Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

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Supporting information

for

Blue-Light-Excited Narrowing Red Photoluminescence in Lead-Free Double Perovskite $Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ with Cryogenic Effect

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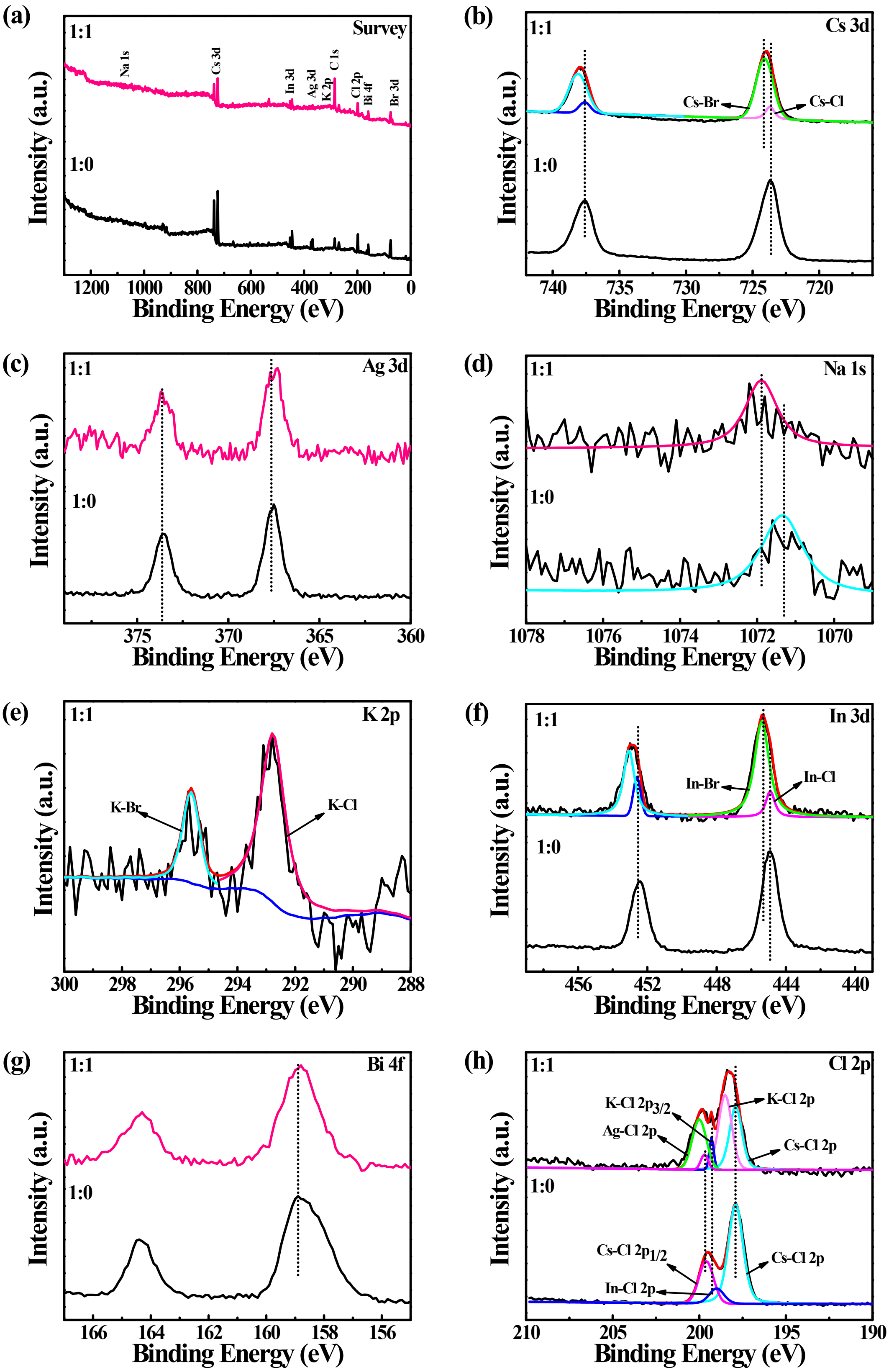
Table S1. The ICP results of $Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$.

To make our ICP-MS results more reliable, blank and standard samples were first used to calibrate the equipment. Then, we measured K and Cs content in $Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ solution dissolved by HNO_3. This data was used to compute the K/Cs ratio of $Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$.

$Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$	K (ug/L)	Cs (ug/L)	K %	Cs %
1:0	0	167.478	0	100
1:0.1	29.649	310.236	24.52	75.48
1:0.4	32.171	137.211	44.35	55.65
1:0.6	32.331	101.524	51.98	48.02
1:1	70.152	182.230	56.68	43.32
1:1.2	44.776	164.838	48.01	51.99



(a)
1:1
Survey
Na 1s
Cs 3d
In 3d
Ag 3d
K 2p
C 1s
Cl 2p
Bi 4f
Br 3d
1:0
Intensity (a.u.)
1200
1000
800
600
400
200
0
Binding Energy (eV)
(b)
1:1
Cs 3d
Cs-Br
Cs-Cl
1:0
Intensity (a.u.)
740
735
730
725
720
Binding Energy (eV)
(c)
1:1
Ag 3d
1:0
Intensity (a.u.)
375
370
365
360
Binding Energy (eV)
(d)
1:1
Na 1s
1:0
Intensity (a.u.)
1078
1076
1074
1072
1070
Binding Energy (eV)
(e)
1:1
K 2p
K-Br
K-Cl
Intensity (a.u.)
300
298
296
294
292
290
288
Binding Energy (eV)
(f)
1:1
In 3d
In-Br
In-Cl
1:0
Intensity (a.u.)
456
452
448
444
440
Binding Energy (eV)
(g)
1:1
Bi 4f
1:0
Intensity (a.u.)
166
164
162
160
158
156
Binding Energy (eV)
(h)
1:1
Cl 2p
K-Cl 2p3/2
K-Cl 2p
Ag-Cl 2p
Cs-Cl 2p
1:0
Cs-Cl 2p1/2
Cs-Cl 2p
In-Cl 2p
Intensity (a.u.)
210
205
200
195
190
Binding Energy (eV)

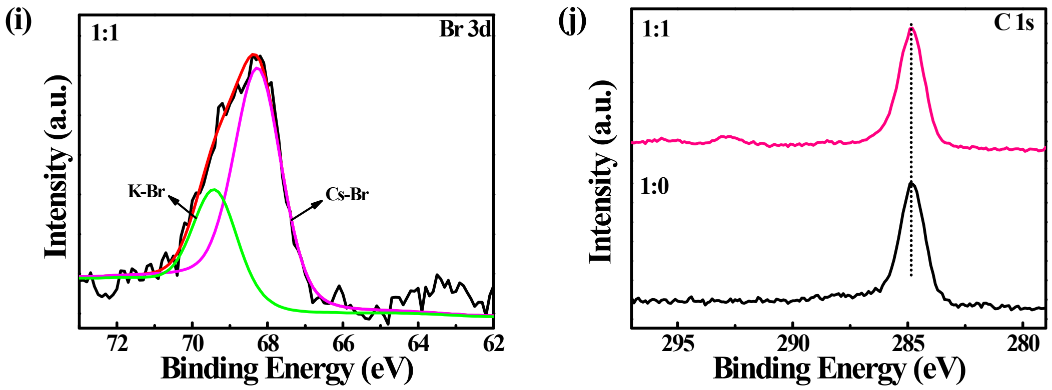


Figure S1. (a) Survey-scan XPS spectra of $Cs_2Ag_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_6$ (1:0) and $Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (1:1). High resolution XPS spectra of: (b) Cs 3d, (c) Ag 3d, (d) Na 1s, (e) K 2p, (f) In 3d, (g) Bi 4f, (h) Cl 2p, (i) Br 3d and (j) C 1s.

Table S2. Fitting values of τ_1, A_1, τ_2, A_2 and τ_{av} at 10 K.

$Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (1:1)	$\tau_1(us)$	A_1	$\tau_2(us)$	A_2	$\tau_{av}(us)$
λ_{ex}= 365 nm	15.30	98	46.90	2	15.97
λ_{ex}= 467 nm	25.33	76	72.84	24	36.69

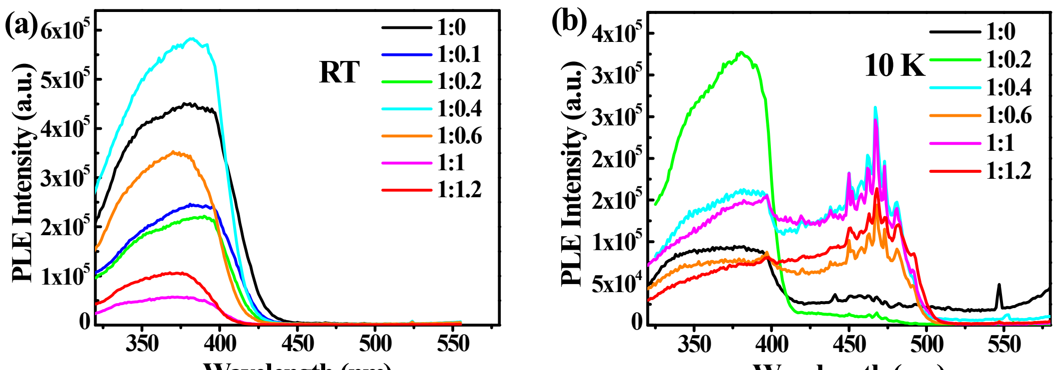


Figure S2. PLE spectra of $Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ at (a) 10 K and (b) room temperature.

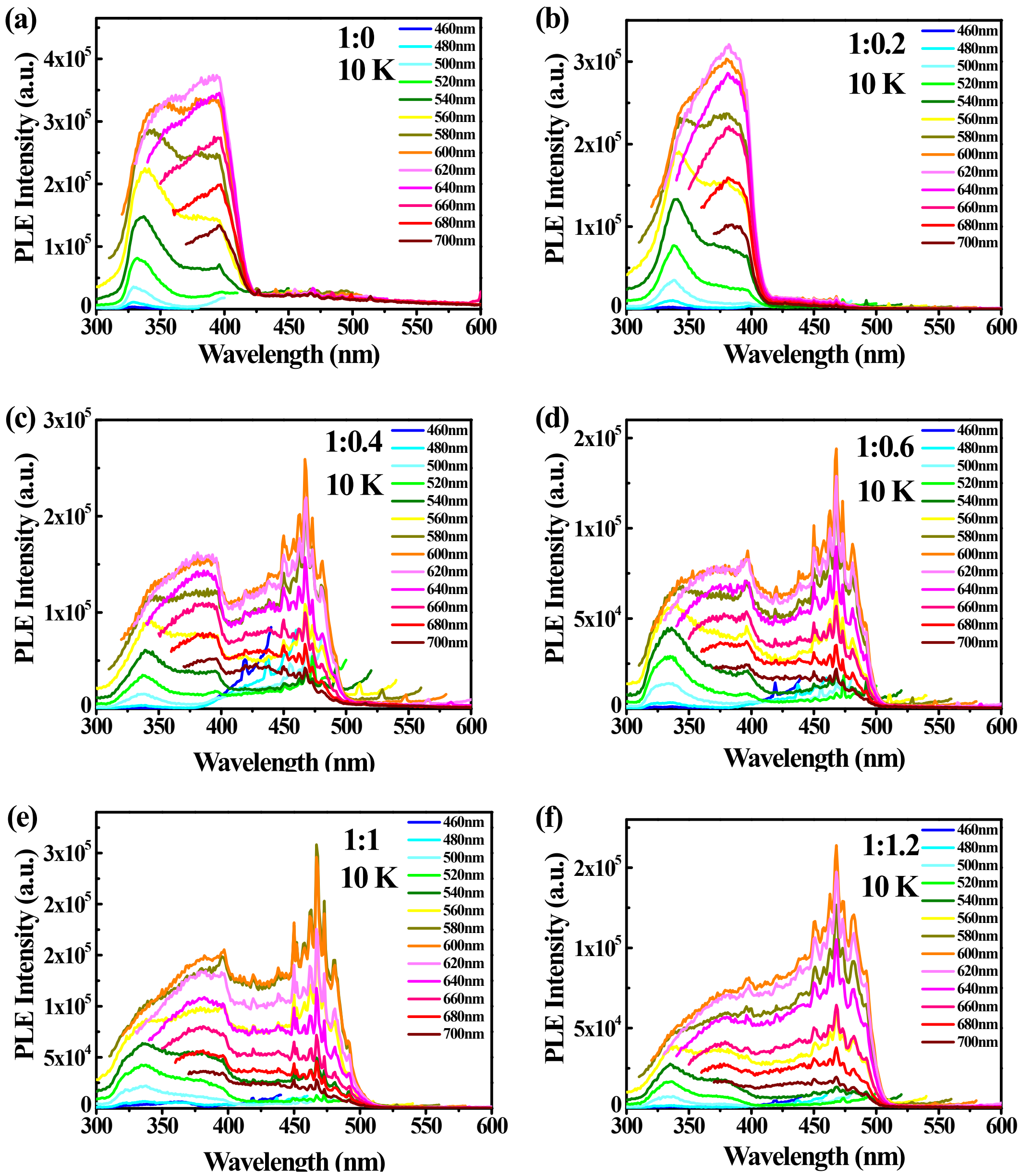


Figure S3. PLE spectra of (a) 1:0.0, (b) 1:0.2, (c) 1:0.4, (d) 1:0.6, (e) 1:1.0 and (f) :1.2 at 10 K.

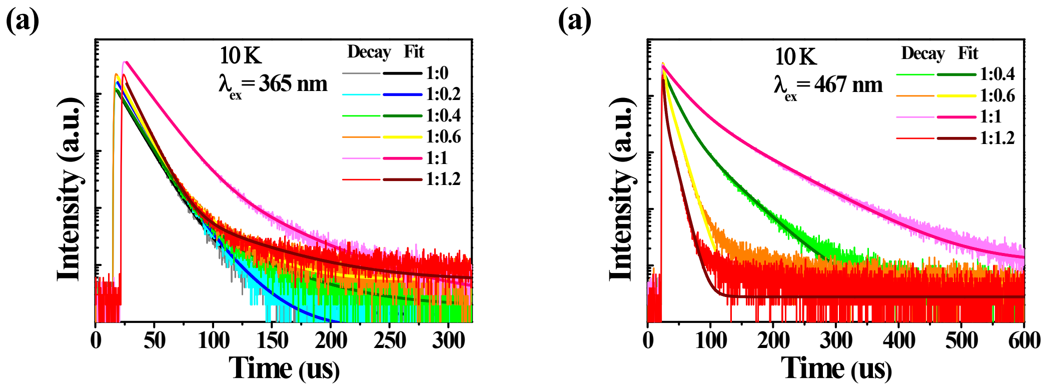


Figure S4. Time-resolved PL spectra of $Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ excited at (a) 365 nm and (b) 467 nm at 10 K.

Table S3. Fitting values of τ_1, A_1, τ_2, A_2 and τ_{av} at 10 K.

10 K（λ_{ex}= 365 nm）	$\tau_1(us)$	A_1	$\tau_2(us)$	A_2	$\tau_{av}(us)$
1:0	12.16	98	28.60	2	12.53
1:0.2	11.97	97	23.95	3	12.36
1:0.4	12.62	99	44.96	1	13.05
1:0.6	10.74	97	29.71	3	11.40
1:1	15.30	98	46.90	2	15.97
1:1.2	10.18	99	54.04	1	10.61

Table S4. Fitting values of τ_1, A_1, τ_2, A_2 and τ_{av} at 10 K.

10 K（λ_{ex}= 467 nm）	$\tau_1(us)$	A_1	$\tau_2(us)$	A_2	$\tau_{av}(us)$
1:0.4	15.35	85	42.69	15	19.51
1:0.6	11.54	51	3.20	49	7.43
1:1	25.33	76	72.84	24	36.69
1:1.2	2.24	71	9.53	29	4.36

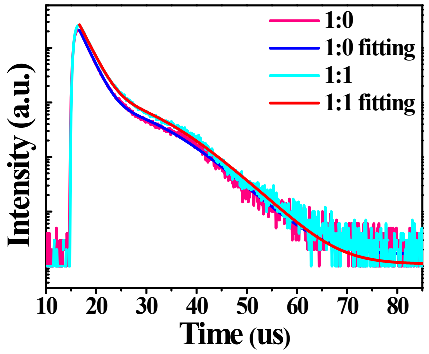


Figure S5. Time-resolved PL spectra of $Cs_2Ag_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_6$ (1:0) and $Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (1:1) excited at 365 nm at room temperature.

Table S5. Fitting values of τ_1, A_1, τ_2, A_2, τ_3, A_3 and τ_{av} at room temperature (RT).

RT（λ_{ex}= 365 nm）	$\tau_1(us)$	A_1 %	$\tau_2(us)$	A_2 %	$\tau_3(us)$	A_3 %	$\tau_{av}(us)$
1:0	5.25	40	5.51	40	1.89	20	4.69
1:1	4.22	29	3.96	49	3.53	21	3.94

Table S6. Fitting parameters of $I(0)$, A and ΔE at 365 nm excitation.

$Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (180-300k)	$I(0)$	$\Delta E / meV$	A
1:0 (λ_{ex}= 365 nm)	85891.3	178.68	851.95
1:0.2 (λ_{ex}= 365 nm)	95276.66	153.33	223.69
1:0.4 (λ_{ex}= 365 nm)	100691.68	148.78	301.76
1:0.6 (λ_{ex}= 365 nm)	62715.98	132.04	123.20
1:1.0 (λ_{ex}= 365 nm)	103966.91	129.84	202.06
1:1.2 (λ_{ex}= 365 nm)	53882.29	118.77	31.63

Table S7. Fitting parameters of I(0), A and ΔE at 467 nm excitation.

$Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (10-180k)	$I(0)$	$\Delta E / meV$	A
1:0.4 (λ_{ex}= 467 nm)	234762.4	42.55	75.18
1:0.6 (λ_{ex}= 467 nm)	126282.3	43.85	206.58
1:1.0 (λ_{ex}= 467 nm)	65312.81	53.74	372.22
1:1.2 (λ_{ex}= 467 nm)	141479.6	44.93	388.31

Table S8. Fitting parameters of $Eg(0)$, S and $\langle \eta\omega \rangle$ at 467 nm excitation.

$Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (180-300k)	$Eg(0)/eV$	S	$\langle \eta\omega \rangle / meV$
1:0 (λ_{ex}= 365 nm)	2.03	4.31	28.08
1:0.2 (λ_{ex}= 365 nm)	2.03	3.77	22.36
1:0.4 (λ_{ex}= 365 nm)	2.03	3.83	29.23
1:0.6 (λ_{ex}= 365 nm)	2.03	4.38	22.04
1:1 (λ_{ex}= 365 nm)	2.03	4.47	30.80
1:1.2 (λ_{ex}= 365 nm)	2.04	3.41	16.18

Table S9. Fitting parameters of $Eg(0)$, S and $\langle \mathrm{h}\omega \rangle$ at 467 nm excitation.

$Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (10-150k)	$Eg(0)/eV$	S	$\langle \mathrm{h}\omega \rangle / meV$
1:0.4 (λ_{ex}= 467 nm)	2.05	0.50	5.30
1:0.6 (λ_{ex}= 467 nm)	2.06	0.75	25.12
1:1.0 (λ_{ex}= 467 nm)	2.04	0.94	1.96
1:1.2 (λ_{ex}= 467 nm)	2.05	1.20	93.49

Table S10. Fitting parameters of Γ_0 , Γ_{op} and $\eta\omega_{\mathrm{op}}$ at 365 nm excitation wavelength.

$Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (10-180k)	Γ_0/meV	Γ_{op}/meV	$\eta\omega_{\mathrm{op}}/meV$
1:0 (λ_{ex}= 365 nm)	399.93	138.28	13.10
1:0.2 (λ_{ex}= 365 nm)	393.97	89.70	8.83
1:0.4 (λ_{ex}= 365 nm)	387.17	215.57	16.01
1:0.6 (λ_{ex}= 365 nm)	378.16	688.30	22.70
1:1 (λ_{ex}= 365 nm)	377.57	132.56	11.16
1:1.2 (λ_{ex}= 365 nm)	362.18	49.44	4.51

Table S11. Fitting parameters of Γ_0 , Γ_{op} and $\eta\omega_{\mathrm{op}}$ at 467 nm excitation wavelength.

$Cs_{2-x}K_xAg_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_{6-x}Br_x$ (10-150k)	Γ_0/meV	Γ_{op}/meV	$\eta\omega_{\mathrm{op}}/meV$
1:0.4 (λ_{ex}= 467 nm)	301.61	2828.32	40.00
1:0.6 (λ_{ex}= 467 nm)	316.67	4378.67	41.71
1:1 (λ_{ex}= 467 nm)	280.06	5353.20	46.49
1:1.2 (λ_{ex}= 467 nm)	302.59	1705.16	35.43