) ₂ Ag][AgAlMo ₆ H ₆ O ₂₄]·3H ₂ O (pyrolysis)	9	94	[14c]
HNa ₂ [(3-pya)(3-Hpya)Ag] ₂ [AlMo ₆ H ₆ O ₂₄]·8H ₂ O (pyrolysis)	9	95	[14c]
$[(3-Hpya)_2Ag][(H_2O)_2Ag]_2[A1Mo_6H_6O_{24}]\cdot 2H_2O$ (pyrolysis)	9	90	[14c]
$[La(HL)(L)(H_2O)_6 \{La(H_2L)_{0.5}(\alpha - PW_{11}O_{39}H)La(H_2O)_4\}]_2 \cdot 8H_2O$	4	60	[14d]
$[Ce(HL)(L)(H_2O)_6 \{Ce(H_2L)_{0.5}(\alpha - PW_{11}O_{39}H)Ce(H_2O)_4\}]_2 \cdot 12H_2O$	4	56	[14d]
$[Pr(HL)(L)(H_2O)_6\{Pr(H_2L)_{0.5}(\alpha - PW_{11}O_{39}H)Pr(H_2O)_4\}]_2 \cdot 8H_2O$	4	45	[14d]

photodegradation of RhB, the final solution was filtered and extracted with diethyl ether, and the organic phase was analyzed by LC–MS. No other organic species were observed; thus, we assumed that the RhB was converted into CO_2 and H_2O .^[15]

To exclude the possibility that soluble metal ions assisted the RhB degradation, two control experiments were conducted (Figures 4 and S12). In the first, RhB solution was stirred with the catalysts overnight. In the second, the RhB solution was readjusted to 3×10^{-4} M by the addition of RhB into the centrifuged solutions after the photocatalytic degradation. As indicated in Figure 4, the degradation of RhB in the two control experiments was almost identical to the rate of the catalyst-free reaction. However, Zn(NO₃)₂ and Co(NO₃)₂ (1×10⁻⁴ M) could gradually degrade RhB (ca. 75% after 4 h, Figure S13) under similar conditions. These results indicated that there were no soluble metal ions in the degradation system and that the catalysts did not decompose or leach ions during this reaction.



Figure 4. Degradation of RhB as a function of irradiation time by 1 under UV light. Black: the RhB solution without catalyst; red: the RhB solution with the catalyst; blue: the filtrate after the RhB solution was stirred with the catalyst overnight; pink: the RhB solution that was readjusted to 3×10^{-4} M by the addition of RhB into the centrifuged solution after the photocatalytic degradation.

The mechanism for the photocatalytic degradation of organic molecules by metal catalysts in aqueous solution was reported^[4a,4b] to involve the following steps: electrons (e^-) of the metal complexes are excited from the valence band (VB) to the conduction band (CB), and simultaneously, the same number of holes (h⁺) are formed in the VB. Then, O₂ or OH⁻ adsorbed on the surfaces of the complexes interact with the electrons (e⁻) of the CB or holes (h⁺) in the VB, respectively, to form hydroxy radicals (•OH). The hydroxy radicals are highly active and decompose the organic pollutants into CO₂ and H₂O (Scheme S1a). The doped catalysts possess a narrower band gap (E_g) than the undoped catalysts, which may accelerate this photocatalytic activity (Scheme S1b).

Conclusions

We have demonstrated the formation of the isostructural coordination polymers 1 and 2 from the reactions of $Zn(NO_3)_2$ or $Co(NO_3)_2$ with tipm and 1,3-H₂BDC under solvothermal conditions. These coordination polymers have a unique 3D framework with a Schläfli symbol $(4\cdot7^2)(6^{2}\cdot7^3\cdot12)(4\cdot6^{2}\cdot7^3)$. Under the irradiation of UV light (365 nm), compounds 1 and 2 exhibit good catalytic activity in the photodegradation of RhB. The partial isomorphic substitution of Zn by Co ions is described, and the resulting doped CPs 1a and 2a have higher photocatalytic activities than the undoped catalysts 1 and 2. As a representative example, 2a can be recycled and reused at least five times without the loss of catalytic photodegradation performance. These results further demonstrate the importance of metal doping to the tuning of the properties of materials.

Experimental Section

General Methods: Chemicals and reagents were obtained from commercial sources and used as received. Tetrakis(4-bromophenyl) methane was prepared from tetraphenylmethane by a literature method.^[10] Infrared spectra (KBr disk, 400–4000 cm⁻¹) were obtained with a Nicolet iS10 spectrometer. Elemental analyses for C, H and N were performed with a Carlo–Erba CHNO-S microanalyzer. Thermogravimetric analysis (TGA) was performed with a TA SDT-2960 analyzer (heating rate of 10 °C/min). The PXRD measurements were performed with a PANalytical X'Pert PRO MPD system (PW3040/60). The solid-state UV/Vis spectra were recorded with a Shimadzu UV-3150 spectrometer at room temperature in the range $\lambda = 200-800$ nm. The UV/Vis absorption spectra of RhB aqueous solutions were recorded with a Varian Cary-50 UV/Vis spectrophotometer.



Tetrakis[4-(1-imidazolyl)phenyl]methane (tipm): A mixture of tetrakis(4-bromophenyl)methane (0.636 g, 1 mmol), imidazole (0.68 g, 10 mmol), K₂CO₃ (0.828 g, 6 mmol) and CuI (0.076 g, 0.4 mmol) was finely ground and then heated under microwave irradiation (720 W) for 90 s (Scheme 1). The resultant mixture was poured into water (10 mL), ethylenediaminetetraacetic acid (EDTA; 0.117 g, 0.4 mmol) and NH₃·H₂O (25-28%, 0.5 mL) were added, and the mixture was stirred for 5 h. The solid product was collected by filtration, washed with water and then purified by recrystallization from MeOH/H₂O (1:4 v/v) to afford yellow crystals, which were dried under vacuum to afford tpim as a light yellow powder, yield 0.528 g [90%, based on tetrakis(4-bromophenyl) methane]. C37H28N8 (584.69): calcd. C 76.01, H 4.83, N 19.17; found C 75.96, H 4.82, N 19.22. IR (KBr disk): $\tilde{v} = 3410$ (m), 3111 (m), 1606 (m), 1517 (s), 1423 (w), 1305 (s), 1245 (w), 1192 (w), 1108 (m), 1057 (s), 963 (m), 818 (s), 737 (m), 658 (m), 559 (m) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 298 K, TMS): δ = 7.87 (s, 4 H, imidazole ring), 7.38 (s, 16 H, benzene ring), 7.29 (s, 4 H, imidazole ring), 7.21 (s, 4 H, imidazole ring) ppm (Figure S1). ¹³C NMR $(75.4 \text{ MHz}, \text{CDCl}_3, 298 \text{ K}): \delta = 144.7, 135.8, 135.4, 132.1, 130.7,$ 120.8, 117.9, 63.7 ppm (Figure S2). HRMS (EI): calcd. for C₃₇H₂₈N₈ [M]⁺ 584.2437; found 584.2442 (error: 0.86 ppm).



Scheme 1. Synthesis of the tipm ligand.

[Zn₂(tipm)(1,3-BDC)₂] (1): A mixture of Zn(NO₃)₂·6H₂O (0.030 g, 0.10 mmol), tipm (0.029 g, 0.05 mmol) and 1,3-H₂BDC (0.016 g, 0.10 mmol) in CH₃CN (0.5 mL) and H₂O (2.0 mL) was sealed in a glass tube and then heated at 150 °C for 24 h. The solution was cooled to room temperature at the rate of 5 °C/h to produce yellow block crystals of **1**, which were collected by filtration, washed with water and EtOH, and dried in air, yield 0.032 g (62% based on tipm). C₅₃H₃₆N₈O₈Zn₂ (1043.64): calcd. C 60.99, H 3.48, N 10.74; found C 60.12, H 3.59, N 10.12. IR (KBr disk): $\tilde{v} = 3454$ (m), 3136 (m), 1614 (s), 1563 (m), 1524 (s), 1374 (s), 1313 (m), 1126 (w), 1068 (s), 966 (m), 828 (m), 753 (s), 728 (m), 655 (m), 561 (w) cm⁻¹.

[Co₂(tipm)(1,3-BDC)₂]·0.5CH₃CN (2·0.5CH₃CN): Compound 2·0.5CH₃CN was separated as blue block crystals by a similar method to that described above for the preparation of 1 with Co(NO₃)₂·6H₂O (0.030 g, 0.1 mmol), tipm (0.029 g, 0.05 mmol) and 1,3-H₂BDC (0.016 g, 0.10 mmol), yield 0.028 g (54% based on tipm). C₅₄H_{37.5}Co₂N_{8.5}O₈ (1051.28): calcd. C 61.69, H 3.60, N 11.32; found C 61.01, H 3.79, N 10.97. IR (KBr disk): $\tilde{v} = 3445$ (m), 3137 (w), 2210 (w), 1608 (s), 1557 (m), 1520 (s), 1372 (s), 1311 (m), 1269 (w), 1124 (s), 1145 (w), 1067 (s), 965 (w), 825 (m), 751 (m), 725 (m), 655 (m), 560 (w) cm⁻¹.

 $[Zn_{(2-2x)}Co_{2x}(tipm)(1,3-BDC)_2]\cdot bH_2O$ (x = 2.4%, b = 0 for 1a, x = 23%, b = 1 for $2a \cdot H_2O$): Compound 1a was separated as orange block crystals by a similar method to that described for the preparation of 1 with Zn(NO_3)_2\cdot 6H_2O (0.030 g, 0.10 mmol), Co(NO_3)_2. 6H_2O (0.030 g, 0.10 mmol), tipm (0.029 g, 0.05 mmol) and 1,3-H_2BDC (0.016 g, 0.10 mmol), yield 0.028 g (55% based on tipm). Compound **2a**·H₂O was separated as red block crystals by the same procedure with Zn(NO₃)₂·6H₂O (0.015 g, 0.05 mmol), Co(NO₃)₂·6H₂O (0.030 g, 0.10 mmol), tipm (0.029 g, 0.05 mmol) and 1,3-H₂BDC (0.016 g, 0.10 mmol), yield 0.021 g (40% based on tipm). The formulas were determined by atomic absorption spectroscopy (AAS) and elemental analyses. Compound **1a**: $C_{53}H_{36}N_8O_8Zn_{1.95}Co_{0.05}$ (1043.33): calcd. C 61.01, H 3.48, N 10.74; found C 60.32, H 3.65, N 10.01. IR (KBr disk): $\tilde{v} = 3432$ (m), 3136 (m), 1612 (s), 1561 (m), 1522 (s), 1367 (s), 1312 (m), 1270 (w), 1126(w), 1068 (s), 966 (m), 827 (m), 750 (s), 728 (m), 655 (m), 561 (w) cm⁻¹. Compound **2a**·H₂O: $C_{53}H_{38}Co_{0.46}N_8O_9Zn_{1.54}$ (1058.69): calcd. C 60.12, H 3.62, N 10.58; found C 59.78, H 3.92, N 10.29. IR (KBr disk): $\tilde{v} = 3431$ (m), 3136 (m), 1612 (s), 1563 (m), 1522 (s), 1368 (s), 1312 (m), 1270 (w), 1125 (m), 1068 (s), 966 (m), 828(m), 750 (s), 728 (m), 651 (w) cm⁻¹.

Crystallographic Data Collection and Refinement: Single crystals of **1**, **2**•0.5CH₃CN, **1a** and **2a**•H₂O suitable for X-ray analysis were obtained directly from the above preparations. With an enhanced X-ray source (Mo- K_a , $\lambda = 0.71073$ Å), the data for **1** and **1a** were recorded with a Rigaku Saturn 724 CCD diffractometer, the data for **2** were recorded with a Bruker D8 QUEST diffractometer, and the data for **2a** were recorded with an Aglient Gemini Atlas diffractometer. Each single crystal was mounted on a glass fibre at 293 K. The cell parameters were refined with the programs CrystalClear (version 1.3, Rigaku Inc.), Bruker-SAINT and CrysAlis-Pro (version 1.171.36.32, Agilent Technologies), respectively, and absorption corrections (multiscan) were applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXL-2013 program.^[16] A large amount of spatially delocalized electron density in the lattice of each compound was found, but acceptable refinement results could not be obtained for this electron density. Thus, the water solvent contribution to the scattering factors has been taken into account with SQUEEZE in the Platon program suite. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. Selected bond lengths and bond angles for 1 and 2 are listed in Table 1. A summary of key crystallographic data for 1, 2, 1a and 2a is given in Table 3.

CCDC-1033791 (for 1), -1033792 (for $2 \cdot 0.5$ CH₃CN), -1041854 (for 1a) and -1041844 (for $2a \cdot H_2$ O) 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/datarequest/cif.

Photocatalytic Activity Study: The photocatalytic activities of the solid samples **1**, **2**, **1a** and **2a** were evaluated for the model degradation of RhB in aqueous solution. An aqueous solution (50 mL) of RhB with a concentration of 0.14 g L^{-1} (ca. $3 \times 10^{-4} \text{ M}$) was mixed with the catalyst (10 mg), magnetically stirred in the dark for 2 h to ensure the equilibrium of adsorption/desorption and then irradiated with a 400W (365 nm) high-pressure mercury lamp. The mixture was stirred continuously with a magnetic stirrer. At regular time intervals, a 1 mL sample was collected, filtered and diluted to 10 mL in a volumetric flask. The UV/Vis absorption maxima of RhB at 554 nm was chosen to monitor the photocatalytic degradation process.

Supporting Information (see footnote on the first page of this article): ¹H and ¹³C NMR spectra of tipm, PXRD patterns, TGA plots and photocatalytic spectra of 1, 2, 1a and 2a.

	1	2 •0.5CH ₃ CN	1a	$2a \cdot H_2O$
Chemical formula	$C_{53}H_{36}N_8O_8Zn_2$	C ₅₄ H _{37.5} N _{8.5} O ₈ Co ₂	$C_{53}H_{36}N_8O_8Co_{0.05}Zn_{1.95}$	$C_{53}H_{38}N_8O_9Zn_{1.54}Co_{0.46}$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	C2/c	C2/c
Crystal size /mm	$0.30 \times 0.30 \times 0.20$	$0.25 \times 0.20 \times 0.10$	$0.40 \times 0.40 \times 0.30$	$0.40 \times 0.30 \times 0.30$
a /Å	41.021(8)	40.575(5)	40.999(8)	40.6544(13)
b /Å	14.365(3)	14.3747(16)	14.353(3)	14.3377(5)
c /Å	20.259(4)	20.156(3)	20.257(4)	20.2429(5)
β /°	108.59(3)	108.058(3)	108.79(3)	108.733(3)
$V/Å^3$	11315(4)	11177(2)	11285(4)	11174.3(6)
Ζ	8	8	8	8
$D_{\rm calcd.}/{\rm gcm^{-3}}$	1.225	1.249	1.228	1.259
F(000)	4272	4312	4271	4341
μ (Mo- K_{α}) /mm ⁻¹	0.903	0.651	0.899	0.856
Total reflections	44732	120694	31068	40156
Unique reflections	9936	10269	12821	14693
Observed reflections $[I > 2\sigma(I)]$	7046	8865	6960	8599
Parameters	640	668	640	662
R _{int}	0.0726	0.0172	0.1107	0.0771
$R^{[a]}$	0.0628	0.0561	0.0800	0.0619
$wR^{[b]}$	0.1561	0.1705	0.2134	0.1969
GOF ^[c]	1.065	1.031	0.993	1.010
Residual peaks /e Å ⁻³	0.807, -0.309	2.073, -0.510	0.766, -0.308	1.554, -0.914

Table 3. Summary	of crystal	data and	structure r	refinement	parameters for	or 1, 2,	1a and 2a.
------------------	------------	----------	-------------	------------	----------------	----------	------------

[a] $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. [b] $wR = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$. [c] GOF = $\{\Sigma w [(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$, n = number of reflections, and p = total number of parameters refined.

Acknowledgments

The authors thank the National Natural Science Foundation of China (NSFC) (grant numbers 21171124, 21271134 and 21373142) and the State Key Laboratory of Organometallic Chemistry of Shanghai Institute of Organic Chemistry (grant number 201201006) for financial support. J. P. L. also highly appreciates the support by the Qing-Lan Project and the "333" Project of Jiangsu Province, the Priority Academic Program Development of Jiangsu Higher Education Institutions, and the "SooChow Scholar" Program of Suzhou University.

- a) H. R. Pouretedal, A. Norozi, M. H. Keshavarz, A. Semnani, J. Hazard. Mater. 2009, 162, 674–681; b) S. S. Martínez, E. V. Uribe, Ultrason. Sonochem. 2012, 19, 174–178; c) L. Alamo-Nole, S. Bailon-Ruiz, T. Luna-Pineda, O. Perales-Perezab, F. R. Romana, J. Mater. Chem. A 2013, 1, 5509–5516; d) M. Mrowetz, C. Pirola, E. Selli, Ultrason. Sonochem. 2003, 10, 247–254.
- [2] a) L. L. Wen, F. Wang, J. Feng, K. L. Lv, C. G. Wang, D. F. Li, Cryst. Growth Des. 2009, 9, 3581–3589; b) J. Lv, J. X. Lin, X. L. Zhao, R. Cao, Chem. Commun. 2012, 48, 669–671; c) P. P. Zhang, J. Peng, H. J. Pang, J. Q. Sha, M. Zhu, D. D. Wang, M. G. Liu, Z. M. Su, Cryst. Growth Des. 2011, 11, 2736–2742; d) Z. M. El-Bahy, A. A. Ismail, R. M. Mohamed, J. Hazard. Mater. 2009, 166, 138–143; e) D. Chatterjee, A. Mahata, J. Photochem. Photobiol. A: Chem. 2002, 153, 199–204.
- [3] a) A. Fujishima, T. N. Rao, D. A. Tryk, J. Photochem. Photobiol. C: Photochem. Rev. 2000, 1, 1–21; b) R. Asahi, T. Morikawa, T. Okwaki, K. Aoki, Y. Taga, Science 2001, 293, 269–271; c) T. E. Dolla, F. H. Frimmela, Acta Hydrochim. Hydrobiol. 2004, 32, 201–213; d) D. Ye, D. Z. Li, W. J. Zhang, M. Sun, Y. Hu, Y. F. Zhang, X. Z. Fu, J. Phys. Chem. C 2008, 112, 17351–17356; e) J. R. Li, Y. Tao, Q. Yu, X. H. Bu, Chem. Commun. 2007, 1527–1529; f) C. Wang, Z. G. Xie, K. E. de-Krafft, W. B. Lin, J. Am. Chem. Soc. 2011, 133, 13445–13454; g) Y. Gong, T. Wu, J. H. Lin, CrystEngComm 2012, 14, 3727–

3736; h) X. L. Wang, J. J. Huang, L. L. Liu, G. C. Liu, H. Y. Lin, J. W. Zhang, N. L. Chen, Y. Qu, *CrystEngComm* **2013**, *15*, 1960–1969.

- [4] a) T. Wen, D. X. Zhang, J. Zhang, *Inorg. Chem.* 2013, *52*, 12–14; b) Y. Q. Chen, G. R. Li, Y. K. Qu, Y. H. Zhang, K. H. He, Q. Gao, X. H. Bu, *Cryst. Growth Des.* 2013, *13*, 901–907; c) L. Liu, J. Ding, C. Huang, M. Li, H. W. Hou, Y. T. Fan, *Cryst. Growth Des.* 2014, *14*, 3035–3025; d) Y. L. Hou, R. W. Y. Sun, X. P. Zhou, J. H. Wang, D. Li, *Chem. Commun.* 2014, *50*, 2295–2297; e) W. Q. Kan, B. Liu, J. Yang, Y. Y. Liu, J. F. Ma, *Cryst. Growth Des.* 2012, *12*, 2288–2298.
- [5] a) C. Wang, Z. G. Xie, K. E. deKrafft, W. B. Lin, J. Am. Chem. Soc. 2011, 133, 13445–13454; b) H. Yang, X. W. He, F. Wang, Y. Kang, J. Zhang, J. Mater. Chem. 2012, 22, 21849–21851; c) X. X. Xu, Z. P. Cui, X. Gao, X. X. Liu, Dalton Trans. 2014, 43, 8805–8813.
- [6] a) M. Li, D. Li, M. O'Keeffe, O. M. Yaghi, *Chem. Rev.* 2014, *114*, 1343–1370; b) T. R. Cook, Y. R. Zheng, P. J. Stang, *Chem. Rev.* 2013, *113*, 734–777; c) Y. B. Xie, H. Yang, Z. Y. U. Wang, Y. Y. Liu, H. C. Zhou, J. R. Li, *Chem. Commun.* 2014, *50*, 563–565; d) M. W. Zhang, M. Bosch, T. Gentle, H. C. Zhou, *CrystEngComm* 2014, *16*, 4069–4083; e) F. Y. Han, Y. J. Lin, W. G. Jia, G. L. Wang, G. X. Jin, *Chem. Commun.* 2008, *44*, 1807–1809; f) H. L. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* 1999, *402*, 276–279; g) M. Eddaoudi, J. Kim, N. Rsi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* 2002, *295*, 469–472; h) F. Luo, J. M. Zhang, S. R. Batten, *Chem. Commun.* 2007, 3744–3746.
- [7] a) D. Liu, H. X. Li, Z. G. Ren, Y. Chen, Y. Zhang, J. P. Lang, *Cryst. Growth Des.* 2009, *9*, 4562–4566; b) D. X. Li, C. Y. Ni, M. M. Chen, M. Dai, W. H. Zhang, W. Y. Yan, H. X. Qi, Z. G. Ren, J. P. Lang, *CrystEngComm* 2014, *16*, 2158–2167; c) H. Y. Bai, J. F. Ma, J. Yang, Y. Y. Liu, H. Wu, J. C. Ma, *Cryst. Growth Des.* 2010, *10*, 995–1016; d) Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* 2001, *123*, 980–981; e) R. Natarajan, G. Savitha, J. N. Moorthy, *Cryst. Growth Des.* 2005, *5*, 69–72; f) R. Natarajan, G. Savitha, P. Dominiak, K. Wozniak, J. N. Moorthy, *Angew. Chem. Int. Ed.* 2005, *44*, 2115–2119.



- [8] a) J. N. Moorthy, R. Natarajan, G. Savitha, P. Venugopalan, *Cryst. Growth Des.* 2006, *6*, 919–924; b) J. Fan, B. E. Hanson, *Inorg. Chem.* 2005, *44*, 6998–7008; c) G. C. Xu, Q. Hua, T. Okamura, Z. S. Bai, Y. J. Ding, Y. Q. Huang, G. X. Liu, W. Y. Sun, N. Ueyama, *CrystEngComm* 2009, *11*, 261–270; d) Q. Hua, Y. Zhao, G. C. Xu, M. S. Chen, Z. Su, K. Cai, W. Y. Sun, *Cryst. Growth Des.* 2010, *10*, 2553–2562; e) L. Luo, P. Wang, G. C. Xu, Q. Liu, K. Chen, Y. Lu, Y. Zhao, W. Y. Sun, *Cryst. Growth Des.* 2012, *12*, 2634–2645.
- [9] C. N. Lü, M. M. Chen, W. H. Zhang, D. X. Li, M. Dai, J. P. Lang, *CrystEngComm* **2015**, *17*, 1935–1943.
- [10] a) J. Choi, H. Y. Yang, H. J. Kim, S. U. Son, *Angew. Chem. Int. Ed.* **2010**, *49*, 7718–7722; b) P. Ganesan, X. Yang, J. Loos, T. J. Savenije, R. D. Abellon, H. Zuihof, E. J. R. Sudhlter, *J. Am. Chem. Soc.* **2005**, *127*, 14530–14531.
- [11] J. A. Hua, Y. Zhao, Q. Liu, D. Zhao, K. Chen, W. Y. Sun, CrystEngComm 2014, 16, 7536–7546.
- [12] a) S. C. Rasmussen, R. L. Schwiderski, M. E. Mulholland, *Chem. Commun.* 2011, 47, 11394–11410; b) F. Wang, Z. S. Liu,

H. Yang, Y. X. Tan, J. Zhang, Angew. Chem. Int. Ed. 2011, 50, 450–453.

- [13] W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, **1966**.
- [14] a) F. H. Chen, F. F. Yan, Q. T. Chen, Y. W. Wang, L. F. Han, Z. J. Chen, S. M. Fang, *Dalton Trans.* 2014, *43*, 13537–13544;
 b) Z. F. Jiang, J. J. Zhu, D. Liu, W. Wei, J. M. Xie, M. Chen, *CrystEngComm* 2014, *16*, 2384–2394; c) Y. Hu, H. Y. An, X. Liu, J. Q. Yin, H. L. Wang, H. Zhang, L. Wang, *Dalton Trans.* 2014, *43*, 2488–2498; d) K. Wang, D. D. Zhang, J. C. Ma, P. T. Ma, J. Y. Niu, J. P. Wang, *CrystEngComm* 2012, *14*, 3205–3212.
- [15] a) M. C. Das, H. Xu, Z. Y. Wang, G. Srinivas, W. Zhou, Y. F. Yue, V. N. Nesterov, G. D. Qian, B. L. Chen, *Chem. Commun.* 2011, 47, 11715–11717; b) Y. Q. Chen, S. J. Liu, Y. W. Li, G. R. Li, K. H. He, Y. K. Qu, T. L. Hu, X. H. Bu, *Cryst. Growth Des.* 2012, 12, 5426–5431.
- [16] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122. Received: January 22, 2015

Published Online: March 9, 2015