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Synthesis of 1,8-naphthyridine and BF₂-based isomers and their application in fluorogenic sensing Cd^{2+}

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Heavy metal cadmium is widely used in industry and agriculture,

and thus it results in high level of cadmium contamination in soil and

crops.¹ Further, toxic Cd^{2+} can be easily absorbed and accumulated in

plants and other organisms. This may lead to various diseases, such as

prostate cancer, lung cancer, and renal cancer.² Therefore it is sig-

nificant to develop effective fluorescent sensors for detecting and

fabricated to detect different kinds of heavy toxic metal ions, because of their simplicity, high sensitivity, and real-time detection.³ Because both Cd^{2+} and Zn^{2+} are in the same group of the periodic table and thus have similar properties and show similar fluorescence changes when Zn²⁺ and Cd²⁺ are coordinated with fluorescent sensors,⁴ it is difficult to distinguish Cd^{2+} from Zn^{2+} in fluorescent sensing. The Cd²⁺ fluorescent sensors have been widely developed in recent five years,⁵ and there still remains a huge challenge for designing fluorescent chemosensors for Cd²⁺.

In recent years, a great number of fluorescent sensors have been

As a bidentate ligand, 1.8-naphthyridine and its derivatives have been widely used to build complexes with metal ions.⁶ However, 1,8-naphthyridine derivatives based fluorescent sensors for transition metals are rare.⁷ In contrast, organic fluorine-boron complexes BODIPY (BODIPY denote boron dipyrromethene and its derivatives) have been widely used in fluorescent sensors,⁸ because

monitoring cadmium in the environment or living cells.

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ABSTRACT

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1. Introduction

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channel fluorescent probe toward Cd^{2+} . BF₂ dissociates from the probe upon reaction with CdCl₂, demonstrating a new approach for sensing Cd^{2+} .

> of their high absorption coefficients and fluorescence quantum yields. Still, the research on boron complexes is inadequate.⁹ Though the synthesis and photophysical properties of BF₂ core complexes containing 1,8-naphthyridine were reported in the last two years,¹⁰ the complexes as fluorescent probes for metal ions have not been studied vet.

A series of isomers were synthesized and identified, two isomers of which were developed as the dual-

In this work, based on 1,8-naphthyridine and BF₂, isomers **2**, **2**', 1, 1', P, and P' were synthesized from 2-amino-6-methylpyridine according to the strategy shown in Scheme 1. Isomers 1 and 1'were developed as Cd²⁺-selective fluorescent probe.



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2. Results and discussion

The HRMS data of products from reactions (c), (d), and (e) indicate that there is only one product of each reaction. In ¹H NMR spectra of the product (Fig. 1) from reaction (c), two peaks at 13.42 (intensity=0.33) and 13.47 (intensity=0.65) are ascribed to two kinds of active H atoms. Besides, there are two peaks at 7.62 (intensity=0.3) and 7.43 (intensity=0.7), and the overall intensities in the range of 7 and 10 are 6. As for ¹³C NMR data, there are two kinds of saturated carbon atoms at 17.88 and 17.14, and 26 kinds of aromatic carbon atoms (see Fig. S1). Considering the HRMS and NMR data, it is easy to conclude that there exist isomers 2 and 2' in the products of reaction (e). ¹H NMR spectrum of the product of (e) (Fig. 1) is similar to that of (c). Besides, the HRMS data of the products from reactions (c) and (e) are almost same. Combining with ¹H NMR and X-ray crystal structure (Fig. 2) of (e), it is easy to conclude that \mathbf{P} and \mathbf{P}' are the products of (e), that is, BF₂ dissociates from **1** or **1**' upon reaction with CdCl₂. The bond C9–N3 (1.345 Å) bears a more single bond character than C9–N4 (1.322 Å) (Table 1). The hydrogen bond between H17 and Cl1 (the bond length of H17-Cl1 is 2.414 Å, the angle of N3-H17-Cl1 is 172.70) might be the reason that stabilizes one isomer **P** over **P**'.



Fig. 1. ¹H NMR spectra (400 MHz, DMSO- d_6 , 298 K) of the products from reactions (c), (d), and (e).



Fig. 2. X-ray crystal structure of cadmium complex from reaction (e).

As for compound 1 or 1', ¹H NMR data indicate that the H atom number in the range between 7.0 and 9.5 are the same as those of compound 2 and 2', and there lacks one kind of H atom (Fig. 1). In ¹³C NMR spectrum, there is only one kind of saturated carbon atom at 17.35 and 15 kinds of aromatic carbon atoms (see Fig. S1), suggesting no isomers exist. However, there exist isomers for compounds **P** and **P'**. Considering the characterization data of the products from (d) and (e), it is not difficult to conclude that there exist isomers 1 and 1' of the products from reaction (d). The exchange of 1 and 1' is faster than the NMR time scale and no

Table 1

Selected bond lengths and angle	es
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Cd1–N1	2.304(4)
Cd1–Cl1	2.4366(13)
N3-C9	1.346(6)
N3-C15	1.376(6)
N4-C9	1.322(6)
N4-C10	1.382(6)
N1-Cd1-Cl1* ²	100.45(10)
N1–Cd1–Cl1	130.89(11)
N1* ² -Cd1-N1	89.86(18)
Cl1* ² -Cd1-Cl1	107.63(8)

Symmetry code: *2 = -x + 1/2, -y + 1/2, z.

difference was observed in the ¹H NMR and ¹³C NMR spectra between such isomers.

To analyze further structures of reactions (c), (d), and (e), theoretical calculations were performed on compounds **2**, **2'**, **1**, **1'**, **P** and **P'**. From Fig. **3**, it is obvious that the ground state energy of **2** is less than **2'**, indicating that **2** is more stable than **2'**. As for complexes **1**, **1'**, **P**, and **P'**, **1** is more stable than **1'** and **P** is more stable than **P'**. Combining with the HRMS, ¹H NMR, and ¹³C NMR of **2**, **2'**, **1**, **1'**, **P**, and **P'**, it is concluded that there exist isomers for **2**, **1**, and **P** in solution and the ratios of **2** to **2'**, **P** to **P'** are **3**/7. Crystal data of products from reaction (e) illustrate that there only exists one kind of isomer **P** in crystal state, implying that **P'** is not stable and was not found in crystal state. Scheme 2 illustrates the possible reaction processes of (d) and (e).



Fig. 3. The optimized structures and the ground state energies of 2, 2', 1, 1', P, and P'.



Scheme 2. Possible reaction processes of (d) and (e).

To interpret further the influence of methyl group location on the absorption properties of isomers **2**, **2**', **1**, **1**', **P**, and **P**', timedependent density functional (TD-DFT) calculations were performed. In Table 2, the lowest energy transitions of **2** and **2**' are not completely same, but their calculated transition energies are almost same (Fig. S2, red and green lines). For every kind of isomers **2**, **2**', **1**, and **1**', the highest occupied molecular orbital (HOMO) is mainly located on the 1*H*-benzo[*d*]imidazoly unit and the lowest unoccupied molecular orbital (LUMO) is on the naphthyridine group (Fig. 4 and Table 3). As for isomers **P** and **P**', the HOMO of **P** is mainly located on the 1*H*-benzo[*d*]imidazoly unit and that of \mathbf{P}' is on the CdCl₂ (Table 4). From Table 5 and Fig. S3, the lowest energy transitions of 1 and 1' are completely same (HOMO-1 to LUMO and HOMO-1 to LUMO+1), and their calculated transition energies are almost same. As shown in Table 6, the lowest energy transition of P comes from HOMO-2 to LUMO. HOMO-3 to LUMO+2, and HOMO to LUMO+2. As for \mathbf{P}' , the lowest energy transition comes from the HOMO-5 to LUMO, HOMO-6 to LUMO, HOMO-4 to LUMO+1, and HOMO-4 to LUMO+3. It is obvious that the lowest energy transitions of **P** and **P**' are different, but their calculated transition energies are close to each other (see Fig. S4, red and green lines). The theoretical results indicate that the excited-states of **2** and **2**' are nearly same, and similar results are obtained for 1, 1', P, and P'. The calculated absorption-peak positions are in good agreement with the experimental results (see Figs. S2-S4). Such theoretical and experimental results suggest that methyl group location impose no influence on the absorption properties of isomers.

Table 2

Excitations of 2 and 2' that contribute to their transitions in 300–400 nm range, along with their relative contributions given by their expansion coefficient

Orbital transition	λ_{ex}/nm		Oscillator strength	
	2	2′	2	2′
HOMO-1→LUMO	358.40	260.15	0.2772	0.4025
HOMO→LUMO	370.16	360.15	0.2392	0.4925



Fig. 4. Frontier molecular orbitals of $\mathbf{2}$ and $\mathbf{2}'$ relevant to their transitions in 300–400 nm range.

Addition of 1.2 equiv CdCl₂ (Cd²⁺, 2.4×10^{-5} M) into the ethanol solution of **1** and **1**' $(2.0 \times 10^{-5} \text{ M})$ in about 30 s made the absorption maximum shift from 353 to 365 nm (see Fig. S5). Upon titration of Cd²⁺ and with excitation at 357 nm, a new fluorescence emission peak at about 485 nm appeared and the intensity was enhanced with 435 nm emission intensity decreased (Φ_{fl} changed from 0.092 to 0.105, Fig. 5), indicating a Cd^{2+} -selective dual-emissive-type signaling behavior. That is, to say, position and intensity of the emission maxima of **1** and **1**' change in the presence of Cd^{2+} . Fig. S6 demonstrates the relationship between the concentration of Cd²⁺ and the emission intensity at the specific wavelength. The red-shift of the emission peak can be ascribed to the orbital recombination, and the increase of emission intensity is most likely the result of rigidification and coplanarity of the complex. Inset part of Fig. 5 demonstrates the fluorescence change of 1 and 1' in ethanol solution upon addition of CdCl₂ and under the irradiation at 365 nm, which is consistent with the fluorescence spectroscopy change of 1 and $\mathbf{1}'$ under the same condition. X-ray crystal structure of $\mathbf{P}(Fig. 2)$ indicates a 1:2 stoichiometry for cadmium ion and isomer 1 and 1'. The detection limit is 2.4×10^{-5} M.

Upon addition of the same amount of the various metal ions $(2.4 \times 10^{-5} \text{ M})$ separately, Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} can

Table 3

Frontier molecular orbitals of 1 and 1^\prime relevant to their transitions in 300–450 nm range



make the absorption peak red-shift minutely and the great absorption spectra change upon addition of Fe^{3+} can be ascribed to the absorption spectra of FeCl₃ (Fig. S7).¹¹ as for emission spectra, only Cd²⁺ increased the emission of **1** and **1**', and made the emission peak red-shift about 50 nm. Under identical conditions, however, Na⁺, Mg²⁺, Al³⁺, K⁺, Ca²⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Hg²⁺, and Pb²⁺ quenched the fluorescence and very little emission intensity enhancement were observed in emission spectroscopy with Na⁺, Al³⁺, K⁺, Zn²⁺, and Pb²⁺, (Fig. 6 and dark bars of Fig. 7). When 1.2 equiv Cd²⁺ was added to the solution of **1** and **1'** in the presence of 1.2 equiv of other metal ions, a similar fluorescent spectroscopy change to that with Cd²⁺ ions only was observed, except Co²⁺, Ni²⁺, and Cu²⁺ (red bars of Fig. 7), indicating the stronger binding ability of Cd²⁺ than that of other ions excluding Co²⁺, Ni²⁺, and Cu²⁺.

Experiments to explore the counterion effect on the Cd^{2+} -selective properties of **1** and **1**' were also performed (Fig. 8). Nitrate, acetate, sulfate, and bromide had similar influence as chloride when it comes to Cd^{2+} salts except iodide, demonstrating that the anions do not coordinate the metal ions while compounds **1** and **1**' reacts with Cd^{2+} . This indicates that compound **1** and **1**' as a fluorescent sensor has a much wider application range in sensing Cd^{2+} ions.

3. Conclusion

In summary, based on 1,8-naphthyridine and boron trifluoride, A series of isomers were synthesized and characterized. Two isomers BF₂ core complexes **1** and **1**' were developed as fluorescent probe toward Cd^{2+} . We found that addition of Cd^{2+} into ethanol solution of the probe made the emission peak red-shift and intensity increase, indicating a dual-channel

Table 4

Frontier molecular orbitals of ${\bf P}$ and ${\bf P}'$ relevant to their transitions in 300–450 nm range



Table 5

Excitations of 1 and 1' that contribute to their transitions in 300–450 nm range, along with their relative contributions given by their expansion coefficient

Orbital transition	λ _{ex} /nm		Oscillator strength	
	1	1′	1	1′
$\begin{array}{l} HOMO-1 \rightarrow LUMO \\ HOMO-1 \rightarrow LUMO+1 \end{array}$	460.61 328.24	460.31 326.16	0.3648 0.3222	0.3841 0.3141

Table 6

Excitations of **P** and **P'** that contribute to their transitions in 300-450 nm range, along with their relative contributions given by their expansion coefficient

Orbital transition	λ _{ex} /nm		Oscillator s	trength
	Р	P ′	Р	Ρ′
HOMO-6→LUMO		373.64		0.4127
HOMO−5→LUMO		399.98		0.1349
$HOMO-4 \rightarrow LUMO+1$		397.96		0.0792
$HOMO-4 \rightarrow LUMO+3$		303.03		0.3219
HOMO−2→LUMO	411.39		0.7841	
$HOMO-3 \rightarrow LUMO+2$	312.39		0.4503	
$HOMO \rightarrow LUMO+2$	321.03		0.0837	



Fig. 5. Emission spectroscopy change of **1** and **1**' in ethanol $(2.0 \times 10^{-5} \text{ M})$ upon addition of CdCl₂. The excitation wavelength was 357 nm. Inset: Photograph of **1** and **1**' in ethanol $(2.0 \times 10^{-5} \text{ M})$ under the irradiation at 365 nm (left: **1** and **1**' only, right: after addition of Cd²⁺).



Fig. 6. Fluorescence spectroscopy change of 1 and 1' (2.0×10^{-5} M) upon addition of different metal cations (1.2 equiv) in ethanol solution.

fluorescent sensing behavior. Crystal structure reveals that BF_2 dissociates from the probe while cadmium chloride reacts with 1 and 1', demonstrating a new approach for sensing cadmium ion.

4. Experimental section

4.1. Materials and instruments

All of the chemicals were purchased from commercial suppliers and used without further purification. All of the reactions were



Fig. 7. Relative fluorescent responses of **1** and **1**' $(2.0 \times 10^{-5}$ M, ethanol) upon addition of different metal salts (the ratio of salt ion to **1** and **1**' is 1.2 equiv, dark bars) and relative fluorescence change of the mixture of **1**, **1**' and Cd²⁺ after addition of the appropriate metal ions (The ratio of other salt ion to **1** and **1**' is 1.2 equiv, red bars). The excitation wavelength was 357 nm. *I* and *I*₀ represent the emission intensity at 435 and 485 nm, respectively. The metal salts represent NaCl, MgCl₂, Al(NO₃)₃, KCl, CaCl₂, CrCl₃, MnCl₂, FeCl₃, CoCl₂, NiCl₂, CuCl₂, ZnCl₂, CdCl₂, HgCl₂, and PbCl₂.



Fig. 8. Fluorescence emission spectra of **1** and **1**' (2.0×10^{-5} M in ethanol) upon addition of different cadmium salts (2.4×10^{-5} M) with excitation at 357 nm.

performed under an argon atmosphere using solvents purified by standard methods. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 NMR spectrometer. Chemical shifts are reported in parts per million using tetramethylsilane (TMS) as the internal standard. Mass spectra were obtained on high resolution mass spectrometer (Micromass Q-Tof MicroTM).

Single-crystal data of the cadmium complex was collected on a Bruker SMART APEX CCD diffractometer with graphitemonochromated MoK α radiation (λ =0.71073 Å) using the ω -scan technique at room temperature.¹² Empirical absorption corrections were applied to the intensities using the SADABS program.¹³ The structure was solved using the program SHELXS-97¹⁴ and refined with the program SHELXL-97.¹⁵ All non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique. The hydrogen atoms of the organic ligands were included in the structure factor calculation at idealized positions using a riding model and refined isotropically.

All spectral characterizations were carried out in HPLC-grade solvents at 20 °C within a 10 mm quartz cell. UV–vis absorption spectroscopy was measured with a TU-1901 double-beam UV–vis spectrophotometer, and fluorescence spectroscopy was determined on a Hitachi F-4500 spectrometer. The fluorescence

quantum yields were measured at room temperature with excitation at 357 nm (Xe lamp in the F-4500 spectrometer) with quinine bisulfate in 1 M H₂SO₄ ($\phi_{\rm fr}$ =0.546) selected as the Ref. 16.

Density functional theory (DFT) calculations with Becke's three parameterized Lee–Yang–Par (B3LYP) ex-change functional with 6-31G(d) and $6-31G^{**}+LanL2DZ$ basis sets were carried out for the geometry optimizations of compounds **2**, **2'**, **1**, **1'**, **P**, and **P'** using a suite of Gaussian 09 programs. The energies and oscillator strengths with 80-120 lowest energy electronic transitions, which involve calculations of singlet-excited-state energies of the complexes, were obtained using time-dependent DFT (TD-DFT) with the same basis sets.

4.2. Synthetic procedure and characterization data

4.2.1. 2-Methyl-1,8-naphthyridine.¹⁷ Sodium-3-

nitrobenzenesulfonate (17.5 g, 77.7 mmol), boric acid (2.4 g, 38.8 mmol), and ferrous sulfate heptahydrate (1.4 g, 0.5 mmol) were added to 23.1 mL of 98% sulfuric acid. After cooling to 0 °C, glycerol (12.5 mL), 2-amino-6-methylpyridine (4.3 g, 40.0 mmol), and hot water (50 °C, 22.5 mL) were slowly added to above mixture. The reaction solution was refluxed for 4 h at 135 °C and cooled to room temperature. 40% water solution of NaOH was used to mediate pH to 7 and chloroform was used to extract the product. The organic phase was concentrated in vacuum to give the crude product and the final product was obtained by column chromatography (200–300 mesh, 3/1 ethyl acetate/petroleum ether) (3.0 g, 25.9% yield).

Characterization of 2-methyl-1,8-naphthyridine: HRMS (EI) *m/z*: calcd for C₉H₉N₂ [M+H]⁺, 145.0766; found, 145.0768. ¹H NMR (400 MHz; CDCl₃; TMS) 9.08 (d, 1H), 8.13–8.16 (m, 1H), 8.08 (d, 1H), 7.43–7.45 (m, 1H), 7.28 (d, H), 2.82 (s, 3H). ¹³C NMR: $\delta_{\rm C}$ (100 MHz, CDCl₃): 163.1, 160.0, 153.3, 136.9, 136.7, 123.0, 121.4, 120.8, 25.7.

4.2.2. 1,8-Naphthyridine-2-aldehyde.¹⁸ 2-Methyl-1,8-

naphthyridine (1.1592 g, 8.0 mmol) and SeO_2 (1.2452 g, 11.2 mmol) were added to 20 mL of 1,4-dioxane. The mixture were refluxed for 4 h in nitrogen atmosphere and filtered. The filtrate was concentrated in vacuum to give the crude product and the final product was obtained by column chromatography (200–300 mesh, ethyl acetate) (0.71 g, 56.6% yield).

Characterization of 1,8-naphthyridine-2-aldehyde: HRMS (EI) m/z: calcd for C₉H₇N₂O [M+H]⁺, 159.0588; found, 159.0561. ¹H NMR: (400 MHz; DMSO; TMS) 10.15 (s, 1H), 9.24–9.26 (m, 1H), 8.71 (d, 1H), 8.60–8.62 (m, 1H), 8.08 (d, 1H), 7.78–7.80 (m, 1H). ¹³C NMR (100 MHz, DMSO): 194.3, 155.8, 155.5, 155.0, 140.5, 138.3, 125.6, 124.9, 118.5.

4.2.3. 2-(4-Methyl-1H-benzo[d]imidazoly)-1,8-naphthyridine (2) and 2-(7-methyl-1H-benzo[d]imidazoly)-1,8-naphthyridine (2').¹⁹ 1,8-Naphthyridine-2-aldehyde (0.4300 g, 2.8 mmol), NaHSO₃ (0.9017 g, 8.7 mmol), and 1,2-diamino-3-methylbenzene (0.4436 g, 3.6 mmol) were added to 10 mL of ethanol, and the mixture was refluxed for 8 h in nitrogen atmosphere. The reaction solution was concentrated in vacuum to give the crude product and the final product was obtained by column chromatography (200–300 mesh, ethyl acetate) (0.2087 g, 29.6% yield).

Characterization of 2-(4-methyl-1*H*-benzo[*d*]imidazol-2-yl)-1,8-naphthyridine: HRMS (EI) *m/z*: calcd for $C_{16}H_{12}N_4$ [M+H]⁺, 261.1062; found, 261.1142. ¹H NMR (400 MHz; DMSO-*d*₆) 13.47 (s, 0.33H), 13.43 (s, 0.65H), 9.15–9.17 (m, 1H), 8.65–8.61 (m, 2H), 8.59–8.54 (d, 1H), 7.70–7.66 (m, 1H), 7.62 (d, 0.3H), 7.43 (d, 0.7H), 7.19–7.16 (m, 1H), 7.03–7.15 (m, 1H), 2.65 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆): 155.8, 154.9, 154.8, 152.2, 152.0, 150.9, 150.0, 144.2, 144.0, 140.0, 139.4, 138.1, 135.4, 125.0, 124.3, 123.4, 123.2, 123.1, 122.8, 122.7, 120.9, 120.6, 117.5, 110.4, 100, 17.9, and 17.1. 4.2.4. BF₂-based compounds 1 and 1'. Boron trifluoride etherate (0.2 mL, 1.6 mmol) were added slowly to 10 mL of chloroform solution of 2-(4-methyl-1H-benzo[d]imidazol-2-yl)-1,8-naphthyridine (0.2000 g, 0.8 mmol) at room temperature, and the mixture was stirred for 1 h. The final product 1 or 1' was obtained by filtration of the reaction solution (0.2236 g, 94.0% yield).

Characterization of **1** and **1**': HRMS (EI) m/z: calcd for C₁₆H₁₁BF₂N₄ [M-BF₂+2H]⁺, 261.1062; found, 261.1145. ¹H NMR (400 MHz; DMSO-d₆) 9.28-9.30 (m, 1H), 8.94 (d, 1H), 8.64-8.70 (m, 2H), 7.82-7.86 (m, 1H), 7.70 (d, 1H), 7.49-7.51 (m, 1H), 7.38-7.49 (m, 1H), 2.73 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆): 185.53, 155.80, 154.70, 147.79, 146.70, 141.00, 139.07, 133.26, 127.15, 126.98, 126.15, 124.68, 124.50, 121.37, 112.41, and 17.35.

4.2.5. Complexes **P** *and* **P**'. A solution of CdCl₂ (0.0134 g, 0.06 mmol) in 0.5 mL of water was added slowly to a solution of **1** (0.0152 g, 0.05 mmol) in 9 mL ethanol at room temperature. The mixture was stirred for 10 min, then the yellow precipitate was removed by filtration. Pale-yellow crystals of the cadmium complex large enough for single crystal X-ray diffraction were grown by slow volatilization of the filtrate in air for a few days (0.0128 g, 35.8% vield).

The structure of the complex was confirmed by HRMS, ¹H NMR, and X-ray crystal structure determination. Selected data for P: HRMS (EI) calcd for $C_{32}H_{24}CdCl_2N_8$ [1/2M-1/2CdCl₂+H]⁺, 261.1062; found, 261.1130. ¹H NMR (400 MHz; DMSO-*d*₆) 13.45 (s, 0.69H), 13.42 (s, 1.31H), 9.16 (s, 2H), 8.65-8.54 (m, 6H), 7.70-7.67 (m, 2H), 7.58 (d, 0.91H), 7.41 (d, 1.44H), 7.20-7.16 (m, 2H), 7.04-7.13 (m, 2H), 2.64 (s, 6H). The relevant crystal data and structural parameters are: formula: C₃₂H₂₄CdC₁₂N₈O. *M*=719.90, orthorhombic. Unit cell parameters: *a*=8.8201(3) Å, *b*=15.1311(5) Å, c=22.3128(7) Å. $\alpha=90^{\circ}$, $\beta=90^{\circ}$, $\gamma=90^{\circ}$, V=2977.82(17) Å³, T=273(2) K, space group Pccn, Z=4, 27,210 reflections collected, 2626 independent reflections [R(int)=0.0645]. Final R indices $[I > 2\sigma(I)]$ R₁=0.0483 and wR₂=0.0872. *R* indices (all data) R₁=0.1074 and *wR*₂=0.1194.

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Supplementary data

CCDC 932784 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. The details of characterization data, UV-vis absorption spectroscopy, and the computational study are available. Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.tet.2013.11.096.

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