

# Some New Organic–Inorganic Hybrid Semiconductors Based on Metal Halide Units: Structural, Optical and Related Properties†

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The structural, optical and related properties of organic–inorganic hybrid semiconductors based on the organic molecules (cations)  $\text{CH}_3\text{NH}_3$ ,  $\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3$ ,  $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3$ ,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_3$ ,  $(\text{H}_2\text{N})_2\text{CS}(\text{CH}_2)_4\text{SC}(\text{NH}_2)_2$ ,  $\text{H}_3\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SC}(\text{NH}_2)_2$ ,  $\text{C}_{10}\text{H}_{21}\text{SC}(\text{NH}_2)_2$ ,  $\text{O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{SC}(\text{NH}_2)_2$ , 1-naphthylmethylammonium  $\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3$ , 9-anthrylmethylammonium  $\text{C}_{14}\text{H}_9\text{CH}_2\text{NH}_3$  and 1-pyrenylmethylammonium  $\text{C}_{16}\text{H}_9\text{CH}_2\text{NH}_3$  and the inorganic units  $\text{MX}_n$  (anions) ( $\text{M} \equiv \text{Bi, Sb, Sn, Pb, Cu, Ag}$ ;  $\text{X} \equiv \text{I, Br, Cl}$ ) are described. There is evidence that the position, intensity and shape of the excitonic bands depend on the order/disorder of the inorganic component and on the electronic interaction between organic and inorganic components. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS semiconductors; low-dimensional systems; crystal structure; optical properties; photoluminescence spectra

## INTRODUCTION

During the past decade a number of organic–inorganic hybrid semiconductors have been prepared and studied in our institute<sup>1–17</sup> and by others<sup>18–29</sup>. The organic component can be an alkylamine ( $\text{RNH}_2$ ) or alkylenediamine ( $\text{H}_2\text{NR}'\text{NH}_2$ ), benzylamine ( $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ), naphthylmethylamine ( $\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_2$ ), anthrylmethylamine ( $\text{C}_{14}\text{H}_9\text{CH}_2\text{NH}_2$ ), etc., while the inorganic component can consist of metal halide ( $\text{MX}_n$ ) units forming a three- or

lower-dimensional (LD) network. The  $\text{MX}_n$  network can be ordered or disordered.<sup>1,6,14,15,18,19</sup> The optical absorption spectra of these hybrid systems can exhibit both Frenkel-type excitonic bands, arising from the organic molecules, and Wannier-type excitonic lines, arising from the inorganic network. The position, intensity and shape of these bands or lines depend on several different factors, e.g. the dimensionality and structure of the metal halide network, the nature of the organic and inorganic components, the temperature and the pressure. There exist a wide variety of spectra, so one can cover the whole spectral region from the UV to the near-IR with excitonic bands of inorganic and/or organic components.

It has been found that these hybrid systems can be used as elements of non-linear optical devices,<sup>20</sup> light-emitting diodes (LEDs)<sup>21,22</sup> and optical

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microcavities.<sup>23</sup> It is expected that advanced devices will be fabricated if there are electronic interactions between the organic and inorganic components.<sup>16,26–32</sup>

In this paper the structural, optical and related properties of some new organic–inorganic hybrid semiconductors based on the organic molecules (cations)  $\text{CH}_3\text{NH}_3$  (abbreviated as  $\text{C}_1$ ),  $\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3$  ( $\text{C}'_6$ ),  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3$  ( $\text{C}_{6-1}$ ),  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3$  ( $\text{C}_1\text{C}_{6-1}$ ),  $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_3$  ( $\text{C}_1\text{OC}_{6-2}$ ),  $(\text{H}_2\text{N})_2\text{CS}(\text{CH}_2)_4\text{SC}(\text{NH}_2)_2$  ( $\text{C}_4\text{S}_2$ ),  $\text{H}_3\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}_3$  ( $\text{C}_6\text{O}_2$ ),  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SC}(\text{NH}_2)_2$  ( $\text{C}_{6-2}\text{S}$ ),  $\text{C}_{10}\text{H}_{21}\text{SC}(\text{NH}_2)_2$  ( $\text{C}_{10}\text{S}$ ),  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{SC}(\text{NH}_2)_2$  ( $\text{ONC}_{6-1}\text{S}$ ), 1-naphthylmethylammonium  $\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3$  ( $\text{C}_{10-1}$ ), 9-anthrylmethylammonium  $\text{C}_{14}\text{H}_9\text{CH}_2\text{NH}_3$  ( $\text{C}_{14-1}$ ) and 1-pyrenylmethylammonium  $\text{C}_{16}\text{H}_9\text{CH}_2\text{NH}_3$  ( $\text{C}_{16-1}$ ) and the inorganic units  $\text{MX}_n$  (anions)  $\text{M} \equiv \text{Bi, Sb, Sn, Pb, Cu, Ag}$ ;  $\text{X} \equiv \text{I, Br, Cl}$ ) are described. Dimensionality, dielectric confinement, temperature and pressure effects are similar to those observed previously in other similar systems (see Refs. 1–29 and references cited therein). Herein, emphasis is on the properties related to the order/disorder of the inorganic component and to the electronic interaction between organic and inorganic components.

## EXPERIMENTAL

The hybrid semiconductors were prepared by treatments of the organic ammonium salts with the corresponding  $\text{MX}_3$  ( $\text{M} \equiv \text{Bi, Sb}$ ),  $\text{MX}_2$  ( $\text{M} \equiv \text{Sn, Pb}$ ) and  $\text{MX}$  ( $\text{M} \equiv \text{Ag, Cu}$ ) inorganic precursors in organic solvents (e.g. acetone, methanol, acetonitrile, dimethylformamide, dimethylsulphoxide) or in aqueous  $\text{HX}$  (for details see Refs 2–17). Usually, from big organic molecules and  $\text{MX}_2$  in aqueous solutions, two types of crystals were obtained, the  $\text{MX}_4$ -based compounds (2D) and the  $\text{MX}_3$ - or  $\text{MX}_5$ -based compounds (1D). The optical absorption (OA), photoluminescence (PL) and photoconductivity (PC) spectra were mainly recorded at room temperature as in Refs 11–13, 16, 17 and 33 (see also Ref 34).

## RESULTS AND DISCUSSION

The low-dimensional organic–inorganic hybrid semiconductors described herein exhibit a variety

of structural, optical and related properties. The most important are the properties related to the order/disorder in the metal halide network and to the electronic interaction between organic and inorganic components. The results from these new systems are summarised in Table 1 (see data reported in Refs 1–29 for comparison).

The compounds  $(\text{C}'_6)\text{MX}_4$ ,  $(\text{C}_{6-1})_2\text{MX}_4$  and  $(\text{C}_1\text{C}_{6-1})_2\text{MX}_4$  ( $\text{M} \equiv \text{Pb, Sn}$ ;  $\text{X} \equiv \text{I, Br, Cl}$ ) consist of perovskite-type sheets of corner-sharing octahedra alternating with sheets of organic ammonium molecules. The difference between the structures of compounds  $(\text{C}'_6)\text{MX}_4$  and (some) compounds  $(\text{C}_{6-1})_2\text{MX}_4$  or (some) compounds  $(\text{C}_1\text{C}_{6-1})_2\text{MX}_4$  is that in the former the inorganic network is ordered<sup>14,15</sup> while in the latter it is disordered.<sup>1,6,16,18,19</sup> Fig. 1 shows the OA and PL spectra of thin deposits of  $(\text{C}'_6)\text{PbX}_4$  and Fig. 2 the PC spectra of single crystals of some compounds of the type  $(\text{C}'_6)\text{PbBr}_x\text{I}_{4-x}$ . It was observed that the excitonic peaks of  $(\text{C}'_6)\text{MX}_4$  occur at shorter wavelengths than those of the corresponding  $(\text{C}_{6-1})_2\text{MX}_4$  or  $(\text{C}_1\text{C}_{6-1})_2\text{MX}_4$  compounds (see also Refs 1 and 14–16). Moreover, the OA spectra of  $(\text{C}'_6)\text{MX}_4$  show sharp bands at shorter wavelengths than those of the excitonic bands, which could be attributed to the higher excitonic states. The corresponding bands in the spectra of  $(\text{C}_{6-1})_2\text{MX}_4$  and  $(\text{C}_1\text{C}_{6-1})_2\text{MX}_4$  are broadened,<sup>1,14–16</sup> perhaps because of the disorder of the inorganic network. However, in both cases of 2D systems the excitonic peaks are more pronounced than those of the corresponding 3D systems, even at room temperature (see also Refs 1, 10 and 34). For 1D and 0D (or intermediate) systems based on metal halide networks, the peak positions are shifted to higher energies (see Table 1). The PL and PC spectra are Stokes shifted in comparison with the OA spectra. Also, the spectra of some mixed halide crystals exhibit peaks at intermediate positions (Fig. 2 and Table 1). The peak positions of the OA, PL and PC spectra of mixed halide complexes obey linear dependences against the composition (see also Refs 2–5). The OA spectra of  $\text{PbI}_3$ - and  $\text{PbI}_5$ -based compounds (1D) exhibit strong excitonic peaks at 401 and 412 nm respectively and some weak peaks or shoulders at ca 480–510 nm owing to imperfect ‘self-assembly’ and the resulting presence of some  $\text{PbI}_4$  (2D) phases. The PL bands corresponding to the weak OA peaks or shoulders are sharp, showing Stokes shifts, i.e. they occur at 490–520 nm (see e.g. Fig. 5 in Ref. 16 and

Table 1. Structural data and OA, FL and PR peak positions (nm) of some hybrid systems<sup>a</sup>

Compound	Dimensionality	OA(I)	FL(I)	OA(O)	PR(O)
(C <sub>6-1</sub> ) <sub>2</sub> SnI <sub>4</sub>	(CS)	2D	580	610	≤230
(C <sub>6</sub> )SnI <sub>4</sub>	(CS)	2D	557	588	≤230
(C <sub>6-1</sub> ) <sub>2</sub> PbI <sub>4</sub>	(CS)	2D	516	534	230–80
(C <sub>1</sub> C <sub>6-1</sub> ) <sub>2</sub> PbI <sub>4</sub>	(CS)	2D	515	527	230–280
(C <sub>1</sub> OC <sub>6-2</sub> ) <sub>2</sub> PbI <sub>4</sub>	(EA)	2D	512		230–280
(C <sub>6</sub> )PbI <sub>4</sub>	(CS)	2D	482	500	≤230
(C <sub>10</sub> S) <sub>2</sub> PbI <sub>4</sub>	(EA)	2D	480	500	≤230
(C <sub>6-2</sub> S) <sub>2</sub> PbI <sub>4</sub>	(EA)	2D	477	495	≤230
(C <sub>6</sub> )PbI <sub>3</sub> Br	(EA)	2D	460	481	≤230
(C <sub>6</sub> )PbI <sub>2</sub> Br <sub>2</sub>	(EA)	2D*	448	472	≤230
(C <sub>6</sub> )PbI <sub>2</sub> Br <sub>1.4</sub>	(EA)	2D*	434		≤230
(C <sub>6-2</sub> S) <sub>3</sub> PbI <sub>5</sub>	(CS)	1D	412		230–280
(C <sub>14-1</sub> ) <sub>x</sub> Pb <sub>x</sub> I <sub>2y+x</sub>		1D*	411		300–420
(C <sub>16-1</sub> ) <sub>2</sub> Pb <sub>6</sub> I <sub>14</sub>	(EA)	1D*	411		300–420
(C <sub>10</sub> S) <sub>x</sub> Pb <sub>y</sub> I <sub>2y+x</sub>		1D*	410		≤230
(C <sub>6-1</sub> ) <sub>x</sub> Pb <sub>y</sub> I <sub>2y+x</sub>		1D?	405		230–280
(C <sub>4</sub> S) <sub>2</sub> Pb <sub>y</sub> I <sub>2y+x</sub>		1D?	403		≤230
(C <sub>10-1</sub> )PbI <sub>3</sub>	(CS)	1D	401		240–320
(C <sub>10-1</sub> )SnI <sub>3</sub>	(EA)	1D*	401		240–320
(C <sub>1</sub> ) <sub>4</sub> PbI <sub>6</sub> 2H <sub>2</sub> O	(CS)	0D	372		≤230
(C <sub>6</sub> )SnBr <sub>4</sub>	(EA)	2D	446		≤230
(C <sub>6-1</sub> ) <sub>2</sub> PbBr <sub>4</sub>	(CS)	2D	397		≤230
(C <sub>6</sub> )PbBr <sub>4</sub>	(CS)	2D	390	402	≤230
(C <sub>10-1</sub> ) <sub>2</sub> PbBr <sub>4</sub>	(EA)	2D	380		240–320
(C <sub>6</sub> O <sub>2</sub> ) <sub>x</sub> Pb <sub>y</sub> Br <sub>2y+x</sub>		2D?	377		≤230
(C <sub>6-1</sub> ) <sub>x</sub> Pb <sub>y</sub> Br <sub>2y+x</sub>		2D?	326		230–280
(C <sub>14-1</sub> ) <sub>x</sub> Pb <sub>y</sub> Br <sub>2y+x</sub>		1D?	326		360, 376, 398
(C <sub>6</sub> ) <sub>2</sub> SnBr <sub>6</sub>	(CS)	0D	325		≤230
(ONC <sub>6-1</sub> S) <sub>x</sub> Pb <sub>y</sub> Br <sub>2y+x</sub>		0D?	319		240–320
(C <sub>1</sub> ) <sub>4</sub> PbBr <sub>6</sub> xH <sub>2</sub> O	(EA)	0D	312		≤230
(C <sub>6</sub> )PbCl <sub>4</sub>	(CS)	2D	332	342	≤230
(C <sub>10-1</sub> ) <sub>2</sub> PbCl <sub>4</sub>		2D*	327		240–320
(C <sub>14-1</sub> ) <sub>x</sub> Pb <sub>y</sub> Cl <sub>2y+x</sub>			284		345–415
(C <sub>1</sub> ) <sub>4</sub> PbCl <sub>6</sub> xH <sub>2</sub> O	(EA)	0D	279		≤230
(C <sub>10-1</sub> ) <sub>x</sub> Cu <sub>y</sub> Br <sub>x+y</sub>		0D?	274		240–320
(C <sub>10-1</sub> ) <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	(EA)	0D*	500		240–320

<sup>a</sup> Formula found from crystal structure determination (CS) or elemental analysis (EA); OA(I), optical absorption of inorganic; FL(I), fluorescence of inorganic; OA(O), optical absorption of organic; PR(O), phosphorescence of organic; \* dimensionality estimated from the OA spectra and/or the composition; blanks, data not obtained or not clear.

Fig. 5 below). Also, similar effects were observed in the OA spectra of some PbI<sub>4</sub>-based complexes because of the presence of PbI<sub>3</sub> or PbI<sub>5</sub> species, and likewise in other compounds based on metal halide units (see also Ref. 17). 2D compounds with disordered networks 'react' with CH<sub>3</sub>NH<sub>3</sub>X and PbX<sub>2</sub> to give a bilayer structure, e.g. (CH<sub>3</sub>NH<sub>3</sub>)(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH<sub>3</sub>)<sub>2</sub>Pb<sub>2</sub>I<sub>7</sub>, while compounds with ordered networks do not 'react'. In some cases (with impurities in the crystals), shoulders are observed at the low-energy side of the excitonic peaks. These shoulders are due to bound excitons and at low temperatures become more intense than those of

(free) excitons (see also Refs 1 and 18). Under hydrostatic pressure the excitonic peaks are red shifted as in the case of PbI<sub>2</sub>- and other PbX<sub>2</sub>-based compounds (see Ref 1 and references cited therein).

As indicated in Table 1, in some cases of hybrid systems the OA excitonic peak of the inorganic component is close to the low-energy OA band of the organic component. In these cases, strong phosphorescence (PR) bands due to organic components and the absence of fluorescence (FL) bands of inorganic components are observed. For example, Fig 3 shows the OA and PL spectra of (C<sub>10-1</sub>)<sub>2</sub>

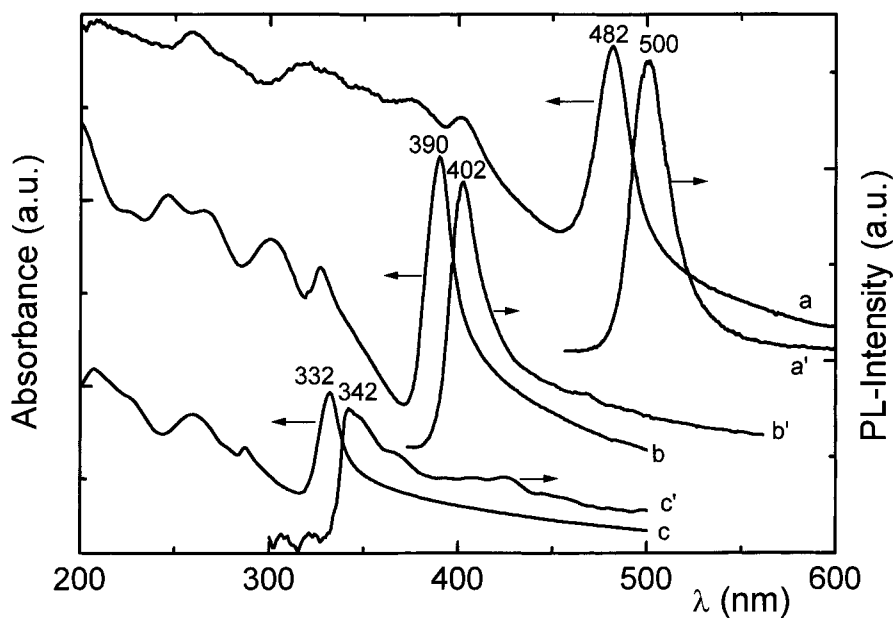


Fig. 1. OA (a, b, c) and PL (a', b', c') spectra of  $(C_6)PbI_4$  (a, a'),  $(C_6)PbBr_4$  (b, b') and  $(C_6)PbCl_4$  (c, c')

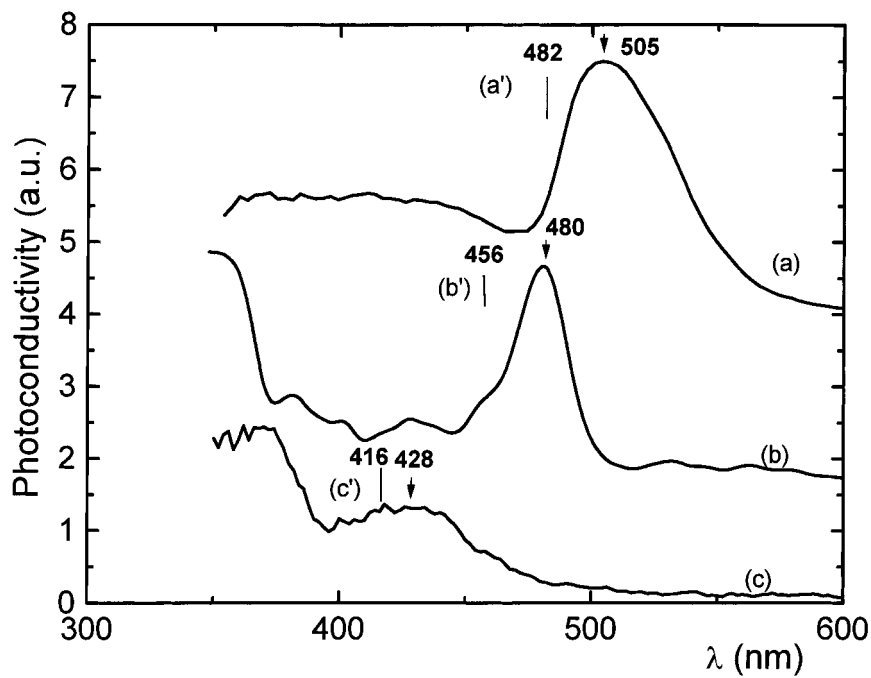


Fig. 2. PC spectra (a, b, c) of  $(C_6)PbI_4$  (a),  $(C_6)PbI_{2.6}Br_{1.4}$  (b) and  $(C_6)_2PbIBr_3$  (c). Vertical bars indicate the peak position of the corresponding OA spectra (a', b', c')

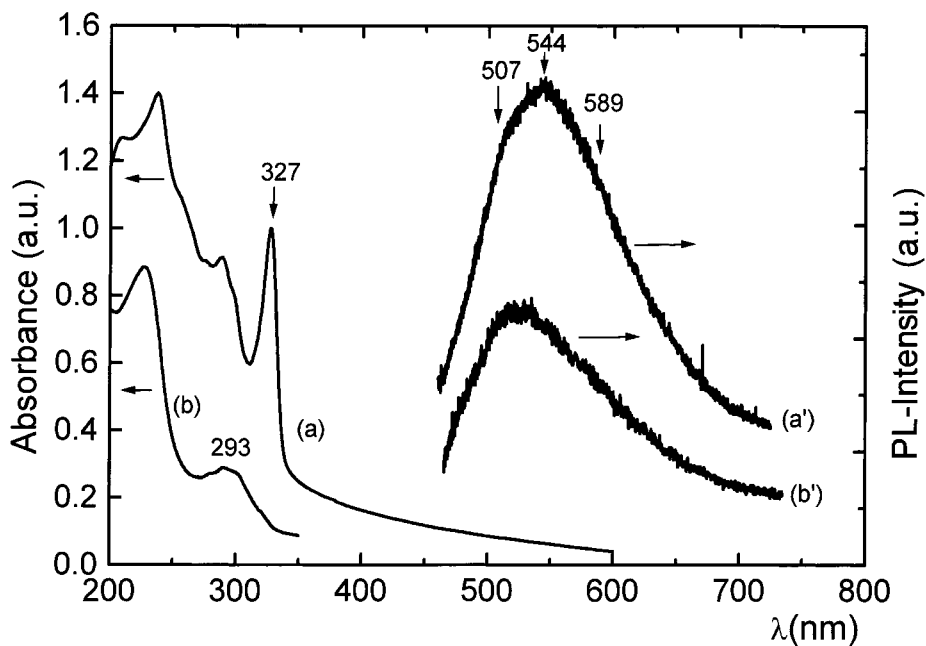


Fig. 3. OA (a, b) and PL (a', b') spectra of  $(C_{10-1})_2PbCl_4$  (a, a') and  $(C_{10-1})Cl$  (b, b')

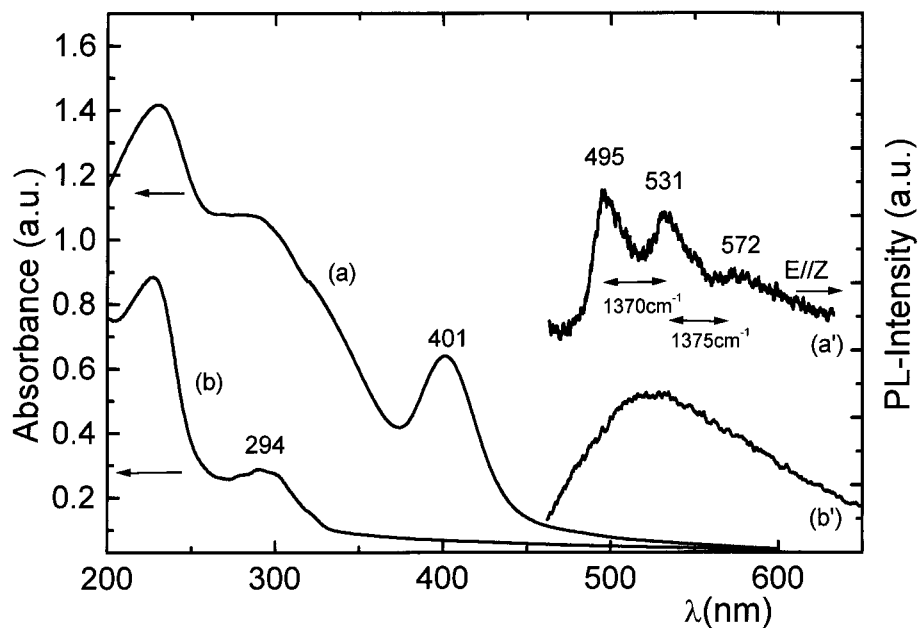


Fig. 4. OA (a, b) and PL (a', b') spectra of  $(C_{10-1})_1PbI_3$  (a, a') and  $(C_{10-1})I$  (b, b'): thin deposits (a, b) and single crystals (a', b') ( $Z = b$ -axis)

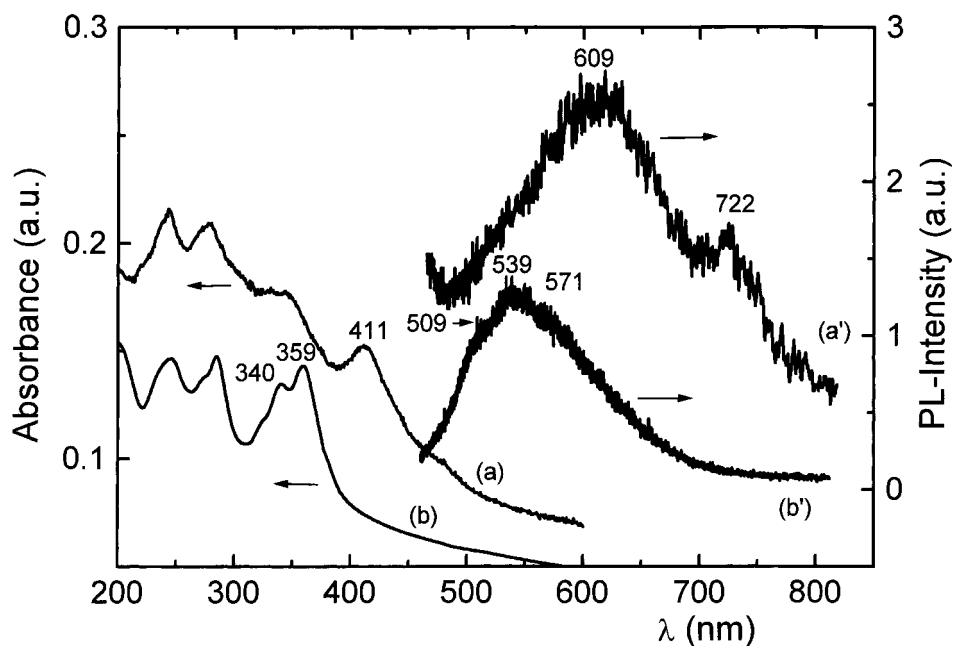


Fig. 5. OA (a, b) and PL (a', b') spectra of  $(C_{16-1})_2Pb_6I_{14}$  (a, a') and  $(C_{16-1})I$  (b, b'): thin deposits (a, b) and polycrystalline pellets (a', b')

$PbCl_4$  (2D),<sup>29</sup> Fig. 4 shows the spectra of  $(C_{10-1})_1PbI_3$  (1D) and Fig. 5 shows the spectra of  $(C_{16-1})_2Pb_6I_{14}$  (1D). Also, in these figures the OA and PL spectra of the corresponding (pure) organic molecules are shown for comparison.

In some organic–inorganic hybrid low-dimensional semiconductor systems (if these have no impurities), it has been predicted theoretically that (dipole–dipole) interactions between the Frenkel excitons of organic components and the Wannier excitons of inorganic components could take place. These interactions give rise to several effects. The Wannier exciton luminescence, for example, is quenched and the organic (Frenkel) luminescence is efficiently turned on when the excitonic band of the inorganic component occurs close to the excitonic band of the organic component.<sup>30–32</sup> Such energy transfer effects have been observed in the PR spectra of some  $PbBr_4$ -based systems<sup>26–28</sup> as well as some  $PbCl_4$ -based systems<sup>29</sup> at low temperatures. We found that the PR band of the organic component in metal halide-based systems could be observed as an intense band with the vibronic pro-

gression at room temperature when excited with visible (laser) excitation lines, e.g. 457.9 nm (Figs 3(a'), 4(a'), 5(a') and 6(a')). The results indicate that the observed phosphorescence could be caused by energy migration from the excitonic states (and perhaps from the impurity states) of the metal halide network to the excited triplet state of the organic component (chromophore). The interaction effect is weaker in the PR spectra of  $(C_{10-1})_2PbCl_4$  (Fig. 3) and  $(C_{10-1})_2PbBr_4$  (see also Refs 26–29) than in those of  $PbI$ -based systems (Figs 4 and 5), where the vibronic progressions in PR spectra are easily observed at room temperature. Vibronic progressions were observed in the PR spectra of  $SnI$ -based complexes but not in the spectra of  $CuBr$ - or  $BiI$ -based compounds. It seems that the magnitude of the excitonic Bohr radius and the dimensionality of the inorganic component play important roles in the mechanism of this energy migration to the triplet states in a way similar to that reported in Refs 30–32 for other systems. However, details of these effects in metal halide and other systems will be reported elsewhere.

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