Synthesis and characterization of a series of complexes with enhanced visible-light photocatalytic hydrogen evolution

Yanju Huang¹, Jiayin Wang¹ and Jun Zhang²

Abstract
The complexes \([\text{Ni}(\text{HNOR})_2]_n\cdot5n\text{H}_2\text{O}\) (1), \([\text{Cd}(\text{HNOR})_2]_n\) (2), \([\text{Zn}(\text{HNOR})_2\cdot2\text{H}_2\text{O}]_n\cdot2n\text{NO}_3\) (3), and \([\text{Co}(\text{H}_2\text{NOR})_2\cdot2\text{H}_2\text{O}]_n\cdot2n\text{NO}_3\) (4) (\(\text{H}_2\text{NOR}\)=norfloxacin) are synthesized by a hydrothermal process. The structures of the complexes are determined by single-crystal X-ray diffraction. The complexes are also characterized by infrared and elemental analysis. At the same time, the promoter catalytic properties of the complexes are studied under visible light, with complex 1 enhancing the catalytic performance of gCN from 407.4 to 914.1 \(\mu\text{mol h}^{-1}\text{g}^{-1}\) and complex 4 enhancing the catalytic performance of gCN from 407.4 to 943.9 \(\mu\text{mol h}^{-1}\text{g}^{-1}\). Complexes 1 and 4 significantly enhance visible-light photocatalytic hydrogen evolution.

Keywords
complex, gCN, hydrothermal process, photocatalytic hydrogen evolution, promoter catalytic materials

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Complexes \([\text{Ni}(\text{HNOR})_2]_n\cdot5n\text{H}_2\text{O}\) (1), \([\text{Cd}(\text{HNOR})_2]_n\) (2), \([\text{Zn}(\text{HNOR})_2\cdot2\text{H}_2\text{O}]_n\cdot2n\text{NO}_3\) (3), and \([\text{Co}(\text{H}_2\text{NOR})_2\cdot2\text{H}_2\text{O}]_n\cdot2n\text{NO}_3\) (4).

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Introduction

Metal complexes are formed by the central atom providing the empty orbital and the coordinating atom providing the lone pair of electrons. In such complexes, oxygen and nitrogen atoms—due to their electronic configuration, electronegativity, and so on—can coordinate with many metals, and there are many different possible bonding modes.1–4 Due to their unique structural modification and composition diversity, metal complexes have a wide range of applications in catalysis, magnetism, luminescence, electrochemical sensing, and so on.5–9

Since 1982, when Lehn first described the photocatalysis of Ru-pyridine and Co-pyridine complexes, catalysis systems involving complexes have aroused wide academic interest and contribute to greener processes.10,11

Metal complexes can be used as catalytic materials, while their metal-directed self-assembly represents a powerful synthetic methodology for supramolecular architectures that have the advantages of flexible regulation at the molecular level and have characteristics of both inorganic and organic compounds.12–14 This ordered coordination improves their visible-light absorption ability and accelerates photo-generated charge mobility.15–18

Norfloxacin as a ligand was studied many years ago because of its multiple coordination sites; although similar complexes have been synthesized, there are some differences in the structures and X-ray crystallographic studies on similar structures have not been previously reported.19,20 Based on the above considerations, we have synthesized a series of complexes: [Ni(HNOR)2]n·5nH2O (1), [Cd(HNOR)2]n (2), [Zn(HNOR)2·2H2O] (3), and [Co(H2NOR)2·2H2O]n·2nNO3 (4) as promoter catalytic materials of conjugated graphitic carbon nitride (gCN).

Results and discussion

Description of crystal structures

[Ni(HNOR)2]n·5nH2O (1). Single-crystal X-ray diffraction analysis showed that complex 1 crystallizes in the P2/n space group. The asymmetric unit of the complex 1 includes one Ni(II) ion, two HNOR− ligands and five free water molecules (Figure 1(a)). The central Ni(II) atom is coordinated with two oxygen atoms (O1 and O2), and one nitrogen atom (N3) from the HNOR− ligands and symmetric HNOR− ligands to form an octahedral structure. Due to the presence of unequal bond lengths (Table 1), the actual structure of complex 1 is a deformed octahedron (Figure 2(a)).

Hydrogen bonds play an important role in the process of molecular crystal formation due to their electrostatic and directional properties. Oxygen atoms with large electronegativity and a small radius in the HNOR− ligands and in water molecules easily form hydrogen bonds (Table 2). The metal–ligand interactions and the hydrogen bond interactions turn complex 1 into a two-dimensional layered structure (Figure 3).

[Cd(HNOR)2]n (2). Single-crystal X-ray diffraction analysis revealed that the complex [Cd(HNOR)2]n (2) crystallized in the P21/c space group. The asymmetric unit of complex 2 consists of one cadmium ion and two HNOR− ligands (Figure 1(b)). The bond lengths of complex 2 are 2.268(4) Å to 2.303(3) Å for Cd–O and 2.353(4) Å for Cd–N (Table 1). As can be seen from Figure 2(b), complex 2 assumes a slightly deformed octahedral structure. Two asymmetric units of the complex are connected, forming a two-dimensional porous structure (Figure 4). In the porous structure, the solvent accessible volume is 1647.7 Å3, which is 12.2% of the total unit cell volume, as calculated by PLATON (assuming that the guest molecules have been removed).

[Zn(HNOR)2·2H2O] (3). Complex 3 adopts a C2/c space group. There are one zinc ion, two HNOR− ligands, and two coordinated water molecules in the asymmetric unit (Figure 1(c)). The HNOR− ligand and its symmetrical ligand are linked by a zinc ion to form a zero-dimensional “U” shaped structure. The zinc ion is coordinated with six oxygen atoms from the HNOR− ligand and two coordinated water molecules. The Zn–O bond lengths range from 2.020(4) Å to 2.097(3) Å, and the bond angles range from 85.51(14)° to 177.88(17)° (Table 1), forming a deformed octahedral structure (Figure 2(c)).

The π–π stacking interaction is an important spatial arrangement of aromatic compounds, which occurs in the ligands and symmetry two adjacent equivalent ligands, π–π stacking interaction is weak interaction between aromatic rings (Table 3). Through such π–π stacking interactions, complex 3 forms a two-dimensional layered structure (Figure 5). The two-dimensional layered structure is porous. According to the PLATON calculation, assuming that the guest molecules have been removed, the solvent accessible volume is 4634.0 Å3, which is 35.9% of the total unit cell volume.

[Co(H2NOR)2·2H2O]·2nNO3 (4). Complex 4 occupies a P–1 space group. In the asymmetric unit, there are one cobaltion, two H2NOR ligands, two coordinated water molecules, and two free nitrate ions (Figure 1(d)). The cobalt ion is coordinated to six oxygen atoms (Co–O bond lengths are 2.0311(14) Å and 2.1365(17) Å) from H2NOR and coordinated water molecules (Table 1), forming a deformed octahedral structure (Figure 2(d)). Figure 6 shows that asymmetric unit forms a two-dimensional layered structure via weak intermolecular forces (Tables 2 and 3).

Powder X-ray diffraction and infrared spectra

The crystallinity of the materials was analyzed by X-ray powder diffraction (XRD). The samples were milled and mounted on the sampling plate. The XRD patterns were recorded on an Advance Bruker X-ray diffractometer with the Cu Kα radiation (λ = 1.5406 Å, 40 kV, 40 mA), a step size of 0.02°, and a scanning rate of 1 step/0.8 s in the range of 10°–80°. Figure 7(a) shows the complexes 1–4/gCN. It can be seen that the composite photocatalysts can be compared with gCN, and that the experimental confirms that
Figure 1. The asymmetric units of complexes 1–4.

Table 1. Selected bond lengths (Å) and angles (°) for complexes 1–4.

| Complex | Bond Distance | Bond | Distance |
|---------|---------------|------|----------|
| [Ni(HNOR)$_2$]$_n$·5nH$_2$O (1) | Ni–O1 2.088 (3) | Ni–O2 1.994 (3) |
|         | Ni–N3 2.131 (3) | Angle (°) | Ni–O2A 86.81 (11) |
|         | O1–Ni–O1A 82.87 (15) | O1–Ni–O2 89.02 (11) |
|         | O1–Ni–O2A 92.19 (11) | O1–Ni–O2A 178.68 (14) |
|         | O1–Ni–N3A 168.81 (11) | O2–Ni–N3A 85.79 (12) |
|         | O2–Ni–N3 95.06 (12) | N3–Ni–N3A 99.98 (17) |
| [Cd(HNOR)$_2$]$_n$ (2) | Cd–O2 2.268 (4) | Cd–O3 2.303 (3) |
|         | Cd–N3 2.353 (4) | Angle (°) | Cd–O2A 79.89 (13) |
|         | O2–Cd–O2A 180.0 | O2–Cd–O3 89.02 (14) |
|         | O2–Cd–O2A 100.11 (13) | O2–Cd–O2A 89.02 (14) |
|         | O2–Cd–N3A 90.98 (14) | O3–Cd–O3A 180.0 |
|         | O3–Cd–N3 88.20 (14) | O3–Cd–N3A 91.80 (14) |
|         | O3–Cd–N3A 180.0 (3) | N3–Cd–N3A 180.0 |
| [Zn(HNOR)$_2$·2H$_2$O] (3) | Zn–O1 2.020 (4) | Zn–O3 2.097 (3) |
|         | Zn–O4 2.062 (4) | Angle (°) | Zn–O3A 86.2 (4) |
|         | O1–Zn–O1A 177.88 (17) | O1–Zn–O3 85.51 (14) |
|         | O1–Zn–O3A 92.93 (15) | O1–Zn–O3A 86.2 (2) |
|         | O1–Zn–O4A 89.08 (17) | O3–Zn–O4A 174.48 (17) |
|         | O3–Zn–O4 93.0 (2) | O3–Zn–O4A 174.48 (17) |
|         | O4–Zn–O4A 88.3 (4) | (Continued) |
Table 1. (Continued)

| Bond          | Distance   | Bond          | Distance   |
|---------------|------------|---------------|------------|
| Co–O1         | 2.0597 (12)| Co–O2         | 2.0311 (14)|
| Co–O4         | 2.1365 (17)| Angle         | (°)        |
| O1–Co–O1A     | 180.0      | O1–Co–O2      | 88.10 (5)  |
| O1–Co–O4      | 91.57 (7)  | O1–Co–O2A     | 91.90 (5)  |
| O1–Co–O4A     | 88.43 (7)  | O2–Co–O2A     | 180.0      |
| O2–Co–O4      | 87.95 (7)  | O2–Co–O4A     | 92.05 (7)  |
| O4–Co–O4A     | 180.0      |               |            |

Table 1. (Continued)

![Figure 2. Octahedral structures of complexes 1–4.](image)

the characteristic peaks of gCN were also observed in the XRD patterns of composite photocatalysts.

In addition, the bonding vibrations of the materials were observed by infrared (IR). The samples were mixed with KBr before molding to afford a round pill with 99 wt% of KBr. The IR spectra were recorded on a Nicolet 170SX spectrometer, with wavenumbers in the range of 4000–400 cm⁻¹, and with a step size of 1 cm⁻¹. The interactions between the complexes 1–4/gCN and gCN were studied by IR spectroscopy (Figure 7(b)). For the complexes 1–4/gCN and gCN, there are peaks at around 800, 1200–1400, 1600, and 3200 cm⁻¹, corresponding to the bending vibration of the triazine unit, the stretching bands of the heterocyclic C–N, C–O, –NH bonds, and the stretching vibrations of O–H, respectively.²¹ The obtained results confirm the formation of the composite photocatalysts and gCN.

UV-vis diffuse reflection Solid spectra and the Tauc’s plots

The influence of the addition of the complex on the optical properties of the as-prepared materials was observed via UV-Vis diffuse reflection solid (DRS). UV–vis DRS spectra of gCN and complexes 1–4/gCN shown in Figure 8(a), due to the modification of the complexes, all the composite photocatalysts showed a wider visible-light absorption range compared to gCN, leading to enhanced light energy absorption. Moreover, the direct band gaps ($E_g$) of
complexes 1/gCN, 2/gCN, 3/gCN, and 4/gCN, and gCN obtained from Tauc’s plots were 2.70, 2.66, 2.23, 2.61, and 2.54 eV, respectively (Figure 8(b)).

**Migration and separation efficiency of photo-generated charges**

To evaluate the separation of e\(^-\) and h\(^+\) in the materials prepared, photoluminescence (PL) and electrochemical impedance spectroscopy (EIS) were recorded. Figure 9(a) shows the PL spectra of the composite photocatalysts under light excitation at a wavelength of 350nm. It has been reported that a lower PL intensity is specific to a lower rate of recombination of photo-generated electron–hole pairs resulting in higher photocatalytic performance.\(^{22,23}\) The fluorescence intensity of complex 4/gCN is the lowest, while those of complexes 1/gCN and 2/gCN are the highest, followed by complex 3/gCN, which suggests that the combination of gCN with [Co(H\(_2\)NOR)\(_2\)·2H\(_2\)O]\(_n\)·2nNO\(_3\) and [Ni(HNOR)\(_2\)]\(_n\)·5nH\(_2\)O effectively suppresses the recombination of photo-generated e\(^-\) and h\(^+\). Complexes 4/gCN and 1/gCN have much higher photocatalytic activity compared to the other two composite photocatalysts.

The electron–hole pair recombination of the materials was further investigated by EIS spectra. Typically, a material will have a higher current and a smaller resistance, in other words, at the interface and the surface if the frequency of the EIS Nyquist semicircles becomes smaller.\(^{24,25}\) Figure 9(b) indicates that the arc radii of complexes 1/gCN

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**Table 2.** Hydrogen bonds (Å) and angles (°) for complexes 1 and 4.

| Donor–H ... Acceptor | D–H | H ... A | D ... A | Angle |
|----------------------|-----|--------|---------|-------|
| OW1–HW1A ... OW2     | 0.85| 1.99   | 2.838 (8)| 174   |
| OW1–HW1B ... OW3     | 0.79| 1.87   | 2.598 (13)| 153   |
| OW2–HW2A ... O3      | 0.88| 2.18   | 2.990 (6)| 152   |
| OW2–HW2B ... O3      | 0.85 (6)| 1.98 (5)| 2.791 (5)| 160 (8)|
| OW3–HW3A ... OW2     | 0.89| 1.78   | 2.564 (13)| 145   |

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**Figure 3.** Two-dimensional layered structure of complex 1.
Figure 4. The two-dimensional porous structure of complex 2 and porous structure.

Table 3. Relative parameters of intermolecular π–π stacking in complexes 3 and 4.

| Complex | Cg(l) Cg(j) | Distance between centroids (Å) | Cg(l) Cg(j) | Distance between centroids (Å) |
|---------|-------------|--------------------------------|-------------|--------------------------------|
| [Zn(HNOR)$_2$·2H$_2$O] (3) | cg(3) → cg(5)$^i$ | 3.484 (4) | cg(5) → cg(3)$^i$ | 3.484 (4) |
| | cg(5) → cg(5)$^i$ | 3.854 (3) | | |
| [Co(H$_2$NOR)$_2$·2H$_2$O]$_2$·2nNO$_3$ (4) | cg(5) → cg(5)$^i$ | 3.5482 (12) | | |

Defined rings and symbol explanations of complex 3: Cg(3): N1 → C3 → C2 → C1 → C5 → C4; Cg(5): C4 → C5 → C6 → C7 → C8 → C9.
Symmetry codes: i: 1 − x, − y, 2 − z.

Defined rings and symbol explanations of complex 4: Cg(5): C4 → C5 → C6 → C7 → C12 → C13.
Symmetry codes: i: 2 − x, − y, 1 − z.

Figure 5. The two-dimensional porous structure of complex 3.
**Figure 6.** Two-dimensional layered structure of complex 4.

**Figure 7.** XRD patterns and IR spectra of gCN and complexes 1–4/gCN.

**Figure 8.** UV-Vis DRS spectra and Tauc’s plots of gCN and complexes 1–4/gCN.
and 4/gCN are smaller than those of complexes 2/gCN and 3/gCN, which supports the fact that complexes 1/gCN and 4/gCN have better $e^-$ separation rates. Consequently, complexes 1/gCN and 4/gCN exhibit better performance in photocatalytic hydrogen production than complexes 2/gCN and 3/gCN. In other words, $[\text{Ni(HNOR)}_2]_n\cdot5n\text{H}_2\text{O}$ and $[\text{Co(H}_2\text{NOR)}_2\cdot2\text{H}_2\text{O}]_n\cdot2n\text{NO}_3$ are good promoter catalytic materials of gCN.

**Photocatalytic hydrogen production**

Photocatalytic hydrogen production experiments were performed using a Labsolar-6A photocatalytic apparatus connected to a gas chromatograph. The samples (0.05 g) were dispersed in deionized water with triethanolamine (20 vol%, 100 mL) and Pt (H$_2$PtCl$_6\cdot6$H$_2$O) (3.0 wt%). The reactor was then placed under a Xenon lamp (300 W, $\lambda\geq420$ nm) for testing. During the photocatalytic process, the temperature of the reaction system was kept at 15 °C by circulating water and the resulting gas was analyzed by gas chromatography using high purity nitrogen as the carrier gas. As can be seen from Figure 10, complexes 1/gCN and 4/gCN exhibited good photocatalytic hydrogen production performance and a remarkably improved rate of hydrogen production. Compared to the literature, pure gCN exhibits a poor photocatalytic hydrogen production activity (407.4 μmol h$^{-1}$ g$^{-1}$),$^{26}$ complexes 1/gCN (914.1 μmol h$^{-1}$ g$^{-1}$) and 4/gCN (943.9 μmol h$^{-1}$ g$^{-1}$) displayed excellent photocatalytic rates of hydrogen production, being about double that of pure gCN (Figure 11). From the point of view of environmental protection, complexes 1/gCN and 4/gCN are environmentally friendly and can achieve a similar catalytic effect to complex catalysts that are based on CdS nanorods as the photosensitizer.$^{27-30}$

**Conclusion**

In summary, we have prepared four complexes, $[\text{Ni(HNOR)}_2]_n\cdot5n\text{H}_2\text{O}$ (1), $[\text{Cd(HNOR)}_2]_n$ (2), $[\text{Zn(HNOR)}_2\cdot2\text{H}_2\text{O}]$ (3), and $[\text{Co(H}_2\text{NOR)}_2\cdot2\text{H}_2\text{O}]_n\cdot2n\text{NO}_3$ (4), by the combination of a transition-metal salt and norfloxacin. According to the Irving–Williams sequence,$^{31}$ the radius of a Ni(II) ion is smaller than that of a Co(II) ion and the coordination stability between Ni(II) and a nitrogen atom is stronger; thus, Ni ion can coordinate with the nitrogen atom of the ligand, but Co(II) coordinates with the oxygen atom of the ligand. In addition, the stability of the complex formed increases as the period increases; therefore, a Cd(II) ion forms a stable complex more easily with a nitrogen atom than a Zn(II) ion. For the above reasons, these metals lead to different coordination patterns. We subsequently synthesized...
the corresponding complex/carbon nitride photocatalysts and applied photocatalytic hydrogen production experiments, with the results showing that complexes 1/gCN and 4/gCN displayed excellent rates of photocatalytic hydrogen production.

**Experimental**

**Materials**

Analytical grade urea, norfloxacin, NiCl$_2$·6H$_2$O, CdSO$_4$·8H$_2$O, ZnSO$_4$·7H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, and sodium hydroxide were obtained from Shanghai Tengzhun Biotechnology Corporation (Shanghai, China), and were used as received.

**Instruments and measurements**

The IR spectra were recorded on a Nicolet FTIR 170SX spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. Photocatalytic hydrogen production was accomplished using a Labsolar-6A. PL was recorded on an F4500 PL detector. EIS was performed on a CHI760E electrochemical workstation.

**Syntheses and measurements**

**Synthesis of [Ni(HNOR)$_2$]·5nH$_2$O (1).** A mixture of NiCl$_2$·6H$_2$O (0.2377 g, 1.0 mmol) and norfloxacin (0.6387 g, 2.0 mmol) in H$_2$O (20 mL) at room temperature was stirred thoroughly while stirring. The four complexes all use the ligand–metal ratio of 2:1. When the mixture and the pH was adjusted to about 8.0 with NaOH. The obtained cloudy solution was transferred into a 30-mL Teflon-lined autoclave under autogenous pressure and heated at 110 °C for 6 days (Scheme 1). After cooling to room temperature, the resulting green block-shaped crystals of complex 1 were collected by filtration and washed with distilled water. Yield: 77% (0.6048 g, 0.77 mmol) (based on Ni). Anal. calcd for C$_{32}$H$_{44}$F$_2$N$_6$NiO$_{11}$: C, 48.93; H, 5.65; N, 10.70; found: C, 48.94; H, 5.64; N, 10.71. IR (KBr, cm$^{-1}$): 3418w, 1629s, 1574m, 1493s, 1478m, 1394m, 1266m, 1186w, 1004w, 928m, 791w, 746w.

**Synthesis of [Cd(HNOR)$_2$] (2).** The preparation of complex 2 was similar to that of complex 1, except that the mass of the central ion is changed, on using CdSO$_4$·8H$_2$O (0.2085 g, 1.0 mmol) (Scheme 1). Colorless block-shaped crystals of complex 2 were obtained. Yield (based on Cd): 83% (0.6133 g, 0.83 mmol). Anal. calcd for C$_{32}$H$_{24}$CdF$_2$N$_6$O$_6$: C, 52.01; H, 3.27; N, 11.37; found: C, 52.03; H, 3.28; N, 11.36. IR (KBr, cm$^{-1}$): 3156w, 1618s, 1578m, 1489s, 1340m, 1263s, 1021m, 935m, 826w, 743w.

**Synthesis of [Zn(HNOR)$_2$·2H$_2$O] (3).** Complex 3 was synthesized as above using ZnSO$_4$·7H$_2$O (0.2876 g, 1.0 mmol) (Scheme 1). Colorless block-shaped crystals of 3 were collected by filtration and washed with distilled water. Yield: 85% (0.6291 g, 0.85 mmol) (based on Zn). Anal. calcd (% for C$_{32}$H$_{38}$F$_2$N$_6$O$_8$Zn: C, 52.07; H, 5.18; N, 11.38; found (%): C, 52.08; H, 5.18; N, 11.39. IR (KBr, cm$^{-1}$): 3326w, 1629s, 1574m, 1490m, 1263s, 1021m, 935m, 826w, 743w.
Synthesis of \([\text{Co(H}_2\text{NOR)}_2\cdot\text{2H}_2\text{O}·\text{2nNO}_3]_n\) (4). Complex 4 was synthesized as above using \(\text{Co(NO}_3)_2·\text{6H}_2\text{O}\) (0.291 g, 1.0 mmol) and the pH value of the mixture was adjusted to about 6.0 (Scheme 1). Red block-shaped crystals of 4 were collected by filtration and washed with distilled water. Yield: 80% (0.343 g, 0.40 mmol) (based on Co). Anal. calcd (%): \(C\), 46.33; \(H\), 4.86; \(N\), 10.13; found (%): \(C\), 46.34; \(H\), 4.88; \(N\), 10.07. IR (KBr, cm\(^{-1}\)): 3211w, 1621s, 1534m, 1461m, 1350m, 1293w, 1010w, 936m, 826w, 759w.

Synthesis of \(g\text{CN}\) and the composite photocatalysts

\(g\text{CN}\) was obtained by calcining urea in a muffle furnace at 450 °C for 2 h (5 °C/min) in ambient air and the composite photocatalysts were obtained by calcining urea and \([\text{Ni(HNOR)}_2]_n·\text{5nH}_2\text{O}\) (1), \([\text{Cd(HNOR)}_2]_n\) (2), \([\text{Zn(HNOR)}_2·\text{2H}_2\text{O}·\text{nNO}_3\] (3), and \([\text{Co(H}_2\text{NOR)}_2·\text{2H}_2\text{O}·\text{2nNO}_3\]) (4) directly (Scheme 1), and the mass ratio of urea and four complexes is 20:1.

Crystal structure determination and physical measurements

The crystallographic data for these four complexes were collected on a Bruker SMART X-ray diffractometer with a CCD area detector using a graphite-monochromated MoK\(\alpha\) radiation (\(\lambda=0.71073\ \text{Å}\)). The structures of the complexes were solved by direct and subsequent Fourier and differential Fourier synthesis methods, respectively, and then by full-matrix least-squares techniques on \(F^2\) using the program SHELXL. The crystallographic data for the four complexes are summarized in Table 4.

**Table 4.** Crystallographic data for complexes 1–4.

| Complex | 1 | 2 |
|---------|---|---|
| Empirical formula | \(C_{32}H_{44}F_2N_6NiO_{11}\) | \(C_{32}H_{40}F_2N_6O_{14}Co\) |
| \(Dc\) (g/cm\(^3\)) | 1.535 | 1.490 |
| \(\mu\) (MoK\(\alpha\)) (mm\(^{-1}\)) | 0.653 | 0.726 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | \(P2_1/n\) | \(P2_1/c\) |
| Crystal size (mm) | \(0.18 \times 0.19 \times 0.22\) | \(0.19 \times 0.20 \times 0.24\) |
| \(a\) (Å) | 10.6025(10) | 5.5523(4) |
| \(b\) (Å) | 11.4594(10) | 22.2203(15) |
| \(c\) (Å) | 14.0618(13) | 13.5064(10) |
| \(\alpha\) | 90 | 90 |
| \(\beta\) | 90 | 90 |
| \(\gamma\) | 90 | 90 |
| Theta range for data collection | 2.9–28.8 | 3.0–25.0 |
| Limiting indices | \(-14 \leq h \leq 14, -15 \leq k \leq 14, -11 \leq l \leq 18\) | \(-54 \leq h \leq 6, -26 \leq k \leq 21, -16 \leq l \leq 3\) |
| \(V\) (Å\(^3\)) | 1699.1(3) | 1647.7(2) |
| \(Z\) | 2 | 2 |
| \(R_1, wR_2\) | 0.0723, \(wR_2=0.1723\) | 0.0526, \(wR_2=0.1658\) |
| \(F(000)\) | 824 | 744 |
| Goodness-of-fit (GOF) on \(F^2\) | 1.085 | 1.14 |

**Complex**

| 1 | 4 |
|---|---|
| Empirical formula | \(C_{32}H_{44}F_2N_6NiO_{11}\) | \(C_{32}H_{40}F_2N_6O_{14}Co\) |
| \(Dc\) (g/cm\(^3\)) | 1.535 | 1.490 |
| \(\mu\) (MoK\(\alpha\)) (mm\(^{-1}\)) | 0.653 | 0.726 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | \(P2_1/n\) | \(P2_1/c\) |
| Crystal size (mm) | \(0.18 \times 0.19 \times 0.22\) | \(0.19 \times 0.20 \times 0.24\) |
| \(a\) (Å) | 10.6025(10) | 5.5523(4) |
| \(b\) (Å) | 11.4594(10) | 22.2203(15) |
| \(c\) (Å) | 14.0618(13) | 13.5064(10) |
| \(\alpha\) | 90 | 90 |
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| \(V\) (Å\(^3\)) | 1699.1(3) | 1647.7(2) |
| \(Z\) | 2 | 2 |
| \(R_1, wR_2\) | 0.0723, \(wR_2=0.1723\) | 0.0526, \(wR_2=0.1658\) |
| \(F(000)\) | 824 | 744 |
| Goodness-of-fit (GOF) on \(F^2\) | 1.085 | 1.14 |
Author contributions
Y.H. contributed to the material characterization, research, and writing. J.W. contributed to synthesis of complexes and complex/carbon nitride photocatalysts. J.Z. contributed to the structural analysis.

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Availability of data and material
CCDC 1984305-1984307 and 2106398 contain the supplementary crystallographic data for the complexes [Ni(HNOR)2]n·5nH2O (1), [Cd(HNOR)2]n (2), [Zn(HNOR)2·2H2O] (3), and [Co(HNOR)2·2H2O]n·2nNO3 (4).

Code availability
These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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