

Poly[μ_2 -4,4'-bipyridine-di- μ_2 -bromido-cadmium(II)], with novel colour-tunable fluorescence

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The title inorganic–organic hybrid complex, $[\text{CdBr}_2(\text{C}_{10}\text{H}_8\text{N}_2)]_n$, features two-dimensional $[\text{CdBr}_2(4,4'\text{-bipy})]_n$ ($4,4'\text{-bipy}$ is 4,4'-bipyridine) neutral networks, based on the octahedral Cd atom coordinated by four μ_2 -Br and two μ_2 -4,4'-bipy at *trans* positions, yielding a CdBr_4N_2 octahedron. It crystallizes in the orthorhombic system (*Cmmm*). All the crystallographically independent atoms are on special positions, namely Cd on *mmm*, Br on *mm*, N on *mm2*, and C on sites of symmetry *m* or *mm2*. Optical absorption spectroscopy reveals the presence of an optical gap of 3.76 eV, indicating that the complex is a wide-gap semiconductor. Photoluminescence investigation reveals that the complex displays strong colour-tunable emissions, which might originate from a ligand-to-ligand charge-transfer (LLCT) transition. Thermogravimetric differential thermal analysis shows that the complex is thermally stable up to 493 K.

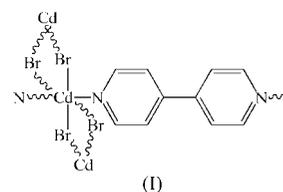
Comment

Inorganic–organic hybrid materials have been of great interest owing to their intriguing structural features and their potential in various applications, such as electrical conductivity, photochemistry, ion exchange, catalysis, biochemistry and nonlinear optical behaviour (Stupp & Braun, 1997; Finn & Zubietta, 2000). A large variety of ligands containing bridging functionalities, such as carboxylates, phosphonates and 4,4'-bipyridine, have been exploited in order to prepare novel inorganic–organic hybrid materials. Being an important class of such materials, metal halide–bipy (bipy is 4,4'-bipyridine) systems have attracted increasing attention in recent years, not only due to their intrinsic aesthetic appeal, but also for their various potential applications.

The ability of bifunctional bipy to act as a rigid rod-like organic building block in the self-assembly of coordination frameworks is well known, such as acting as a charge-compensating cation (Zapf *et al.*, 1997; Lu *et al.*, 2005), a pillar

bonding to an inorganic skeletal backbone (Chen *et al.*, 2003; Wang, Liao *et al.*, 2005), an uncoordinated guest molecule and organic template (Gillon *et al.*, 1999, 2000; Biradha & Mahata, 2005), or a ligand linking a metal and an inorganic framework (Yaghi & Li, 1996; Shi *et al.*, 2000; Wang, Zhou *et al.*, 2005). In addition, bipy has attracted increasing attention due to the delocalized π -electrons in its pyridyl rings, which makes it an excellent candidate for preparing light-emitting complexes with potential in various technical applications, such as sensitizers in solar energy conversion (Hagfeldt & Gratzel, 2000; Balzani & Juris, 2001) and emitting materials for organic light-emitting diodes (Baldo *et al.*, 1998; Gao & Bard, 2000).

Very large-scale structures of metal halide–bipy materials have been reported (Figgis *et al.*, 1983; Lu *et al.*, 1998; Hu *et al.*, 2003), but among these, group 12 (IIB) metal halide–bipy materials are relatively rare. In fact, complexes containing IIB elements are particularly attractive for many reasons: the variety of coordination numbers and geometries provided by the d^{10} configuration of the IIB metal ions, photoelectric properties, fluorescent properties, the widespread applications of IIB compounds, the essential role of zinc in biological systems, and so on. Our recent efforts in synthesizing novel IIB-based complexes have focused largely on systems containing bifunctional ligands, such as 4,4'-bipy. We describe here the synthesis and characterization of the title complex, $[\text{CdBr}_2(4,4'\text{-bipy})]_n$ (I).



X-ray diffraction analysis reveals that complex (I) features two-dimensional layered $[\text{CdBr}_2(4,4'\text{-bipy})]_n$ neutral networks. The divalent metal centres have a slightly distorted octahedral coordination with four μ_2 -Br and two μ_2 -4,4'-bipy in *trans* positions, yielding edge-shared CdBr_4N_2 octahedra (Fig. 1). The CdBr_4N_2 octahedra interconnect with each other *via* two μ_2 -Br atoms, forming a linear inorganic mono-chain running along the *c* direction. The mono-chains in (I) are different from the double chains reported by Lu *et al.* (1999). These mono-chains are bridged by μ_2 -4,4'-bipy ligands to form an inorganic–organic hybrid two-dimensional layer (Fig. 2), which is similar to that reported by Chen *et al.*, (2006), but

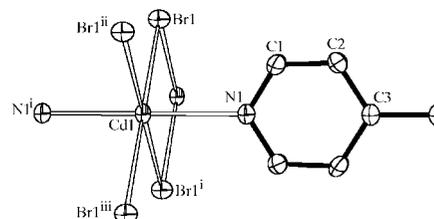


Figure 1

The structure of (I), with displacement ellipsoids drawn at the 40% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y, z$; (ii) $x, y, 1 + z$; (iii) $-x, -y, 1 + z$.]

different from other known two-dimensional metal–4,4'-bipy structures, *e.g.* diamondoid (MacGillivray *et al.*, 1994), brick wall (Gable *et al.*, 1990), ladder (Fujita *et al.*, 1995), square network (Li *et al.*, 1997; Noro *et al.*, 2002), and so forth. These layers stack in an ...*ABAB*... mode along the *b* axis to yield a three-dimensional structure (Fig. 3).

In complex (I), π – π stacking interactions in the layer give rise to 'perfect facial alignment', as shown by the angle of the centroids of three consecutive rings (180°). The two pyridyl rings of the 4,4'-bipy ligand are coplanar, with a dihedral angle of 0° , which is remarkably different from the cases found in many other complexes containing 4,4'-bipy ligands in which the two pyridyl rings are far from being coplanar (Chen *et al.*, 1996; Marinescu *et al.*, 2005). In each layer, neighbouring μ_2 -4,4'-bipy ligands interact through weak π – π contacts with a distance equal to the *c* axis length, *viz.* 3.924 Å.

Optical absorption spectroscopy reveals an optical gap of 3.76 eV (Fig. 4). This suggests that complex (I) is a wide-gap semiconductor, which is consistent with the colour of the crystal, as observed for cases in the literature (Chondroudou *et al.*, 1997; Chondroudou & Kanatzidis, 1998; Aitken *et al.*, 2000; Choi & Kanatzidis, 2000). The gradual slope of the optical absorption edge is indicative of the existence of indirect transitions (Huang *et al.*, 2001). The optical absorption of (I) likely originates from charge-transfer excitations, mainly from the valence band of the Br atoms to the conduction band of the Cd centre.

The solid-state emission spectrum of the title complex was investigated at room temperature and is given in Fig. 5. The fluorescent spectrum study shows that (I) exhibits a broad and strong emission with a maximum wavelength of 491 nm upon

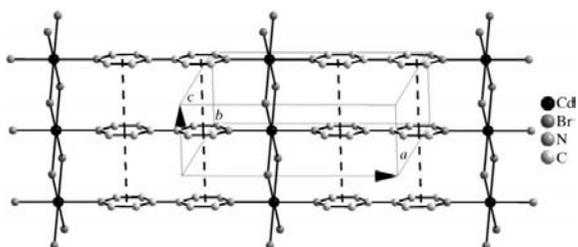


Figure 2
The layered structure of (I), with H atoms omitted for clarity. Dashed lines represent π – π stacking interactions.

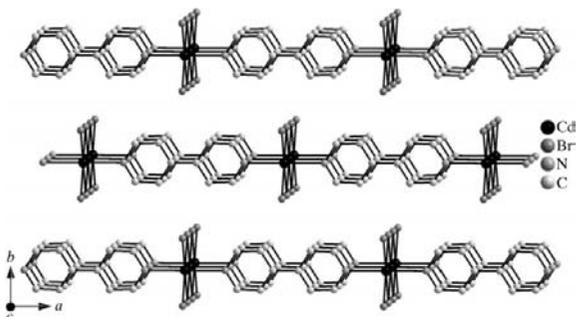


Figure 3
A packing diagram for (I). H atoms have been omitted for clarity.

intensive photo-excitation at 391 nm (Fig. 5), which is red-shifted by 53 nm compared with that of the pure 4,4'-bipy ligand (Chen *et al.*, 2006). Interestingly, complex (I) exhibits a broad and slightly weaker emission with a maximum wavelength of 527 nm upon weak photo-excitation at 315 nm. During the measurement process in a dark room, we opened a small slit of the sample chamber and found that the title complex emitted blue–white light upon intensive photo-excitation at 391 nm, while it emitted green–yellow light upon weak photo-excitation at 315 nm. According to the results reported by Chen *et al.*, 2006, the emission of (I) is probably assigned to the ligand-to-ligand charge-transfer (LLCT) transition (from the highest occupied molecular orbital of the Br atom to the lowest unoccupied molecular orbital of the 4,4'-bipy group). Thus, this complex may be a potential colour-tunable organic luminescent material upon different photo-excitation.

Thermogravimetric differential thermal analysis (TG–DTA) shows that complex (I) is thermally stable up to 493 K and undergoes a two-step decomposition process. The TG–DTA displays an initial mass loss of 35.74% (calculated 36.41%) with an onset temperature of about 493 K, corresponding to the loss of a 4,4'-bipy molecule. A second weight loss of 64.26% (calculated 63.49%), with two small endo-

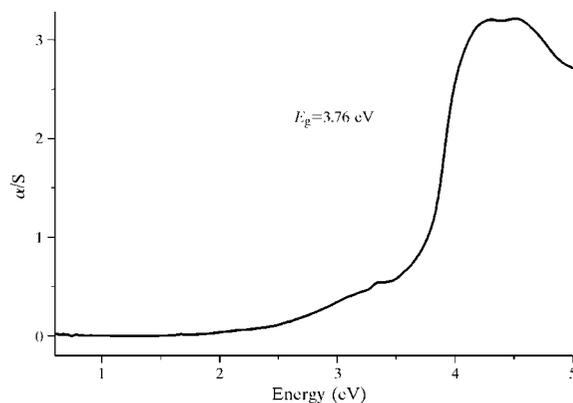


Figure 4
The solid-state diffuse reflectance spectrum for (I).

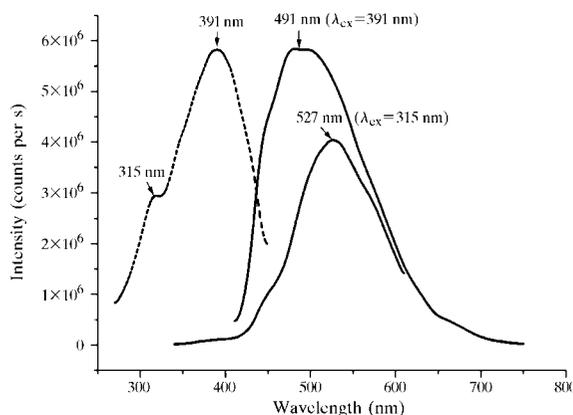


Figure 5
The solid-state emission and excitation spectra of (I) at room temperature. Solid lines: emission spectrum upon photo-excitation at 391 (upper) and 315 nm (lower); dashed line: excitation spectrum.

thermic peaks centred at 446 and 825 K, is found in the range 546–923 K, corresponding to the loss of cadmium bromide. These results are consistent with the composition of the X-ray crystal structure.

In brief, using the hydrothermal reaction of CdBr_2 with 4,4'-bipy, an inorganic–organic hybrid complex with a novel two-dimensional layered structure was obtained. The optical absorption spectrum shows that the title complex may be a candidate as a potential photoelectric material. This complex exhibits broad and strong fluorescent emission bands; and it might have use as a potential colour-tunable organic luminescent material. The scope for the syntheses of new metal halide–bipy complexes with novel structures and properties appears to be very large, and further systematic investigations of this system are in progress.

Experimental

$\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ (0.3 mmol, 103 mg), 4,4'-bipyridine (0.2 mmol, 31 mg) and distilled water (3 ml) were loaded into a Teflon-lined stainless steel autoclave (25 ml) and kept at 473 K for 3 d. After being slowly cooled to room temperature at a rate of 8 K h^{-1} , colourless crystals of (I) suitable for X-ray crystallographic analysis were obtained (yield 31%, based on Cd).

Crystal data

$[\text{CdBr}_2(\text{C}_{10}\text{H}_8\text{N}_2)]$	$V = 580.7 (2) \text{ \AA}^3$
$M_r = 428.40$	$Z = 2$
Orthorhombic, $Cmmm$	Mo $K\alpha$ radiation
$a = 11.787 (3) \text{ \AA}$	$\mu = 8.73 \text{ mm}^{-1}$
$b = 12.554 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 3.9242 (7) \text{ \AA}$	$0.10 \times 0.09 \times 0.06 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer	1912 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	337 independent reflections
$T_{\min} = 0.820$, $T_{\max} = 1.000$ (expected range = 0.486–0.592)	330 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$	28 parameters
$wR(F^2) = 0.042$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.96 \text{ e \AA}^{-3}$
337 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cd1–N1	2.358 (4)	Cd1–Br1 ⁱⁱⁱ	2.7852 (5)
Cd1–N1 ⁱ	2.358 (4)	Cd1–Br1	2.7852 (5)
Cd1–Br1 ⁱⁱ	2.7852 (5)	Cd1–Br1 ⁱ	2.7852 (5)

Br1ⁱⁱ–Cd1–Br1 89.57 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, z + 1$; (iii) $-x, -y, -z - 1$.

All H atoms were positioned geometrically and refined using a riding model, with $\text{C–H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXTL (Sheldrick, 1998); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2004); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3011). Services for accessing these data are described at the back of the journal.

References

- Aitken, J. A., Chondroudis, K., Young, V. G. & Kanatzidis, M. G. (2000). *Inorg. Chem.* **39**, 1525–1533.
- Baldo, M. A., O'Brien, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E. & Forrest, S. R. (1998). *Nature (London)*, **395**, 151–154.
- Balzani, V. & Juris, A. (2001). *Coord. Chem. Rev.* **211**, 97–115.
- Biradha, K. & Mahata, G. (2005). *Cryst. Growth Des.* **5**, 61–63.
- Brandenburg, K. (2004). *DIAMOND*. Release 3.0a. Crystal Impact GbR, Bonn, Germany.
- Bruker (2005). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, C. Y., Lii, K. H. & Jacobson, A. J. (2003). *J. Solid State Chem.* **172**, 252–256.
- Chen, W.-T., Wang, M.-S., Liu, X., Guo, G.-C. & Huang, J.-S. (2006). *Cryst. Growth Des.* **6**, 2289–2300.
- Chen, X. M., Tong, M. L., Luo, Y. J. & Chen, Z. N. (1996). *Aust. J. Chem.* **49**, 835–838.
- Choi, K.-S. & Kanatzidis, M. G. (2000). *Inorg. Chem.* **39**, 5655–5662.
- Chondroudis, K., Hanco, J. A. & Kanatzidis, M. G. (1997). *Inorg. Chem.* **36**, 2623–2632.
- Chondroudis, K. & Kanatzidis, M. G. (1998). *Inorg. Chem.* **37**, 3792–3797.
- Figgis, B. N., Patrick, J. M., Reynolds, P. A., Skelton, B. W., White, A. H. & Healy, P. C. (1983). *Aust. J. Chem.* **36**, 2043–2055.
- Finn, R. & Zubieta, J. (2000). *Chem. Commun.* pp. 1321–1322.
- Fujita, M., Kwon, Y. J., Sasaki, Y. O., Yamaguchi, K. & Ogura, K. (1995). *J. Am. Chem. Soc.* **117**, 7287–7288.
- Gable, R. W., Hoskins, B. F. & Robson, R. (1990). *J. Chem. Soc. Chem. Commun.* pp. 1677–1678.
- Gao, F. G. & Bard, A. J. (2000). *J. Am. Chem. Soc.* **122**, 7426–7427.
- Gillon, A. L., Lewis, G. R., Orpen, A. G., Rotter, S., Starbuck, J., Wang, X.-M., Rodriguez-Martin, Y. & Ruiz-Perez, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3897–3905.
- Gillon, A. L., Orpen, A. G., Starbuck, J., Wang, X.-M., Rodriguez-Martin, Y. & Ruiz-Perez, C. (1999). *Chem. Commun.* pp. 2287–2288.
- Hagfeldt, A. & Gratzel, M. (2000). *Acc. Chem. Res.* **33**, 269–277.
- Huang, F. Q., Mitchell, K. & Ibers, J. A. (2001). *Inorg. Chem.* **40**, 5123–5126.
- Hu, C. H., Li, Q. & Englert, U. (2003). *CrystEngComm*, **5**, 519–529.
- Li, J. M., Zeng, H. Q., Chen, J. H., Wang, Q. M. & Wu, X. T. (1997). *J. Chem. Soc. Chem. Commun.* pp. 1213–1214.
- Lu, J. Y., Cabrera, B. R., Wang, R.-J. & Li, J. (1999). *Inorg. Chem.* **38**, 4608–4611.
- Lu, J., Yu, C., Niu, T. Y., Paliwala, T., Crisci, G., Somosa, F. & Jacobson, A. J. (1998). *Inorg. Chem.* **37**, 4637–4640.
- Lu, Y., Xu, Y., Wang, E. B., Lü, J., Hu, C. W. & Xu, L. (2005). *Cryst. Growth Des.* **5**, 257–260.
- MacGillivray, L. R., Subramanian, S. & Zaworotko, M. J. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1325–1326.
- Marinescu, G., Andruh, M., Julve, M., Lloret, F., Llusar, R., Uriel, S. & Vaissermann, J. (2005). *Cryst. Growth Des.* **5**, 261–267.
- Noro, S., Kitaura, R., Kondo, M., Kitagawa, S., Ishii, T., Mizusaka, H. & Yamashita, M. (2002). *J. Am. Chem. Soc.* **124**, 2568–2583.
- Sheldrick, G. M. (1996). *SADABS*. Version 6.10. University of Göttingen, Germany.
- Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. University of Göttingen, Germany.
- Shi, Z., Feng, S., Zhang, L., Yang, G. & Hua, J. (2000). *Chem. Mater.* **12**, 2930–2935.
- Stupp, S. I. & Braun, P. V. (1997). *Science*, **277**, 1242–1248.
- Wang, C. M., Liao, C. H., Kao, H. M. & Lii, K. H. (2005). *Inorg. Chem.* **44**, 6294–6298.
- Wang, R. H., Zhou, Y. F., Sun, Y. Q., Yuan, D. Q., Han, L., Lou, B. Y., Wu, B. L. & Hong, M. C. (2005). *Cryst. Growth Des.* **5**, 251–256.
- Yaghi, O. M. & Li, H. (1996). *J. Am. Chem. Soc.* **118**, 295–296.
- Zapf, P. J., Haushalter, R. C. & Zubieta, J. (1997). *J. Chem. Soc. Chem. Commun.* pp. 321–322.