

# Demonstration of Particle in a Box Model in Cyanine Dyes

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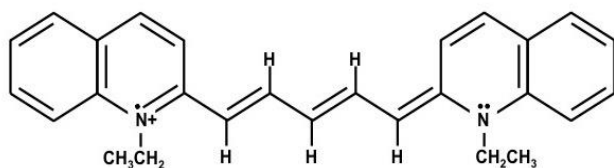
## Introduction:

The particle in a box (PIB) model is a simple case of a quantum mechanical system which allows us to easily find a set of analytic solutions to the Schrödinger equation. The one-dimensional PIB model sets the potential of the Hamiltonian to zero from  $x = 0$  to  $x = a$ , where  $a$  is the length of the potential “well,” and infinity everywhere else, making it impossible for a particle in the box to escape. The eigenvalues ( $E_n$ ) of the system are given by the following equation where  $h$  is Planck’s constant,  $n$  is a quantum number, and  $m$  is the mass of the particle:

$$E_n = \frac{h^2 n^2}{8ma^2} \quad (1)$$

One-dimensional systems are not encountered in reality, but some systems can be approximated as such. In this lab, we assume one-dimensionality on a conjugated chain in a set of dyes. Since the energy levels are quantized, excitation of the electrons will occur at specific energies ( $E$ ), or equivalently, wavelengths ( $\lambda$ ) of light. This equivalence is governed by the following equation where  $c$  is the speed of light:

$$E = \frac{hc}{\lambda} \quad (2)$$



**Figure 1:** 1,1'-diethyl-2,2'-dicarbocyanine iodide. Notice the conjugated chain between the nitrogens.

The dyes each have varying lengths of conjugated chains. The chain in 1,1'-diethyl-2,2'-dicarbocyanine iodide, demonstrated in figure 1, is terminated by two nitrogen atoms. It contains eight  $\pi$ -electrons in the conjugated portion. This is in contrast to 1,1'-diethyl-2,2'-carbocyanine iodide with six and 1,1'-diethyl-2,2'-cyanine iodide with four.

Since only two electrons can occupy a single orbital at a time, the highest occupied orbital in the multi-electron PIB model is  $n = N/2$  where  $N$  is the number of electrons. The lowest unoccupied orbital would be  $n = N/2 + 1$ . Due to the  $n^2$  term in eq. 1, the lowest energy transition ( $\Delta E$ ) between energy levels is between consecutive minimized energy levels. This means that in our system,  $\Delta E$  is between  $n = N/2$  and  $n = N/2 + 1$ . Plugging these values into eq. 1 and subtracting them from another gives this equation:

$$\Delta E = \frac{h^2}{8ma^2} (N + 1) \quad (3)$$

According to the PIB model, the  $\pi$ -electrons should absorb light at quantized wavelengths. We are concerned with the lowest energy transition for reasons later discussed. Practically speaking,  $\Delta E$  appears as an absorption peak with the highest wavelength ( $\lambda_{\max}$ ), from eq. 2. Depending on the dye, the number of  $\pi$ -electrons

will change, and so will  $\lambda_{\text{max}}$ , as a result. From the measured  $\lambda_{\text{max}}$ , we can determine  $\Delta E$  and, due to eq. 1, determine the length of the box of the PIB model. Computationally, we can use software to numerically solve the Schrödinger equation and determine the actual length of the box by measuring the distance between each of the atoms consecutively from nitrogen to nitrogen. This value can be used as a value to compare the length calculated from the PIB model from the experimental data.

## Methods:

For the experimental section, the following dyes were obtained: 1,1'-diethyl-2,2'-cyanine iodide, 1,1'-diethyl-2,2'-carbocyanine iodide and 1,1'-diethyl-2,2'-dicarbocyanine iodide. Approximately one milligram of each dye was weighed, recorded and dissolved in 100 mL of methanol, as measured by a volumetric flask. The Pasco spectrometer was calibrated using a blank of methanol and the absorbance of the dye solutions were each measured. The peak with the longest wavelength was determined by first taking the derivative of the 5-point moving average of the absorption spectra; a change in sign from positive to negative denotes a local maximum. The derivative was graphically enlarged to determine exactly where the last zero was and with what uncertainty.  $\Delta E$  was calculated for each from eq. 2 then the PIB model box length was calculated using eq. 3. This process was repeated for each dye.

For the computational section of the lab, the software Gaussian 16 was used.<sup>1</sup> Each of the dyes were first modelled to visual accuracy. Next, the following heading was added to the Gaussian Input File (gjf file):

```
%chk=INPUT.chk
# opt hf/3-21g geom=connectivity

Dye

1 1
```

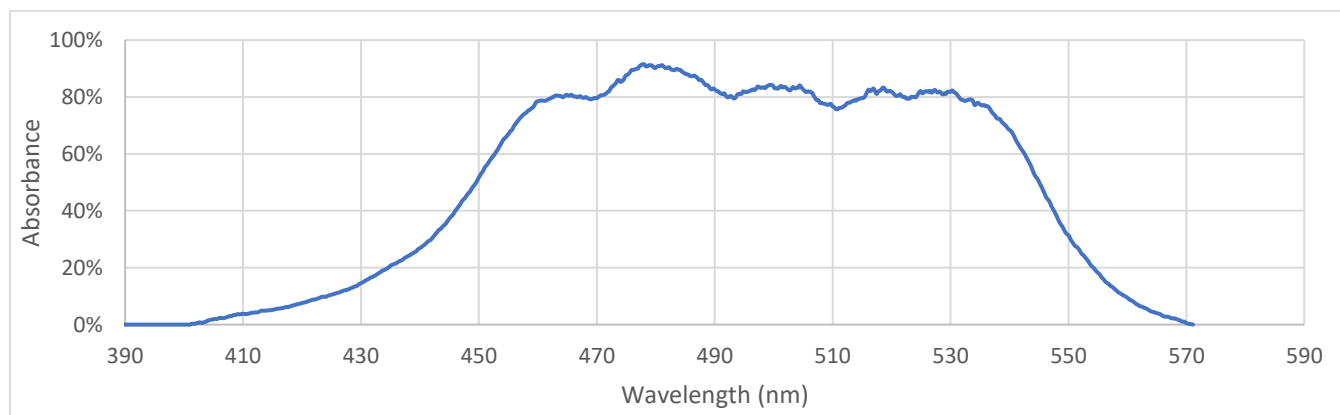
Explicitly, the geometry was optimized using the STO3-21G basis set assuming Hartree-Fock approximation. The charge of the molecule was set to +1. Each of the compounds underwent this process and the resulting check files (.chk) were used as the output. The check files were then imported into Gaussview and the measure tool was used to calculate the distance between each atom in the conjugated chain. The distances were recorded and summed to determine the calculated box length. The experimental box lengths were then compared to the literature box lengths.

## Results and Discussion:

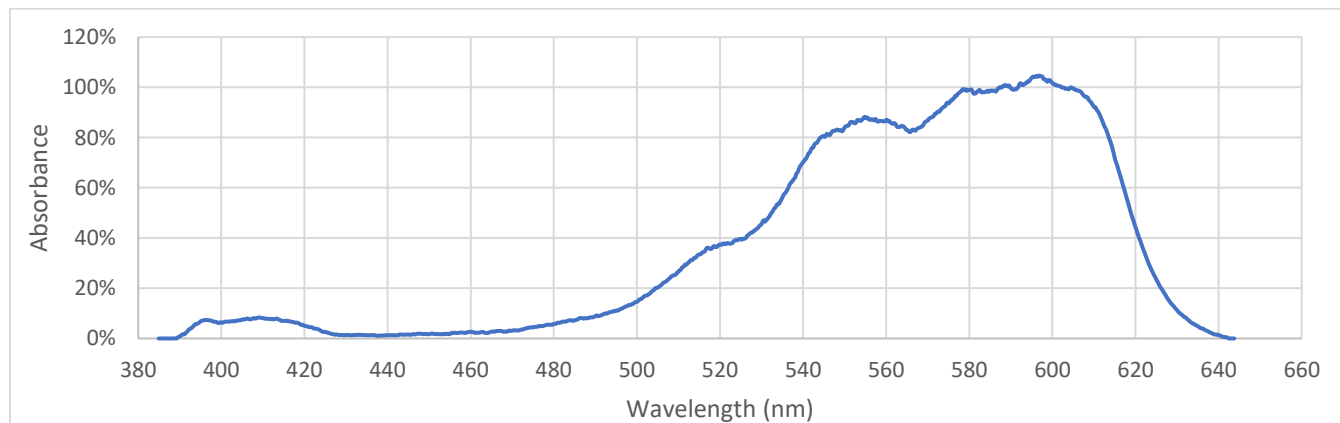
**Table 1:** Collected data from experiments, calculations and literature.  $\lambda_{\max}$  is the peak with the longest wavelength. The box lengths are from the PIB model. The corrected box length extends the box length by including more atoms in the conjugated chain.

	$\lambda_{\max}$ (nm)	Experimental box length (Å)	Literature box length (Å)	Computed box length (Å)	Corrected box length (Å)
1,1'-diethyl-2,2'-cyanine iodide	527±2	8.94±0.02	9.46±0.01 <sup>2</sup>	5.68232±0.00001	8.62754±0.00001
1,1'-diethyl-2,2'- carbocyanine iodide	596±1	11.25±0.01	12.3±0.1 <sup>2</sup>	8.29738±0.00001	11.10379±0.00001
1,1'-diethyl-2,2'- dicarbocyanine iodide	692±1	13.74±0.01	14.7±0.1 <sup>2</sup>	11.06559±0.00001	13.87083±0.00001

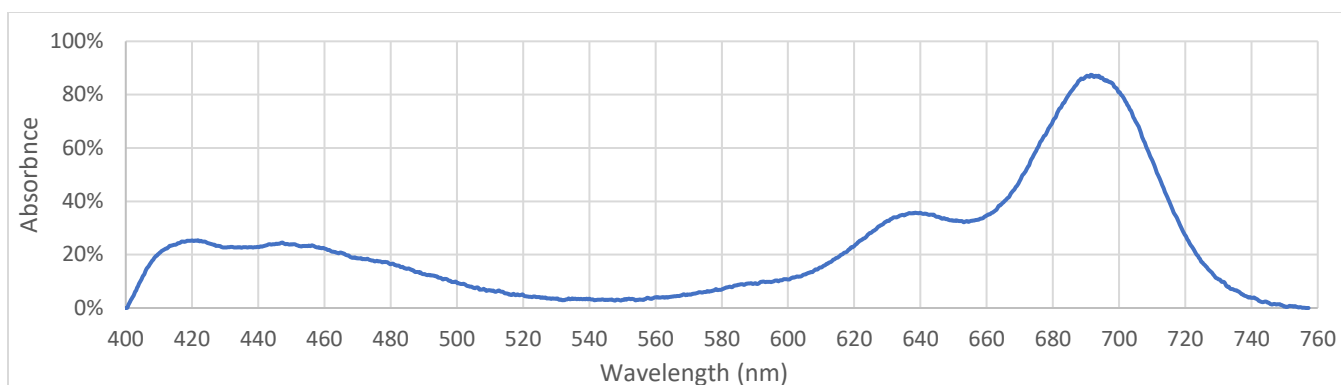
For the remainder of the discussion each of the dyes will be referred to as Dye-4 (1,1'-diethyl-2,2'-cyanine iodide), Dye-6 (1,1'-diethyl-2,2'-carbocyanine iodide) and Dye-8 (1,1'-diethyl-2,2'-dicarbocyanine iodide) for shorthand. The absorption spectra of the Dyes are shown in figures 2-4. There are multiple peaks despite having a single compound because every other excitation has a separate energy. The transition from  $n = N/2$  to  $n = N/2 + 1$  is theoretically possible but it will have a different energy than the peak of interest.



**Figure 2.** Graph of the absorption spectra for Dye-4. The last peak is difficult to determine visually.

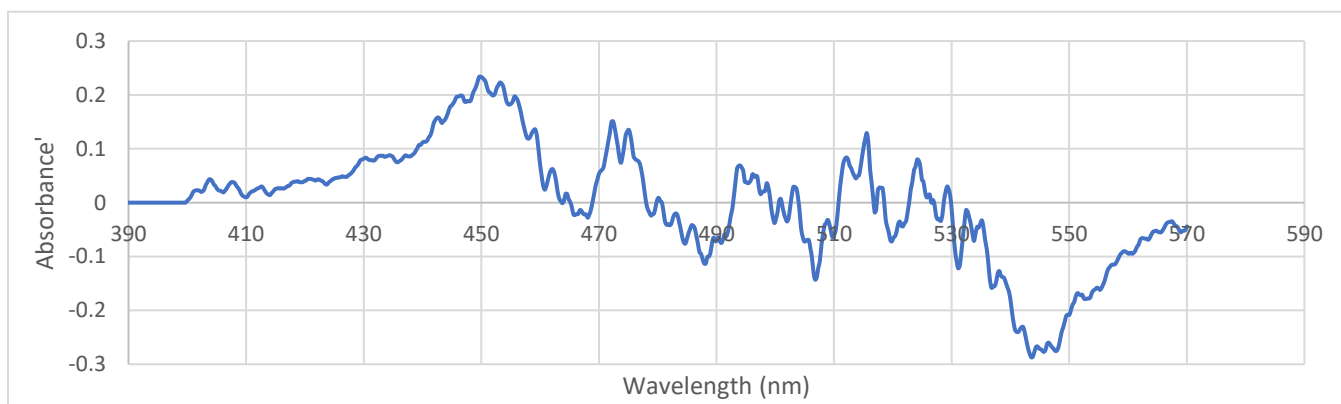


**Figure 3.** Graph of the absorption spectra for Dye-6. The last peak is much clearer here.

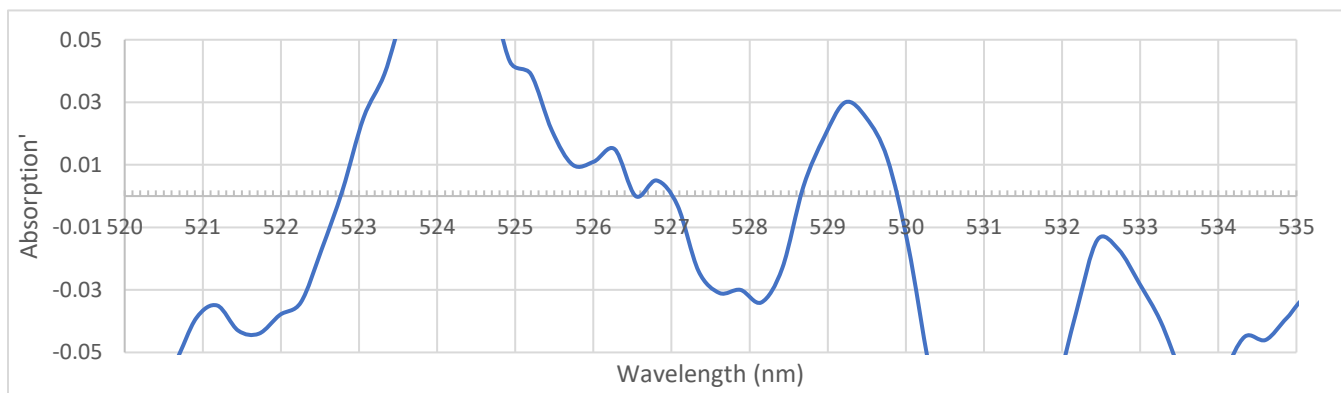


**Figure 4.** Graph of the absorption spectra for Dye-8.

Using Excel, the discrete derivative of the five-point derivative of the absorbance was calculated. The last sign-change from positive to negative was graphically enlarged to exactly determine  $\lambda_{\max}$ . The zero was determined which indicates a local maximum in the absorption spectra. The uncertainty was calculated for each as being at least five times the minimum increment in wavelength of the spectrometer. Since the increment was on average 0.25 nm, the uncertainty in each zero is at least 1.25 nm. Additionally, Dye-4 in particular exhibited noisy behavior, and so the uncertainty was increased to include the multiple sign changes. The derivative graph and its corresponding zero are shown in figures 5 and 6.



**Figure 5.** Graph of the derivative of the absorption spectra for Dye-4. Notice the noisy change of sign from positive to negative near 530nm.



**Figure 6.** Figure 5 zoomed into the 530nm section to show the zero. The zero here is estimated to be 528nm with an uncertainty to include all parts of the noise. The zero is certainly after 526nm but before 530nm, hence the 2nm uncertainty.

From these data, the energy with worst-case scenario uncertainty is calculated with eq. 2. It is important to use  $\lambda_{\max}$  here, or equivalently the peak associated with the lowest energy transition, because we know exactly which excitation this is: the excitation from the highest occupied orbital and the lowest unoccupied orbital. Dye-4 looks like the following:

$$E = \frac{hc}{\lambda} = \frac{1.98645 \times 10^{-25} \text{J/m}}{(527 \pm 2) \times 10^{-9} \text{m}} = (3.77 \pm 0.01) \times 10^{-19} \text{J}$$

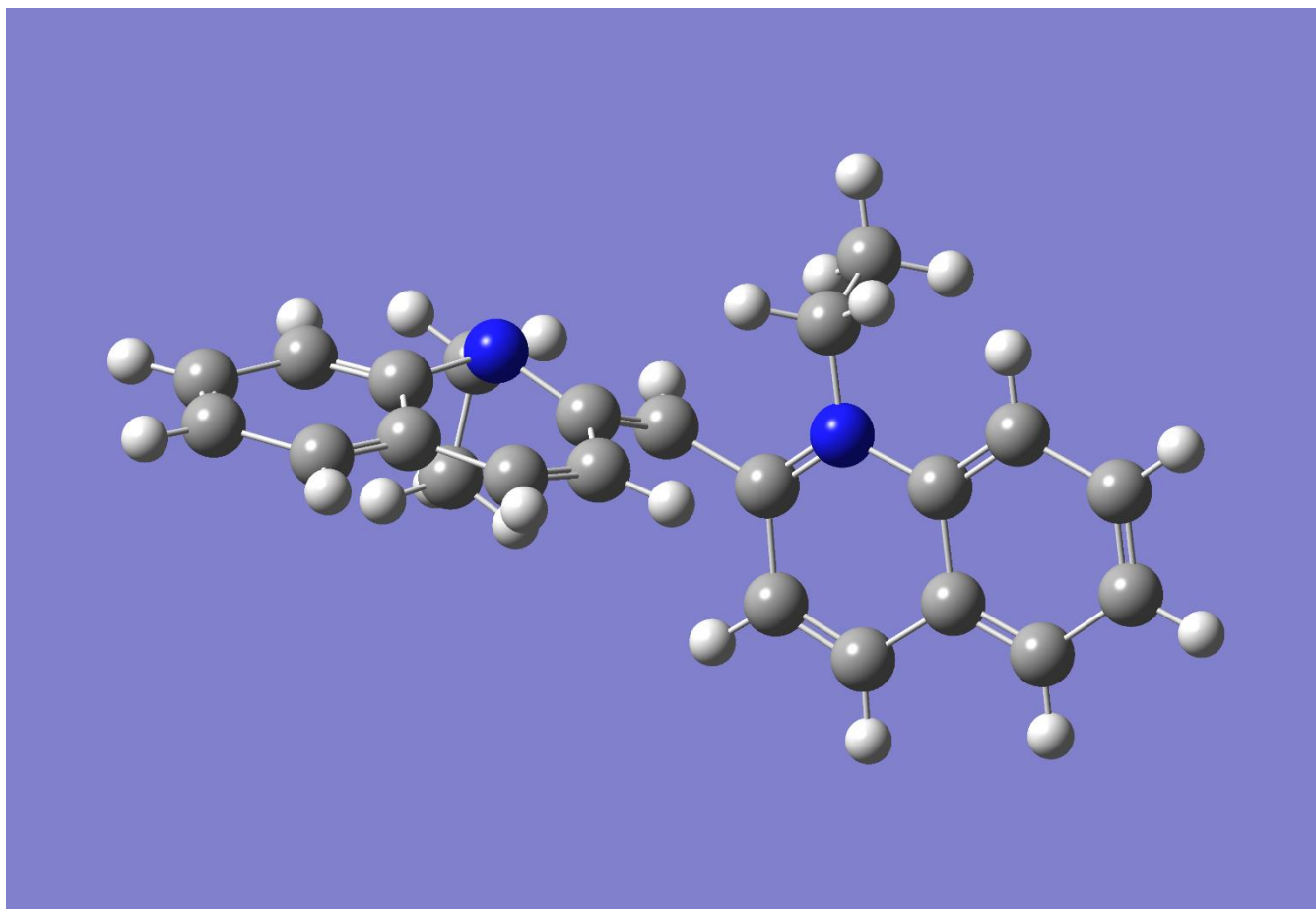
Next, the box length is calculated according to eq. 1. An example with uncertainty is shown. For Dye-4, the number of  $\pi$ -electrons is 4.

$$a = \sqrt{\frac{h^2(N+1)}{8m\Delta E}} = \sqrt{\frac{6.26068 \times 10^{-34} \text{Js}(5)}{8 \times 9.1093837 \times 10^{-31} \text{kg}(3.77 \pm 0.01) \times 10^{-19} \text{J}}} = (8.94 \pm 0.02) \times 10^{-10} \text{m}$$

As expected, the experimental box length increases as the length of the conjugated system is increased. This is also the case for the calculated box lengths. However, all calculations are an underestimate of the experimental box length by 27% on average, or an average of 2.93Å. This is 5% higher than twice the average bond length from all the calculated bond lengths. For each optimized molecule, two more bonds were included: the bond between nitrogen and carbon along the same axis as the conjugated chain. Due to this addition, the calculated box length much more closely approximates the experimental box length with an average underestimate of 1.0% compared to experimental data, or an underestimate of 0.079Å. Interestingly, the trend is such that Dye-4 is an underestimate and Dye-8 is an overestimate.

The literature values were obtained on a set of similar cyanine conjugated dyes: 3,3'-diethylthiacyanine iodides. The differences between the dyes used in our lab are the existence of a sulfur atom in the  $\beta$  position relative to the nitrogens. Also, the quinoline motifs in the lab dyes are replaced with something like an indole motif. As these are different dyes it makes sense that there would be a systemic difference in the box lengths. Although the trend of increasing box length per larger conjugated system remains, the lengths are a 7.4% overestimate compared to our experimental data. To explicitly confirm if these values, we can use the best-case scenario calculation, where if it is possible for the values to agree at all, we say they do. For example, to compare the experimental box length and the corrected calculation for Dye-4 we identify that the experimental value  $(8.94 \pm 0.02) \text{Å}$  the calculated value  $(8.62754 \pm 0.00001) \text{Å}$ . Since the difference between the values  $(.310 \text{Å})$  is larger than the uncertainty combined  $(0.02 \text{Å})$ , there is no possible way the values could agree. This is the case for all comparisons between box lengths for each respective dye.

It is additionally important to consider the optimized structure of the dyes. Dye-4 had an interesting, non-linear conjugated system as shown in figure 7.



**Figure 7.** Dye-4 optimized structure. Notice the non-zero dihedral angle between the quinoline rings.

## Conclusion:

Despite no box lengths agreeing even in the best-case scenario, assuming worst-case scenario error propagation, the corrected calculated values were off by only 1.0% compared to experimental data. This was down from 27% from before the correction of the two additional bonds extending the ‘box’ and effectively the conjugated system. It should be noted that the 1% figure is slightly deceptive as the deviation of the differences is 2.4%. Perhaps this ‘trick’ of adding two extra bonds to the conjugated system may not work if the conjugated system were increased in size to  $N=10$  or higher. Additionally, the addition of those two bonds implies the conjugated system extends past the nitrogens which physically doesn’t make sense. In order to be part of the conjugated system, the carbon behind the nitrogen would have to break benzene’s aromaticity in forming a double bond with the nitrogen additionally causing a carboanion to form on the ring. Due to the stability of nitrogen (I) and benzene, the idea that conjugation would extend to the carbon in the benzene rings seems extremely unlikely.

Many assumptions were made: one-dimensionality and particle in a box seem to be the largest sources of error in this experiment. Electrons here don’t travel in a straight line (remember Dye-4 is not even in a straight line),

nor do they ever hit a wall of potential when they reach the nitrogen. The trends surrounding the length of the conjugated system and  $\lambda_{\text{max}}$  suggest that there truly is a decrease in the HOMO-LUMO gap as the conjugated system increases in size. However, it may not be explained simply by a particle in a box.

## Safety:

Each of the compounds used in this lab are particularly toxic.<sup>3-5</sup> Due to the small quantities used, proper lab procedures should be enough to ensure safety. However, if large enough quantities are consumed, fatality may occur.

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