Exciton-Enhanced Infrared Spectroscopy with Organometallic Perovskite Nanoplatelets

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Chemicals and materials

PbBr₂ (98%, Aladdin), methylamine (CH₃NH₂, 33% in methyl alcohol, Aladdin), octylamine (CH₃(CH₂)₇NH₂, 99%, Aladdin), hydrobromic acid (HBr, 48%, Aladdin), N-dimethylformamide (DMF, analytical grade, Aladdin), toluene (analytical grade, H₂O content 0.018%, Beijing Ouhe Technology Co. Ltd, China), and were used as received without further purification.

Preparation of CH₃NH₂Br (MABr) and CH₃(CH₂)₇NH₂Br (OABr)

CH₃NH₂Br (MABr) and CH₃(CH₂)₇NH₂Br (OABr) were synthesized by the reaction of methylamine and octylamine with HBr (the molar ratio of 1: 1), respectively. 30 mL of methylamine (33% in methyl alcohol) or octylamine was cooled to 0°C with continuous stirring, and the HBr was added slowly. After stirring for 2 h, the precipitate was obtained by rotary evaporation at 60°C, followed by washing and centrifuging with diethyl ether three times, and then dried under vacuum.

Preparation of the CH₃NH₃PbBr₃ nanoplatelet colloids

A series of precursor solutions were prepared in dimethylformamide (DMF) with a fixed total concentration of PbBr₂ (0.05 M) and ammonium ions (0.05 M), but a varying fraction of OABr. The precursor solution (0.50 mL) was added drop-wise into toluene (10 mL) under vigorous stirring to induce crystallization of the desired product. The resulting suspensions were precentrifuged (7000 rpm) to remove the coarse particles and the supernatants were recentrifuged (15000 rpm) and redispersed in neat toluene to obtain the colloids. Three full washing cycles with toluene were carried out for each sample.

Characterization

The morphologies were investigated using a JEOL, JSM-7800F (Japan) Scanning Electron Microscopy (SEM). Photoluminescence (PL) measurements were performed using a Agilent, Cary eclipse (USA) in ambient conditions. Fourier transform infrared (FTIR)
spectra were measured by using a Shimadzu, IRPrestige-21 (Japan). UV-vis absorption spectra were recorded on a FLA6000 (Hangzhou) spectro-photometer.

**SEIRA detection of nitroaromatic molecules on the film of CH₃NH₃PbBr₃ nanoplatelet**

The colloid of CH₃NH₃PbBr₃ nanoplatelet was used to dip-coat on a clear CaF₂ wafer (diameter = 1.5 mm) to form the film of CH₃NH₃PbBr₃ nanoplatelet. Then, A 100μL volume of toluene solution of nitroaromatic molecules, including TNP, PNP, DNT and PNT, respectively, was dropped onto the CH₃NH₃PbBr₃ nanoplatele films and dried in 50°C to remove the solvent. The nitroaromatic molecules on the blank substrate (CaF₂) was also detected by the same method mentioned above. For comparison purpose, the nitroaromatic molecules were also spectroscopically detected on the blank substrate by the same method mentioned above.

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<th>Intercept</th>
<th>Slope</th>
<th>LOD (nmol mm⁻²)</th>
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<tr>
<td>TNP</td>
<td>0.0156</td>
<td>0.0194</td>
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<tr>
<td>PNP</td>
<td>0.0255</td>
<td>0.0317</td>
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</tr>
<tr>
<td>DNT</td>
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<td>0.0287</td>
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<tr>
<td>PNT</td>
<td>0.00116</td>
<td>0.0152</td>
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</table>

*Figure S1. The scanning electron microscopy (SEM) image the CH₃NH₃PbBr₃ nanoplatelet film obtained by dip-coating precursor solutions on a clear CaF₂ wafer.*
**Figure S2.** Infrared spectroscopy of the CH$_3$NH$_3$PbBr$_3$ nanoplatelet film obtained by dip-coating precursor solutions on a clear CaF$_2$ wafer.

**Figure S3.** a) Infrared spectra and b) the selected specific peak heights of PNP molecule (surface density of 2.3 nmol mm$^{-2}$) on the blank substrate (CaF$_2$ wafer only, black) and on the films of the perovskite nanoplatelets obtained with 80% OABr (red).
Figure S4. a) Infrared spectra and b) the selected specific peak heights of DNT molecule (surface density of 2.3 nmol mm⁻²) on the blank substrate (CaF₂ wafer only, black) and on the films of the perovskite nanoplatelets obtained with 80% OABr (red).
**Figure S5.** a) Infrared spectra and b) the selected specific peak heights of PNT molecule (surface density of 2.3 nmol mm$^{-2}$) on the blank substrate (CaF$_2$ wafer only, black) and on the films of the perovskite nanoplatelets obtained with 80% OABr (red).

**Figure S6.** Infrared absorption intensity response to various analyte concentrations. a) TNP, (b) PNP, (c) DNT, (d) PNT. The peak around 1340 cm$^{-1}$ is selected for analysis.