Unveiling interfacial dynamics of zero-dimensional bismuth-based halide perovskite emitters for Electrochemiluminescence Applications

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Supporting Information Contents

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A. Experimental details

Ultrapure fresh water was obtained from a Millipore water purification system (>18M Ω Milli-Q, Millipore). Anhydrous dichloromethane (CH₂Cl₂ or DCM) and tripropylamine (TPrA, 98%) were obtained from TCI (Shanghai) Development Cp., Ltd. and transferred directly into a argon atmosphere glovebox (M. Braun inertgas systems (shanghai) co., ltd) without further purification. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆), was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. and used as received. Acetonitrate (MeCN) was purchased from Acros Organics All the reactions were prepared under Ar atmosphere in the glovebox (< 1 ppm H₂O, < 1 ppm O₂). All syntheses were performed under argon atmosphere in anhydrous solvents, which were dried prior to use following standard procedures.

Characterization

For UV–visible absorption measurements, samples were dissolved in DCM and were carried out on a LAMBDA 1050+ UV/Vis/NIR spectrophotometers (PerkinElmer Inc., USA) using 1 cm path length sealed quartz cells. Photoluminescence measurements were obtained with 340 nm excitation on a RF-5301PC (Shimadzu Scientific Instrument) using 1 cm square sealed quartz cells. Time-resolved PL measurements were made using a time correlated single photon counting setup (PicoQuant GmBH). Temperature dependences of TRPL spectra were collected using an Optistat DN-X cryostat (Oxford Instruments) controlled by a MercuryiTC temperature controller (Oxford Instruments) in the range of 80–340 K. Samples were photoexcited using a laser head providing < 200 ps pulses with a fluence of ~ 30 nJ cm⁻². Ultrafast pump-probe experiments were performed with femtosecond (fs) transient absorption spectroscopy with broadband capabilities. Detailed information of the experimental setup can be found elsewhere.¹ Briefly, the fs-transient absorption spectrometer equipped with UV-visible and near-infrared detectors was used to measure the samples in this study. The white

light continuum probe pulse was generated in a thick sapphire plate (800-1300 nm) and in a CaF_2 crystal (350-700 nm spectral range) using a few µJ pulse energy of the fundamental output of a Ti:sapphire fs regenerative amplifier operating at 800 nm with 35 fs pulses and a repetition rate of 1 kHz. The pump pulses at 355 nm were created from fs pulses generated in an optical parametric amplifier (Newport Spectra-Physics). The sample solution in the sealed cell was constantly stirred to avoid photodegradation in scanned volume. The pump and probe beams were overlapped both spatially and temporally on the sample solution, and the transmitted probe light from the samples was collected on the broad-band UV-visible-near-IR detectors to record the time-resolved excitation-induced difference spectra.

Electrochemistry

For Cyclic voltammogram (CV) and electrochemiluminescence (ECL) experiments, the three-electrode conventional electrochemical cell consisted of a Pt wire (1 mm in diameter) as a counter electrode, a Ag/AgNO₃ as a reference electrode, and a Pt disk (2 mm in diameter) inlaid in PTFE act as a working electrode. The geometric area of the Pt disk electrode was 0.0314 cm². After each experiment, the potential of the Ag/AgNO₃ wire was calibrated with ferrocene as internal standard (+0.197 V vs SCE).² The working electrode was sonicated in Milli-Q deionized water and then in acetone before the experiment. The clean-up procedures of counter and reference electrodes were processed by sonicating in acetone, water, and ethanol, finally were rinsed with D.I. water, dried in ambient condition and then transferred into a glovebox.

All solutions for electrochemical measurements consisted of 2 mM DBI in dry dichloromethane as the solvent with 0.1 M TBAPF₆ as the supporting electrolyte. For the measurement under ambient condition, the electrochemical and ECL cells with sample solution was protected with airtight sealed Teflon cap to avoid any O_2 contamination. To connect with the electrochemical cell, the stainless-steel rods as a conductor were driven

through the cap. CV were obtained on a CHI 760E CH Instruments electrochemical workstation (Chenhua Co., Shanghai, China)

ECL

The ECL spectra were obtained on homemade system coupling a PyLoN charge-coupled device (CCD) camera (Teledyne, USA) cooled to – 100°C with an Acton SpectraPro 2300 monochromator (Acton, MA) as the detector. CV-ECL plots and ECL intensity - time plots were collected on an MPI-E ECL analyzer (Xi'an Remax Analyse Instrument Co., Ltd., Xi'an, China). The PMT was supplied with –800 V.

Preparation of bismuth-based perovskite

Preparation of bismuth-based perovskite adapt the literature method described by Tang *et. al.*.³ Simple solvothermal techniques were used to prepare the samples made of bismuth. After vigorously agitating 30 mL of IPA to dissolve 0.2 g of Bi(NO₃)₃·5H₂O, 0.12 g of MAI was added to the aforementioned solution. An additional 30 minutes of stirring followed the addition of 1 mL of HI solution and a DMF co-solvent with DMF/IPA volume percents of 10%. The mixture was then transferred and sealed into a 50 mL stainless steel autoclave that had a Teflon liner. For six hours, the autoclave reactor was heated to 130 °C, and after that, it was cooled to room temperature. The resultant precipitates were collected and allowed to dry for eight hours at 60 °C.

Electrochemical Kinetics Calculations:

The diffusion coefficient (d), along with the transfer coefficient (α), estimates the heterogeneous electron-transfer rate constant (k^0). The diffusion coefficients given by the Randles-Sevcik equation (1) are,⁴

$$I_{rev} = 2.69 \times 10^5 n^{\frac{3}{2}} A C D^{\frac{1}{2}} v^{\frac{1}{2}}$$
(1)

For an irreversible system, a modified equation is given by equation 2

$$I_{irrev} = 2.99 \times 10^5 nAC(\alpha n'D)^{\frac{1}{2}}$$
 (2)

For equations 1 and 2, where I is peak current (A), n is the number of the exchanged electrons, n' is the total number of electrons transferred before the rate-determining step, α is

the transfer coefficient, A is the active surface area of the working electrode (cm²), D is the diffusion coefficient (cm²/s), and C is the bulk concentration of the participating species (mol cm⁻³), v is the voltage scan rate (V/s).

Through the Tafel plot drawn from the descending parts of the cathodic and anodic peaks of the cyclic voltammogram, α can be determined by the slope of the plot of log(i) versus potential, as shown in equation 3.⁴

$$Slope = \frac{-\alpha F}{2.3RT} or \frac{\alpha F}{2.3RT}$$
(3)

The heterogeneous electron-transfer rate constant (k^0) is estimated by the Gileadi method based on determining the critical scan rate at which the reaction converts from reversible to irreversible or quasi-reversible to irreversible.⁵ The critical scan rate (V_c) is graphically evaluated by E_p plotted against the log of scan rate at low and high scan rates (**Figures S2d-f**). Two different slopes are obtained from two lines fitted for the low and high scan rates, whose intersection provides the critical scan rate, and then the k^0 can be determined by equation 4.⁶

$$\log k^{0} = -0.48\alpha + 0.52 + \log \left(\frac{nF\alpha V_{c}D}{2.3RT}\right)^{\frac{1}{2}}$$
(4)

B. Supporting Data



Figure S1. fs-TA kinetic traces of DMA₃BiI₆ at timescale between 0ps to 2500ps.



Figure S2 Tafel plot of the (a) reduction peak, (b) first oxidation peak and (c) second oxidation peak of DMA₃BiI₆; The plot of E_p against the log of scan rate at low and high scan rates of (d) oxidation reaction (e) first reduction reaction and (f) second reduction reaction of DMA₃BiI₆. Under the condition of 2mM DMA₃BiI₆ in 100 mM TBAPF₆ using DCM as solvent.



Figure S3 (a) SEM image of $MA_3Bi_2I_9$. ECL (red curve) – CV (blue curve) simultaneous measurements by the pulsing potential from (b) approximately 0.0V to -1.8V vs. SCE and (c) approximately 0.0V to +1.2V vs. SCE; (c) $MA_3Bi_2I_9/PE$ in the presence of 10 mM TPrA as the co-reactant for pulsing potential approximately +0.2 to +1.2 V vs. SCE.



Figure S4 TEM image of DMA_3BiI_6 . (a) Low-magnification TEM image showing aggregated DMA_3BiI_6 nanostructures. (b) High-magnification TEM image revealing the DMA_3BiI_6 granule and its nanoscale features.

Temperature (°C)	$\tau_1/\mu s$ (α_1)	$ au_2/\mu s$ ($lpha_2$)	<\alpha > [a] /\mu s	χ^2
340K	0.282 (21.71%)	2.13 (78.29%)	1.73	0.75
310K	0.305 (20.51%)	2.15 (79.49%)	1.77	0.76
280K	0.376 (20.21%)	2.26 (79.79%)	1.88	0.78
250K	0.402 (19.85%)	2.34 (80.15%)	1.96	0.78
220K	0.458 (19.62%)	2.41 (80.38%)	2.03	0.70
190K	0.496 (19.20%)	2.54 (80.80%)	2.15	0.72
160K	0.558 (18.99%)	2.60 (81.01%)	2.21	0.82
130K	0.601 (18.63%)	2.77 (81.37%)	2.37	0.77
100K	0.664 (18.38%)	2.89 (81.62%)	2.48	0.77

Table S1 The kinetics of MA₃Bi₂I₉ monitored at 610 nm at different temperatures.

 $[\mathbf{a}] \langle \tau \rangle = \sum_{i} \alpha_{i} \tau_{i}$

Temperature (°C)	$\tau_1/\mu s(\alpha_1)$	$\overline{\tau_2}/\mu s(\alpha_2)$	$<\tau>$ [a] /µs	χ^2
340K	0.318 (15.95%)	2.35 (84.05%)	2.03	0.75
310K	0.341 (17.96%)	2.58 (82.04%)	2.18	0.85
280K	0.383 (18.49%)	2.70 (81.51%)	2.27	0.78
250K	0.412 (18.63%)	2.80 (81.37%)	2.36	0.86
220K	0.480 (19.19%)	2.94 (80.81%)	2.49	0.86
190K	0.514 (19.96%)	3.15 (80.04%)	2.63	0.87
160K	0.583 (20.02%)	3.36 (79.98%)	2.80	0.74
130K	0.610 (20.76%)	3.56 (79.29%)	2.95	0.91
100K	0.656 (21.00%)	3.94 (79.00%)	3.25	0.71

Table S2 The kinetics of DMA_3BiI_6 monitored at 610 nm at different temperatures

 $[\mathbf{a}] \langle \tau \rangle = \sum_{i} \alpha_{i} \tau_{i}$

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