



# Upconversion in Resonance Energy Transfer Logic

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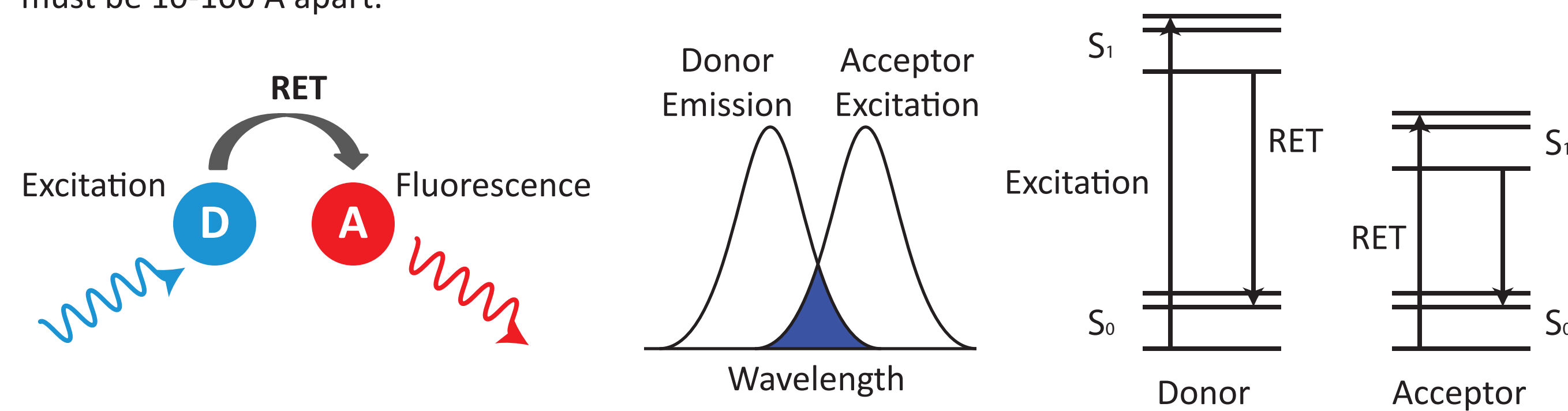
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## Introduction

Self-assembled DNA nano-grids have proven to be excellent molecular breadboards for the precise placement of chromophores. Using Förster resonance energy transfer (RET), networks of these chromophores can perform optical computation by manipulating information in the form of excitons. This computing platform, known as RET logic, offers a promising method for low-cost, nanoscale computation in new domains. However, due to the red-shifting nature of RET, excitons constantly lose energy as they propagate through a network. Without a way to restore this energy, output excitons from one network lack the energy necessary to excite any subsequent network. This limitation places restrictions on the size of any RET circuit, making it difficult to cascade multiple RET networks and create more complex systems. To address this inherent energy loss, we are investigating a possible upconversion mechanism called two-color transfer-induced double-quantum excitation which couples RET and single photon absorption in order to blue-shift red excitons. A semi-classical model for this process has been derived from first principle chemical equations. In addition, a custom dual-beam optical setup has been developed which will allow for experimental verification of the mechanism. If the process is unobservable, the limitations of the optical setup will be used in conjunction with the model to provide rough upper bound calculations on the rate of this upconversion mechanism.

## RET - Resonance Energy Transfer

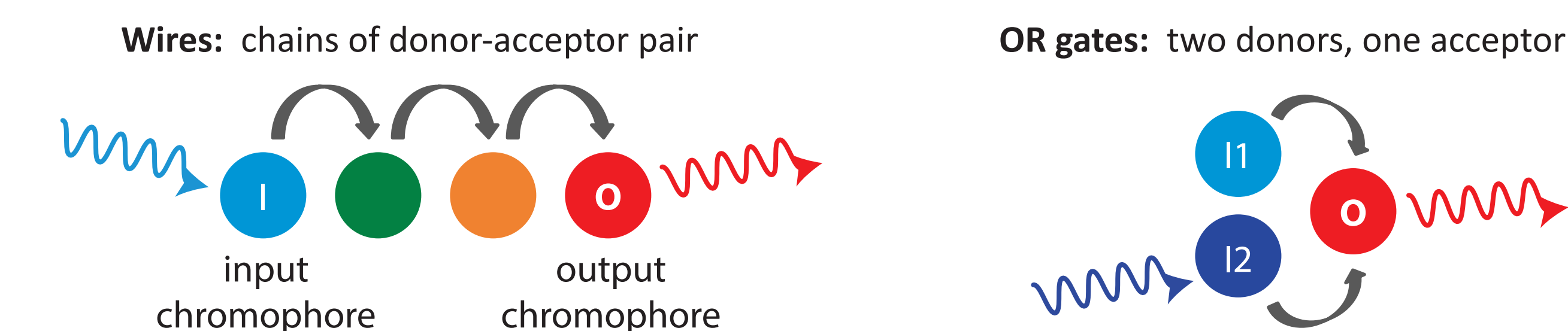
An excited molecule may donate its energy non-radiatively to a neighboring molecule through Förster Resonance Energy Transfer (RET). RET is a weak dipole-dipole coupling mechanism that requires the donor's emission spectrum to overlap the acceptor's excitation spectrum. For RET to occur, the molecules must be 10-100 Å apart.



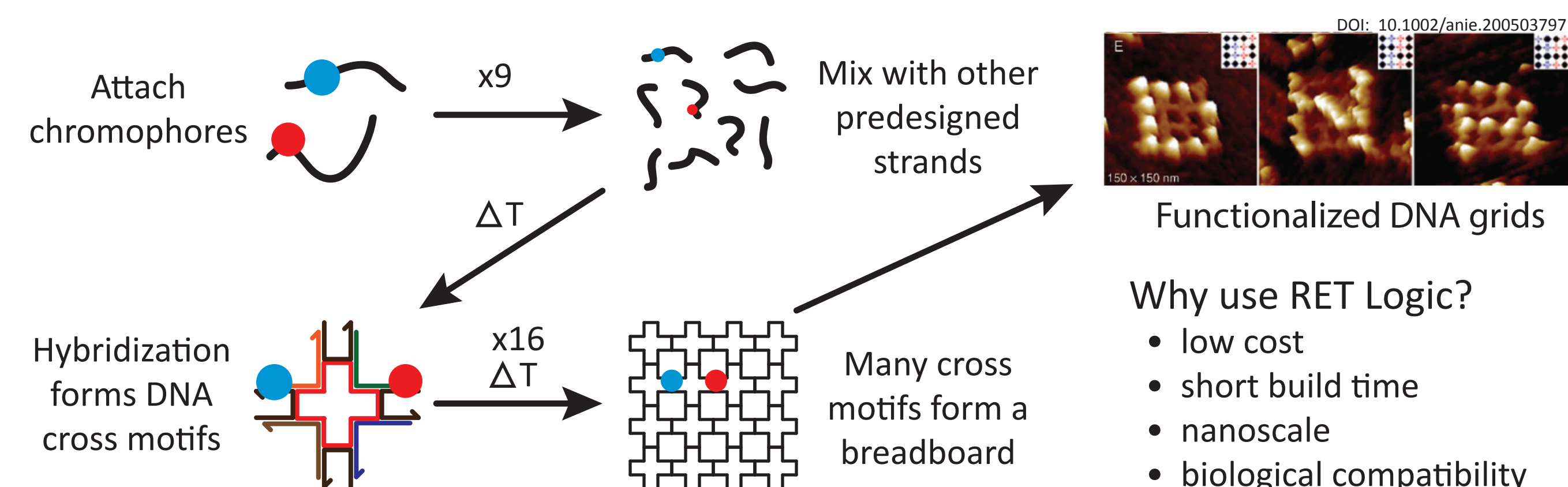
Forster Radius (R<sub>0</sub>)  
• Distance at which transfer efficiency drops to 50%  
Transfer Rate:  
 $R_0^6 = \frac{9000(\ln 10)\kappa^2\phi_D^0}{128\pi^5 N_A n^4} \int I_D(\lambda)\epsilon_A(\lambda)\lambda^4 d\lambda$   
 $k_{RET} = \frac{1}{\tau_{D_0}} \left[ \frac{R_0}{r} \right]^6$  where r is the separating distance and τ is the intrinsic lifetime

## RET Logic

Using RET, networks of chromophores that perform simple computation can be self-assembled on DNA grids. Short wavelength photons act as inputs, exciting designated input chromophores and creating excitons in the system. These excitons hop from chromophore to chromophore according to the network's inner transfer efficiencies. Red shifted fluorescent photons are recorded as the network's output. Below are a few simple example networks:



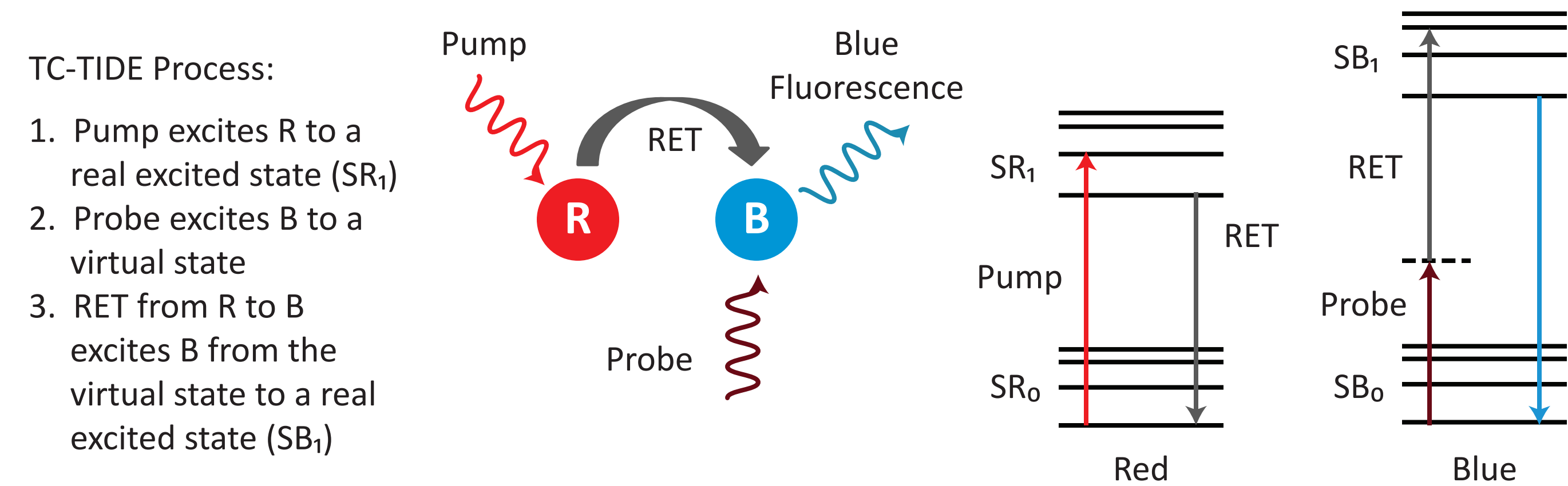
With a specific RET network in mind, preprogrammed DNA strands are functionalized with the correct chromophores and mixed with other preprogrammed strands to create DNA nano-grids. These structures act as molecular breadboards for the precise arrangement of RET networks.



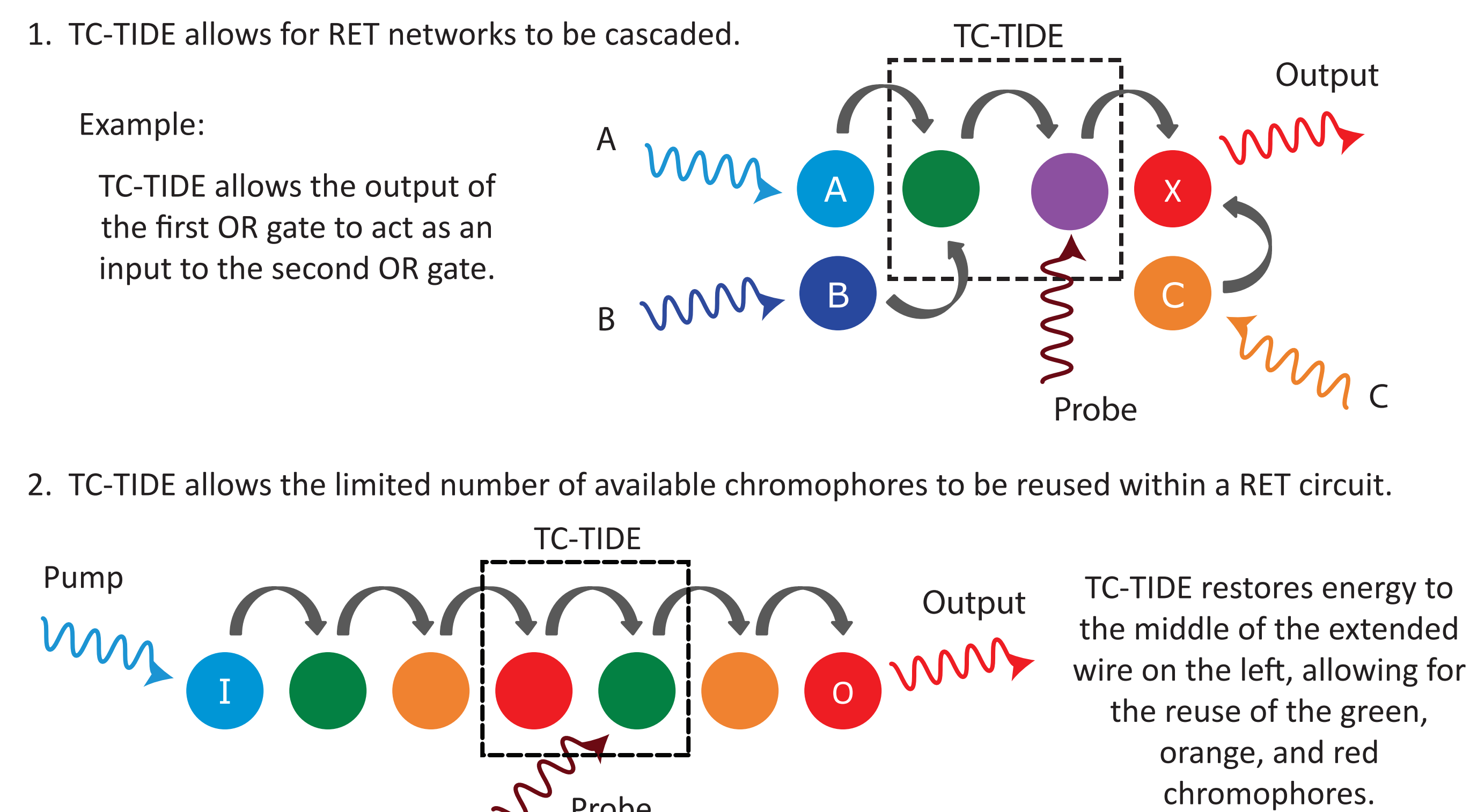
- Why use RET Logic?
- low cost
  - short build time
  - nanoscale
  - biological compatibility

## Two-Color Transfer-Induced Double-Quantum Excitation

Two-color transfer-induced double-quantum excitation is a theoretical upconversion mechanism that allows red-shifted chromophores (R) to act as donors to blue-shifted chromophores (B). Using two excitation sources called the pump and the probe, TC-TIDE couples RET and single photon absorption.

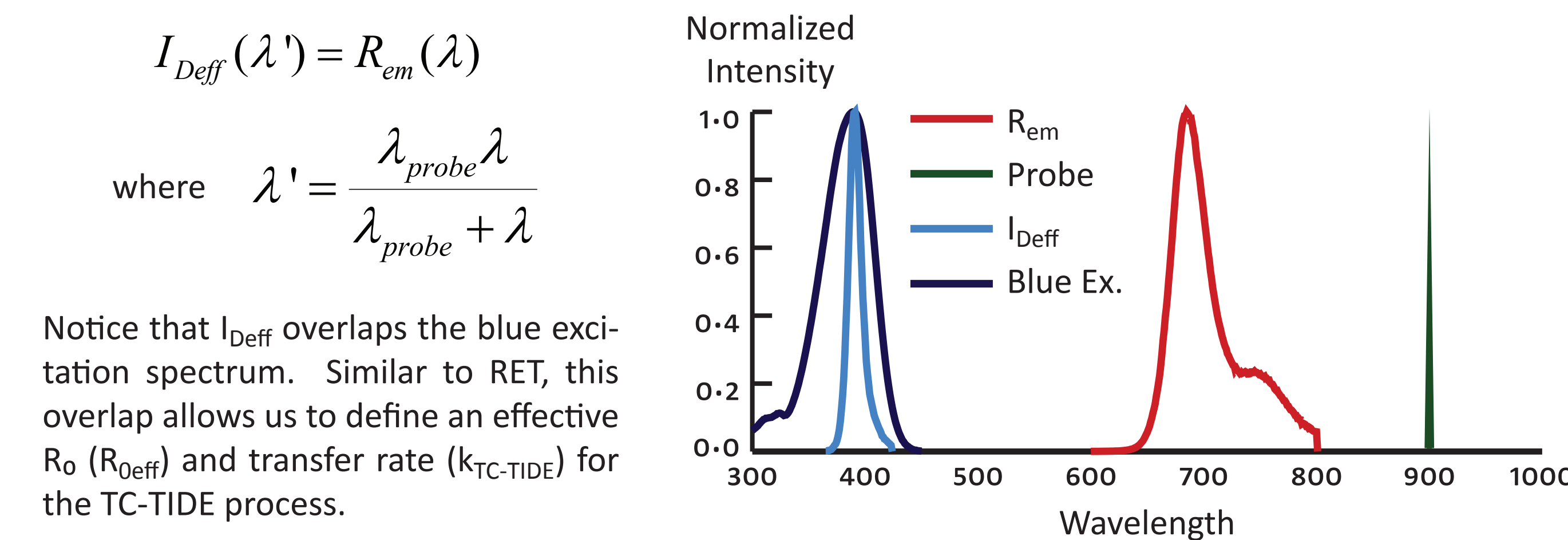


Conventional RET requires donors to be blue-shifted with respect to the acceptor. By allowing red chromophores to transfer energy to blue chromophores, TC-TIDE theoretically solves two previously unsolvable problems with standard RET logic.



## TC-TIDE Chromophore Pairs

For a "good" TC-TIDE chromophore pair, the total energy of the red exciton and the probe photon must be great enough to excite the blue chromophore. Thus, we define the Effective Donor Spectrum I<sub>Deff</sub> as the sum of these two energy sources. In wavelength space, this is calculated as the effective wavelength of the monochromatic probe and the red chromophore's emission wavelengths (R<sub>em</sub>).

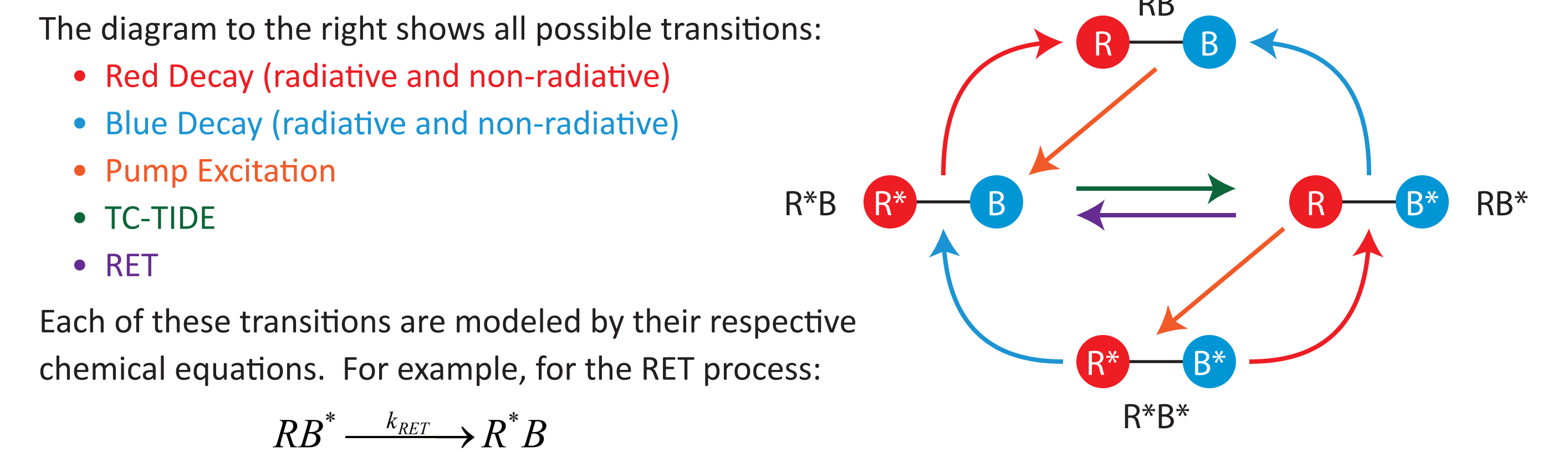


$I_{Deff}(\lambda') = R_{em}(\lambda)$   
where  $\lambda' = \frac{\lambda_{probe}\lambda}{\lambda_{probe} + \lambda}$   
Notice that I<sub>Deff</sub> overlaps the blue excitation spectrum. Similar to RET, this overlap allows us to define an effective R<sub>0</sub> (R<sub>0eff</sub>) and transfer rate (k<sub>TC-TIDE</sub>) for the TC-TIDE process.

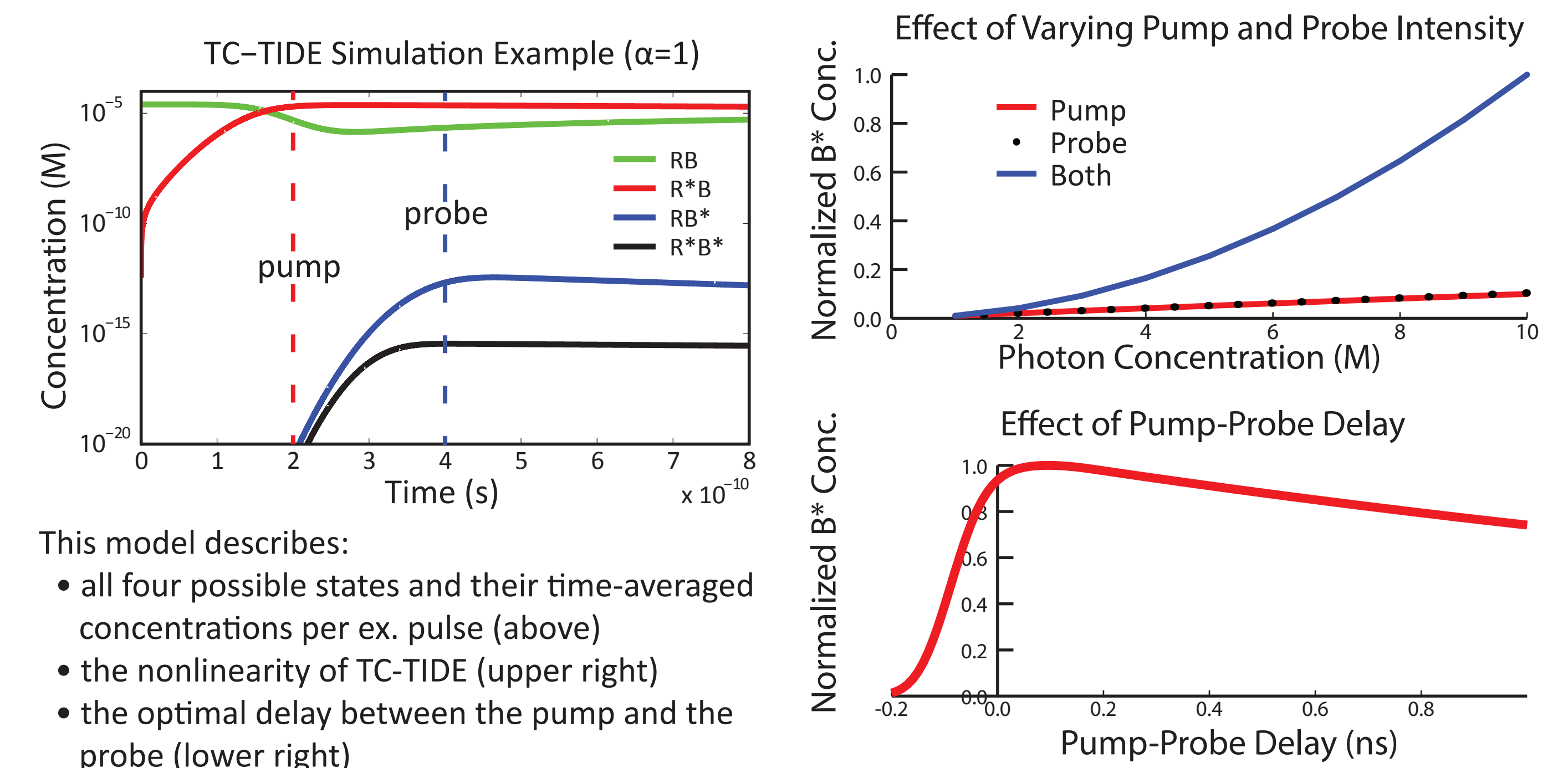
- Choosing the excitation sources:
- The pump is chosen to maximize the excitation of the red chromophore.
  - The probe is chosen to maximize R<sub>0eff</sub>.

## Modeling TC-TIDE Chromophore Pairs

From the ground state, a red and blue chromophore pair (RB) can transition to one of three excited states: R\*B, RB\*, and R\*B\* (where \* denotes the excited state).



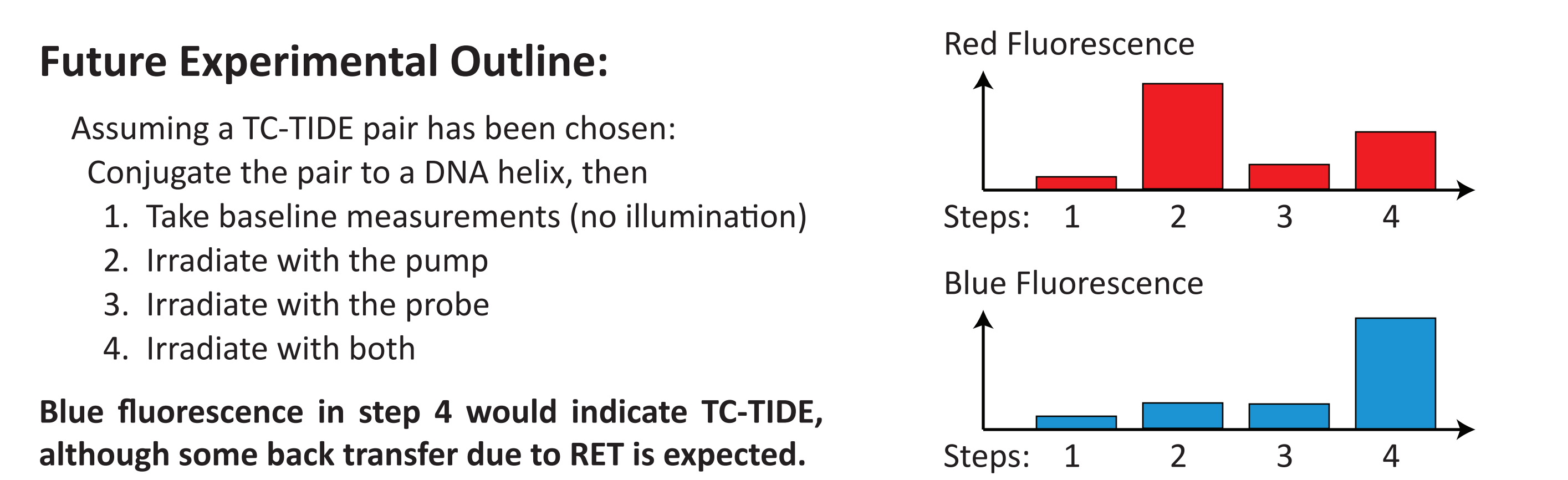
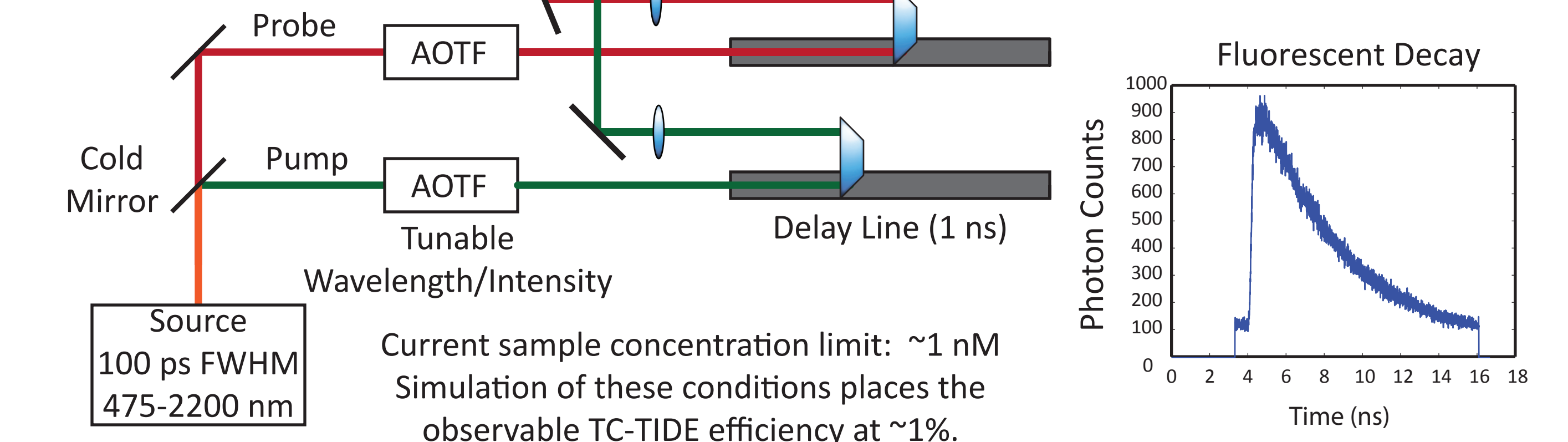
Each of these transitions are modeled by their respective chemical equations. For example, for the RET process:  
 $RB^* \xrightarrow{k_{RET}} R^*B$   
where k<sub>RET</sub> is RET transfer rate described earlier. Using these chemical equations and the TC-TIDE rate formulated previously, differential equations describing the creation and destruction of RB, R\*B, RB\*, and R\*B\* are derived and solved numerically. Based on the initial conditions, this model can simulate TC-TIDE for different efficiencies (values of α) and reveal the following trends.



This model describes:  
• all four possible states and their time-averaged concentrations per ex. pulse (above)  
• the nonlinearity of TC-TIDE (upper right)  
• the optimal delay between the pump and the probe (lower right)

## Optical Setup and Experimentation

To experimentally demonstrate TC-TIDE, we need an optical setup with two excitation sources (the pump and the probe). We must also have control over the delay between these two beams as well as their wavelengths and intensities. Thus, we have constructed the following optical setup.



Blue fluorescence in step 4 would indicate TC-TIDE, although some back transfer due to RET is expected.