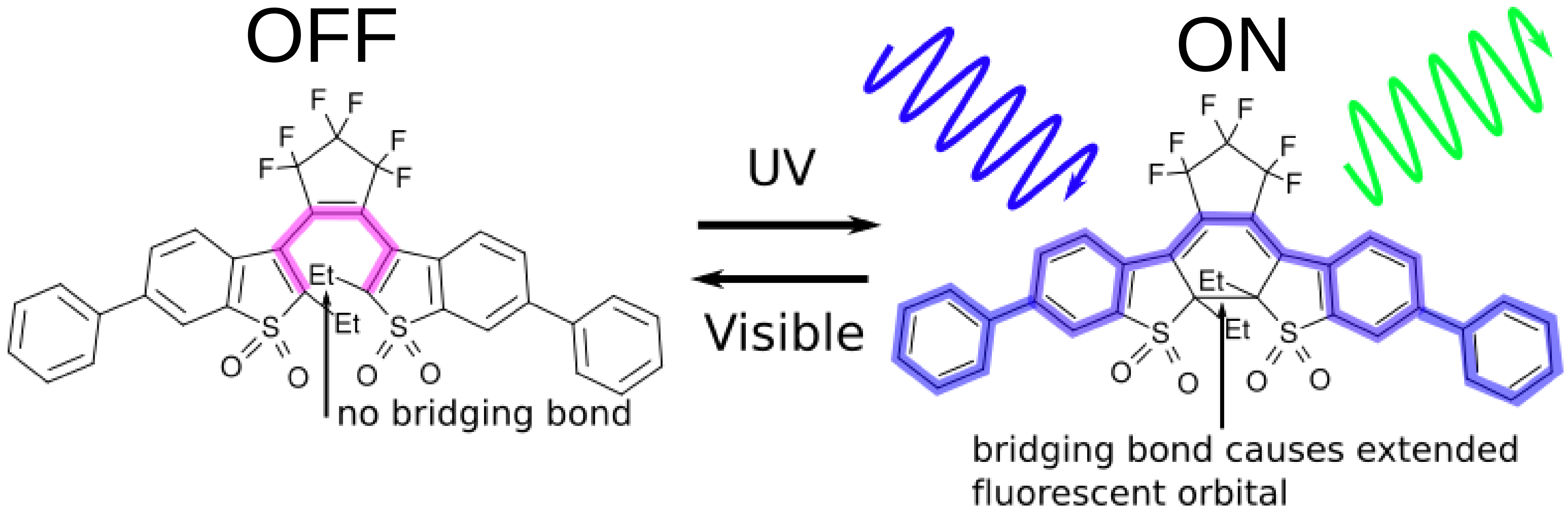
Using Switchable Fluorescent Molecules to Image Tracks and Measure Energy in Large Liquid Double Beta Decay Detectors

Eric Spieglan, Evan Angelico, Andrey Elagin, Joao Shida, Henry Frisch

Fluorescent Dyes that You Can Turn OFF or ON



Highly transparent to visible light
Can absorb a UV photon and turn ON by changing shape and electronic structure

Can **repeatedly** absorb a visible photon and fluoresce
Eventually turns OFF after emitting >1000 photons

Diarylethenes with switchable fluorescence have been synthesized by various workers, and research on diarylethenes as molecules with photoswitchable properties is extensive; see bibliography for recent reviews

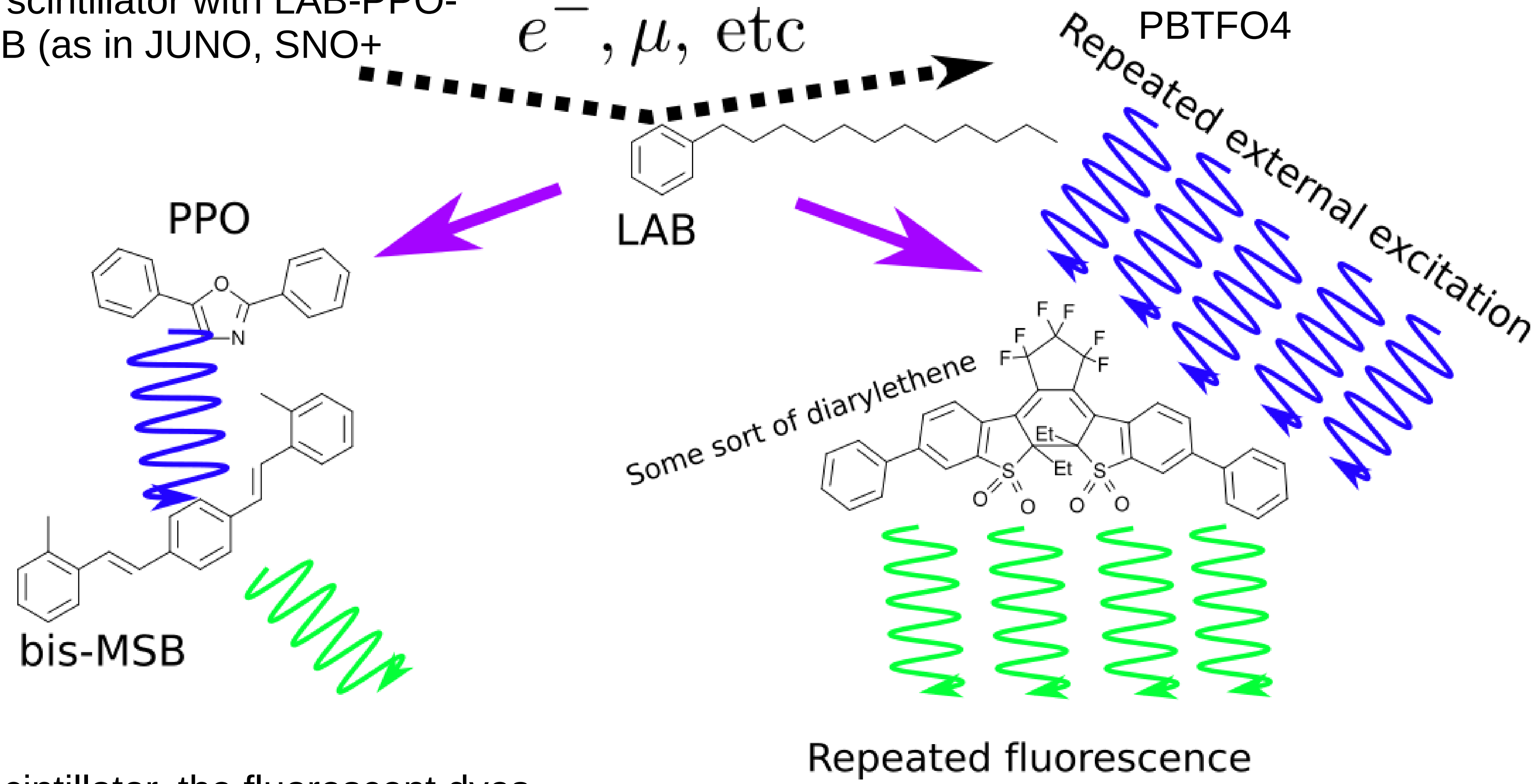
Kakishi Uno, Hiroyuki Niikura, Masakazu Morimoto, Yukihide Ishibashi, Hiroshi Miyasaka, and Masahiro Irie. In situ preparation of highly fluorescent dyes upon photoirradiation. Journal of the American Chemical Society, 133(34):13558–13564, 2011.

Instead of Scintillator, Make Switchillator

When an ionizing particle excites a molecule of solvent…

Liquid scintillator with LAB-PPO-bisMSB (as in JUNO, SNO+ etc)

Switchillator with LAB-PBTFO4



In a scintillator, the fluorescent dyes fluoresce and give you <1 photon to detect; JUNO targets >1200 photoelectons/MeV out of ~9500 photons/MeV

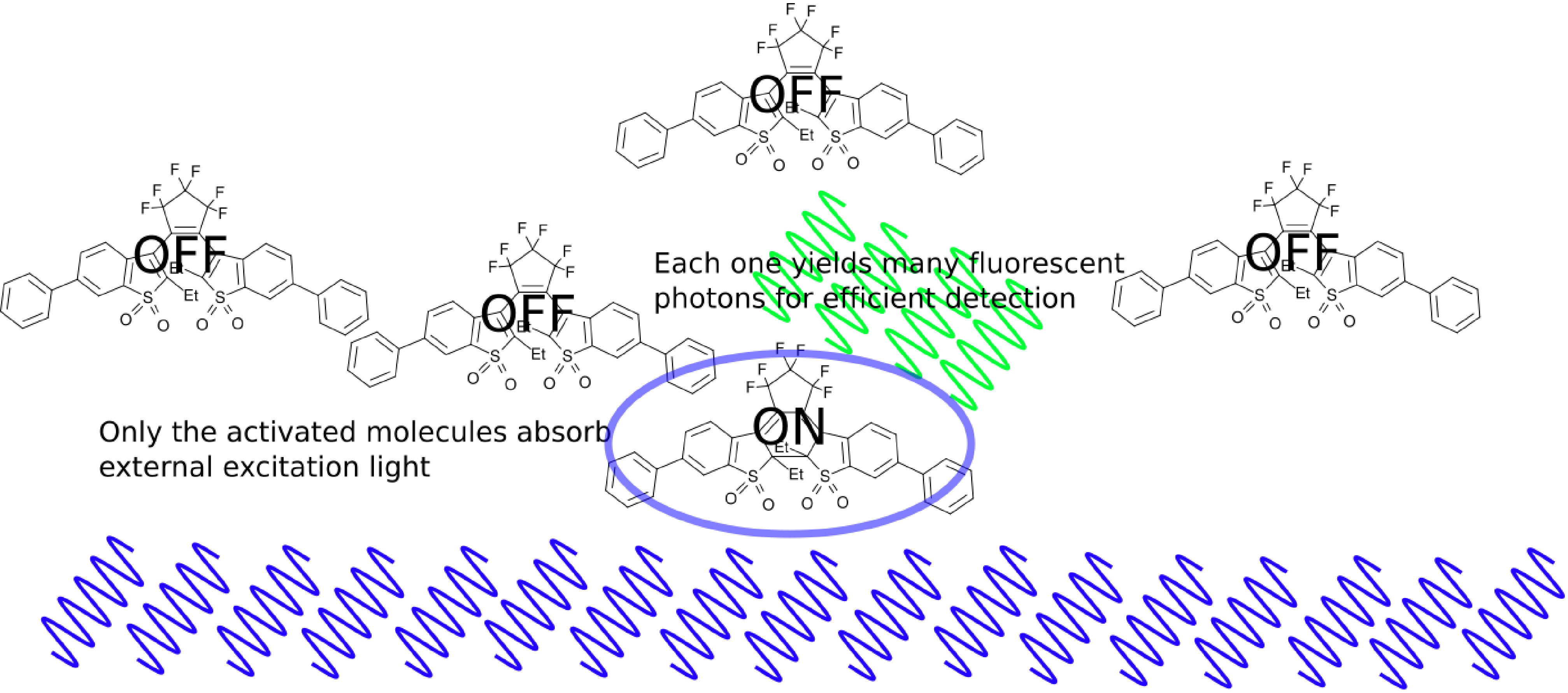
In a switchillator, the switchable fluorescent dye switches ON, and can be externally stimulated to yield many photons before switching OFF

What’s the Point?

Count switched-ON fluorescent molecules instead of photons

Detecting a photon is at best ~10% efficient in large scintillator detectors

With >1000 photons/molecule, detection could be almost fully efficient



Each one yields many fluorescent photons for efficient detection

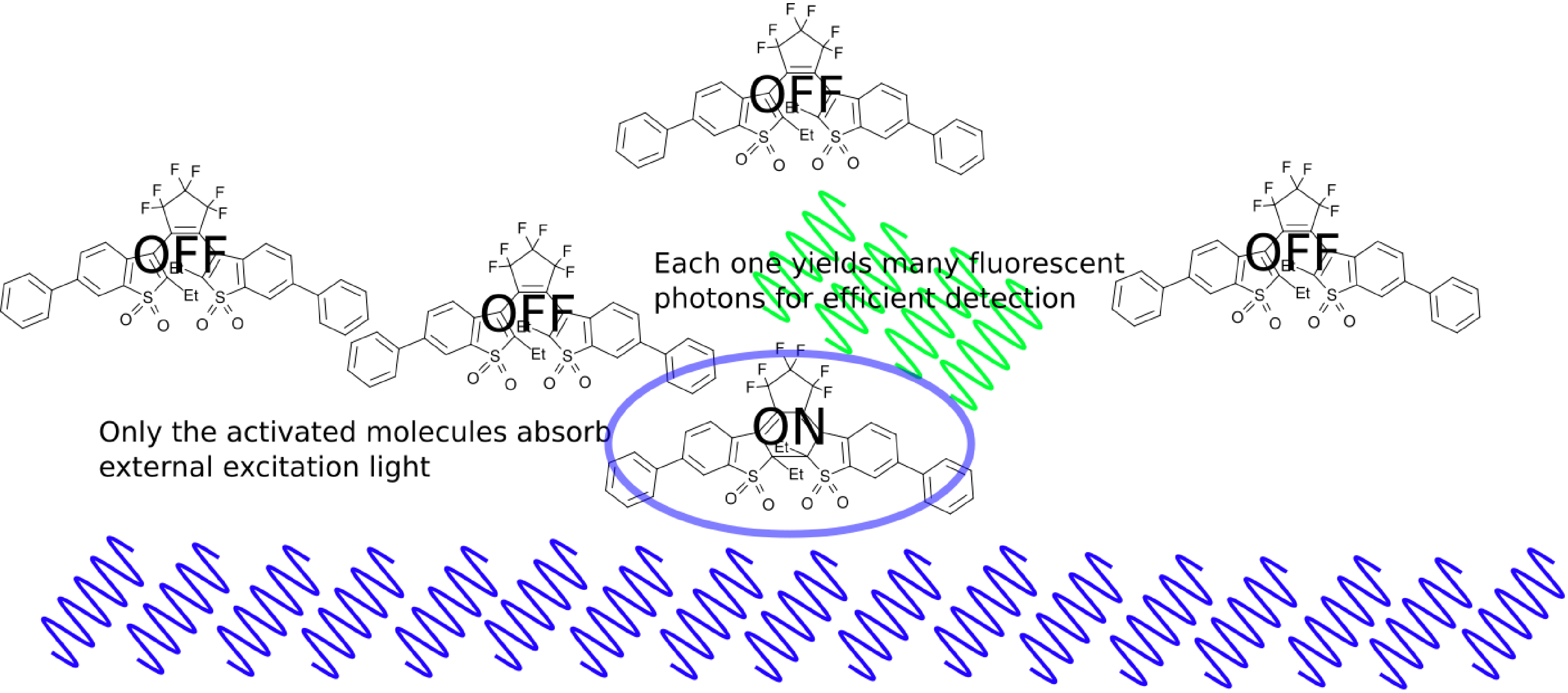
Only the activated molecules absorb external excitation light

Energy Resolution

Count switched-ON fluorescent molecules instead of photons

Achievable light yields in scintillators are >10,000 photons/MeV

Counting that many molecules could allow energy resolution <1%



Each one yields many fluorescent photons for efficient detection

Only the activated molecules absorb external excitation light

Initial Localization

Use Cherenkov light to form a hypothesis about the event location

Point a laser at the hypothesis region and scan the beam around it until something fluoresces

The number of photons of laser light required is proportional to the cross-sectional area of the hypothesis region

If the arrival time of the photons is precisely known, a several-cm hypothesis can be formed with only a few photons

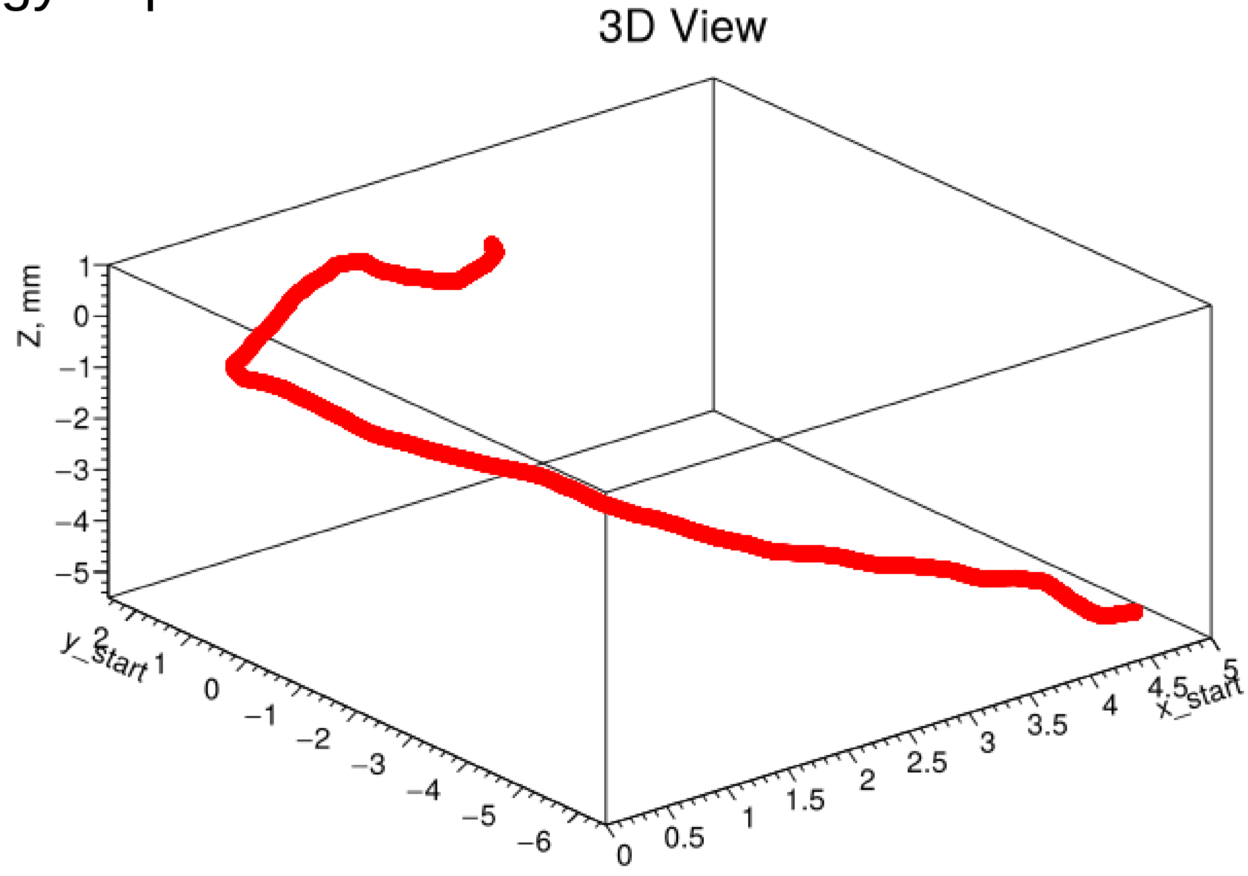
R. Jiang and A. Elagin, “Space-Time Discriminant to Separate Double-Beta Decay from 8B Solar Neutrinos in Liquid Scintillator,” arXiv:1902.06912 [physics.ins-det].

Imaging

Switched-ON fluors are produced at the track, and stay near the track

Liquid diffusion is slow-- D << (0.1 mm)^2/s in relevant solvents

The energy deposition information remains available for readout



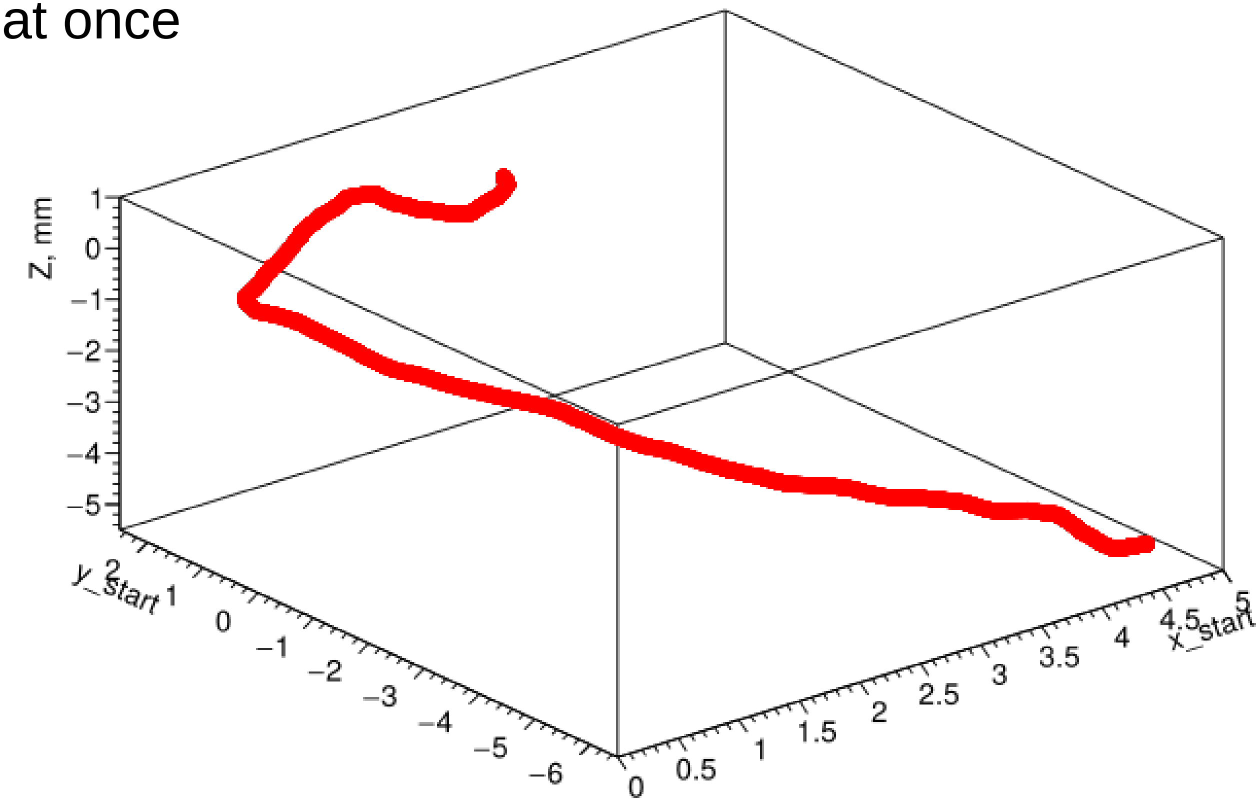
Simulation of ^{130}Te event in detector similar to KamLAND-Zen

Imaging

Illuminate the event with a narrow beam of excitation light; fluorescence indicates to intersection with a piece of the track

The amount of fluorescent light obtained should be proportional to local energy deposition, allowing for identifying the endpoint of a track

Other structured illumination likely affords faster imaging by reading out more of the event at once



Simulation of ^{130}Te event in detector similar to KamLAND-Zen

A Practical Concern: Selectivity

When you light up ~10^4 fluorescent molecules it’s important not to switch ON any of the other 10^{26} that weren’t activated by the event

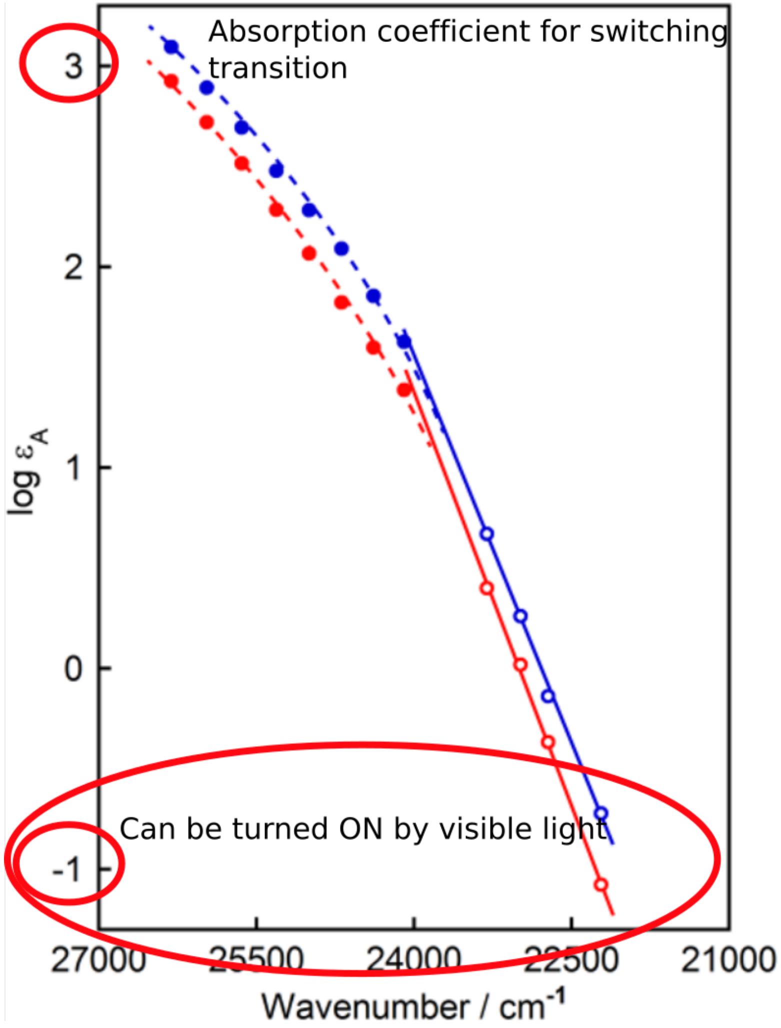
The OFF isomer must have a sufficiently low absorption cross-section for excitation light

Exponential tails of the switching transition must fall off strongly with increasing wavelength

Known to vary from 0.5 to 1.5

$$\varepsilon(E) \propto \varepsilon(E_{00})[-\frac{\sigma(E_{00}-E)}{k_B T}]$$

Optical absorption of a diarylethene that can switch ON with visible light



Ryota Kashihara, Masakazu Morimoto, Syoji Ito, Hiroshi Miyasaka, and Masahiro Irie. Fluorescence photoswitching of a diarylethene by irradiation with single-wavelength visible light. Journal of the American Chemical Society, 139(46):16498–16501, 2017.

Switching OFF Again

A few possibilities:

- The ON isomer has a small chance to switch OFF instead of fluorescing, yielding many photons on average but slow to switch off
- Resonant two-photon (NIR) processes with high yield are usually possible; see backup slides
- Reactive dopant in the mixture to slowly and selectively capture ON isomers
- Four well-separated bands to turn ON, turn OFF, excite fluorescence and emit fluorescence? (likely most difficult)

References

[1] David L Andrews. Mechanistic principles and applications of resonance energy transfer. Canadian Journal of Chemistry, 86(9):855–870, 2008.

[2] Sofia Andringa, SNO+ collaboration, et al. Sno+ present status and prospects. In Journal of Physics: Conference Series, volume 1137, page 012053. IOP Publishing, 2019. 2

[3] Yuhei Arai, Syoji Ito, Hajime Fujita, Yusuke Yoneda, Takahiro Kaji, Satoshi Takei, Ryota Kashihara, Masakazu Morimoto, Masahiro Irie, and Hiroshi Miyasaka. One-colour control of activation, excitation and deactivation of a fluorescent diarylethene derivative in super-resolution microscopy. Chemical Communications, 53(29):4066–4069, 2017.

[4] E Barrez, G Laurent, C Pavageau, M Sliwa, and R M´etivier. Comparative photophysical investigation of doubly-emissive photochromic-fluorescent diarylethenes. Physical Chemistry Chemical Physics, 20(4):2470–2479, 2018.

[5] Isadore B Berlman. Handbook of flourescence spectra of aromatic molecules. New York: Academic Press, 1971, 2nd ed., 1971.

[6] Christian Buck and Minfang Yeh. Metal-loaded organic scintillators for neutrino physics. Journal of Physics G: Nuclear and Particle Physics, 43(9):093001, 2016.

[7] Michelle J Dolinski, Alan WP Poon, and Werner Rodejohann. Neutrinoless doublebeta decay: status and prospects. Annual Review of Nuclear and Particle Science, 69:219–251, 2019.

[8] Andrey Elagin. personal communication, 11 2019.

[9] Sayo Fukumoto, Takuya Nakashima, and Tsuyoshi Kawai. Photon-quantitative reaction of a dithiazolylarylene in solution. Angewandte Chemie International Edition, 50(7):1565–1568, 2011.

[10] Florencia Gillanders, Luciana Giordano, Sebasti´an A D´ıaz, Thomas M Jovin, and Elizabeth A Jares-Erijman. Photoswitchable fluorescent diheteroarylethenes: substituent effects on photochromic and solvatochromic properties. Photochemical & Photobiological Sciences, 13(3):603–612, 2014.

[11] Masahiro Irie, Tuyoshi Fukaminato, Kenji Matsuda, and Seiya Kobatake. Photochromism of diarylethene molecules and crystals: memories, switches, and actuators. Chemical Reviews, 114(24):12174–12277, 2014.

[12] Masahiro Irie and Masakazu Morimoto. Photoswitchable turn-on mode fluorescent diarylethenes: strategies for controlling the switching response. Bulletin of the Chemical Society of Japan, 91(2):237–250, 2017.

References

[13] Yong-Chul Jeong, Sung Ik Yang, Kwang-Hyun Ahn, and Eunkyoung Kim. Highly fluorescent photochromic diarylethene in the closed-ring form. Chemical Communications, (19):2503–2505, 2005.

[14] Ryota Kashihara, Masakazu Morimoto, Syoji Ito, Hiroshi Miyasaka, and Masahiro Irie.

Fluorescence photoswitching of a diarylethene by irradiation with single-wavelength

visible light. Journal of the American Chemical Society, 139(46):16498–16501, 2017.

[15] Shuichi Kinoshita, Nobuhiko Nishi, Akiya Saitoh, and Takashi Kushida. Urbach tail of

organic dyes in solution. Journal of the Physical Society of Japan, 56(11):4162–4175, 1987. 3

[16] Tatsuhiro Nagasaka, Tomohiro Kunishi, Hikaru Sotome, Masafumi Koga, Masakazu Morimoto, Masahiro Irie, and Hiroshi Miyasaka. Multiphoton-gated cycloreversion reaction of a fluorescent diarylethene derivative as revealed by transient absorption spectroscopy. Physical Chemistry Chemical Physics, 20(30):19776–19783, 2018.

[17] Tetsuya Nakagawa, Yosuke Miyasaka, and Yasushi Yokoyama. Photochromism of a spiro-functionalized diarylethene derivative: multi-colour fluorescence modulation with a photon-quantitative photocyclization reactivity. Chemical communications, 54(26):3207–3210, 2018.

[18] Oleksii Nevskyi, Dmytro Sysoiev, Jes Dreier, Simon Christoph Stein, Alex Oppermann, Florian Lemken, Tobias Janke, J¨org Enderlein, Ilaria Testa, Thomas Huhn, et al. Fluorescent diarylethene photoswitchesa universal tool for super-resolution microscopy in nanostructured materials. Small, 14(10):1703333, 2018.

[19] Michaela Schever. Status of the jiangmen underground neutrino observatory. Ukrainian Journal of Physics, 64(7):635–635, 2019.

[20] Yuta Takagi, Tomohiro Kunishi, Tetsuro Katayama, Yukihide Ishibashi, Hiroshi Miyasaka, Masakazu Morimoto, and Masahiro Irie. Photoswitchable fluorescent diarylethene derivatives with short alkyl chain substituents. Photochemical & Photobiological Sciences, 11(11):1661–1665, 2012.

[21] Kakishi Uno, Hiroyuki Niikura, Masakazu Morimoto, Yukihide Ishibashi, Hiroshi Miyasaka, and Masahiro Irie. In situ preparation of highly fluorescent dyes upon photoirradiation. Journal of the American Chemical Society, 133(34):13558–13564, 2011.

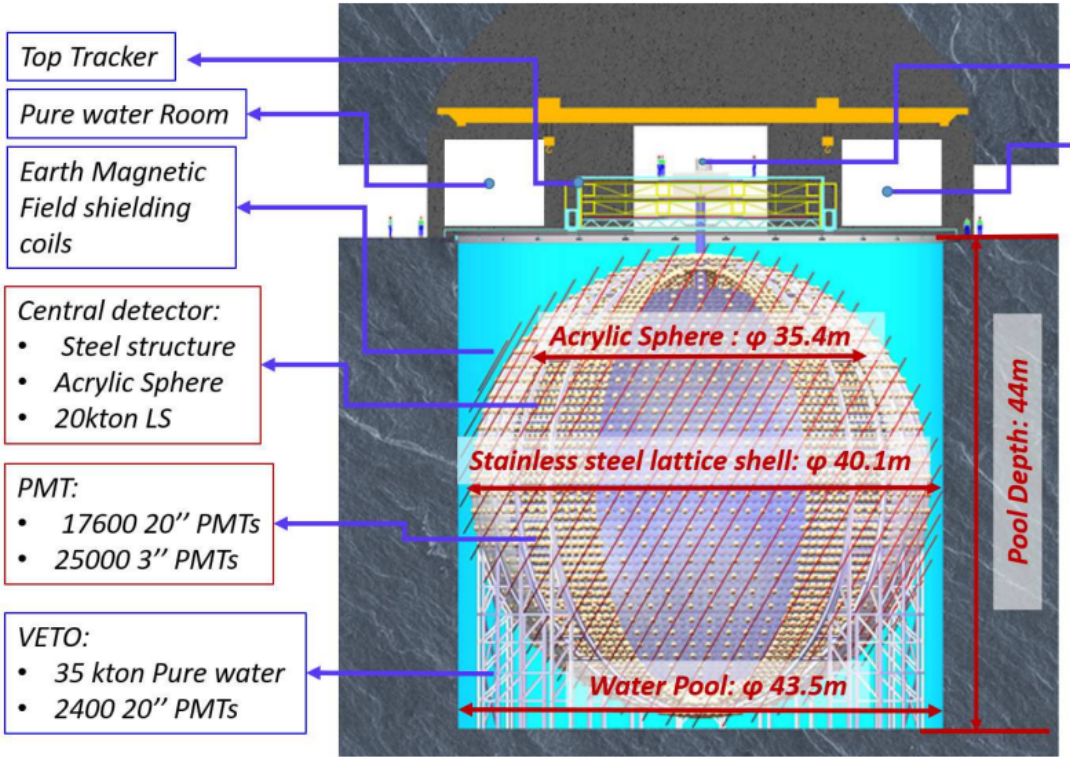
[22] Kyoko Yagi and Masahiro Irie. Photochromic and fluorescent properties of a diarylethene dimer. Chemistry letters, 32(9):848–849, 2003.

[23] R. Jiang and A. Elagin, “Space-Time Discriminant to Separate Double-Beta Decay from 8B Solar Neutrinos in Liquid Scintillator,” arXiv:1902.06912 [physics.ins-det].

Backup

Photodetection Efficiency in JUNO

The LS recipe, which is optimized from Daya Bay experiment 8, consists of Linear Alkyl Benzene (LAB) as solvent, 2.5 g/L 2,5-diphenyloxazole (PPO) as the fluor and 3 mg/L p-bis-(o-methylstyryl)-benzene (bis-MSB) as the wavelength shifter. The comprehensive light yield is required to be larger than 1200 photon-electrons (P.E.)/MeV and the attenuation length should be longer than 20 m at 430 nm wavelength



Top Tracker

Pure water Room

Earth Magnetic Field shielding coils

Central detector:
- *Steel structure*
- *Acrylic Sphere*
- *20kton LS*

PMT:
- *17600 20'' PMTs*
- *25000 3'' PMTs*

VETO:
- *35 kton Pure water*
- *2400 20'' PMTs*

Metal Loaded Organic Scintillators are Scalable but Energy Resolution is Insufficient

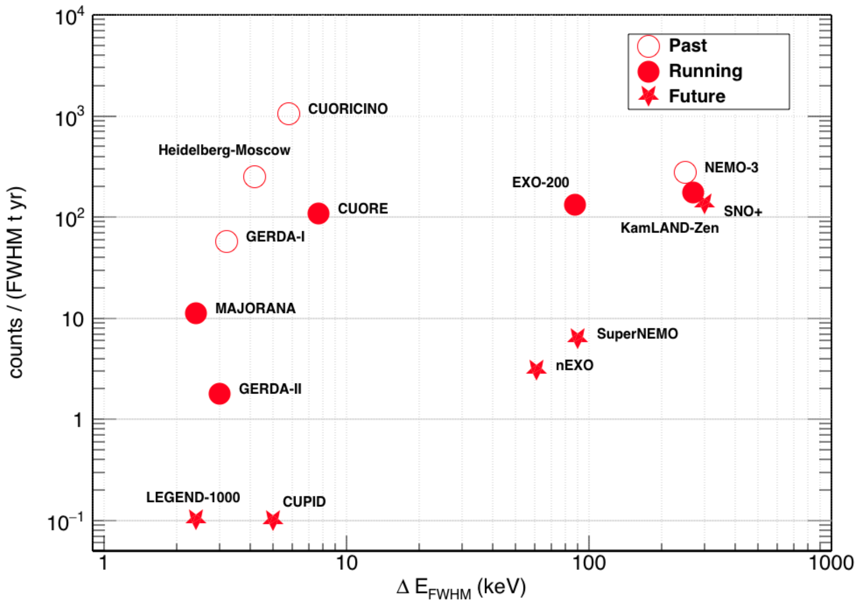
- ^{130}Te is an advantageous isotope due to its abundance and large Q
- Metal-loaded organic scintillators scale well to large sizes to take advantage of this
- Energy resolution based on a Poisson rate can't be better than Q/N$^{1/2}$ where N is the number of things detected in an event

$$e^- \xrightarrow{\epsilon_a} LAB \xrightarrow{\epsilon_b} PPO \xrightarrow{\epsilon_c} Photodetector$$

$$e^- \xrightarrow{\epsilon'_a} LAB \xrightarrow{\epsilon'_b} \begin{matrix}\text{Switching}\\ \text{Fluor}\end{matrix} \xrightarrow{\epsilon'_c} Photodetector$$

- In LAB-based scintillators over 10,000 photons/MeV are possible, which could allow better than 1% energy resolution
- However, transmitting a photon through the scintillator and then detecting it is typically <10% efficient, and SNO+ expects ~400 pe/MeV
- Improving the efficiency of the chain from solvent to photodetector would be useful

$$\frac{S}{B} \propto \left(\frac{Q}{\Delta E}\right)^6 \frac{T^{2\nu}_{1/2}}{T^{0\nu}_{1/2}}$$

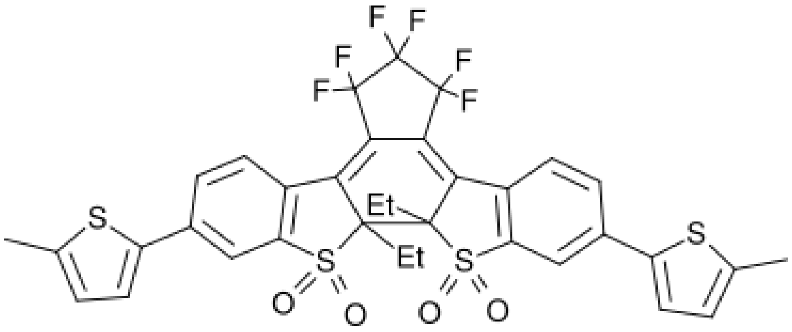


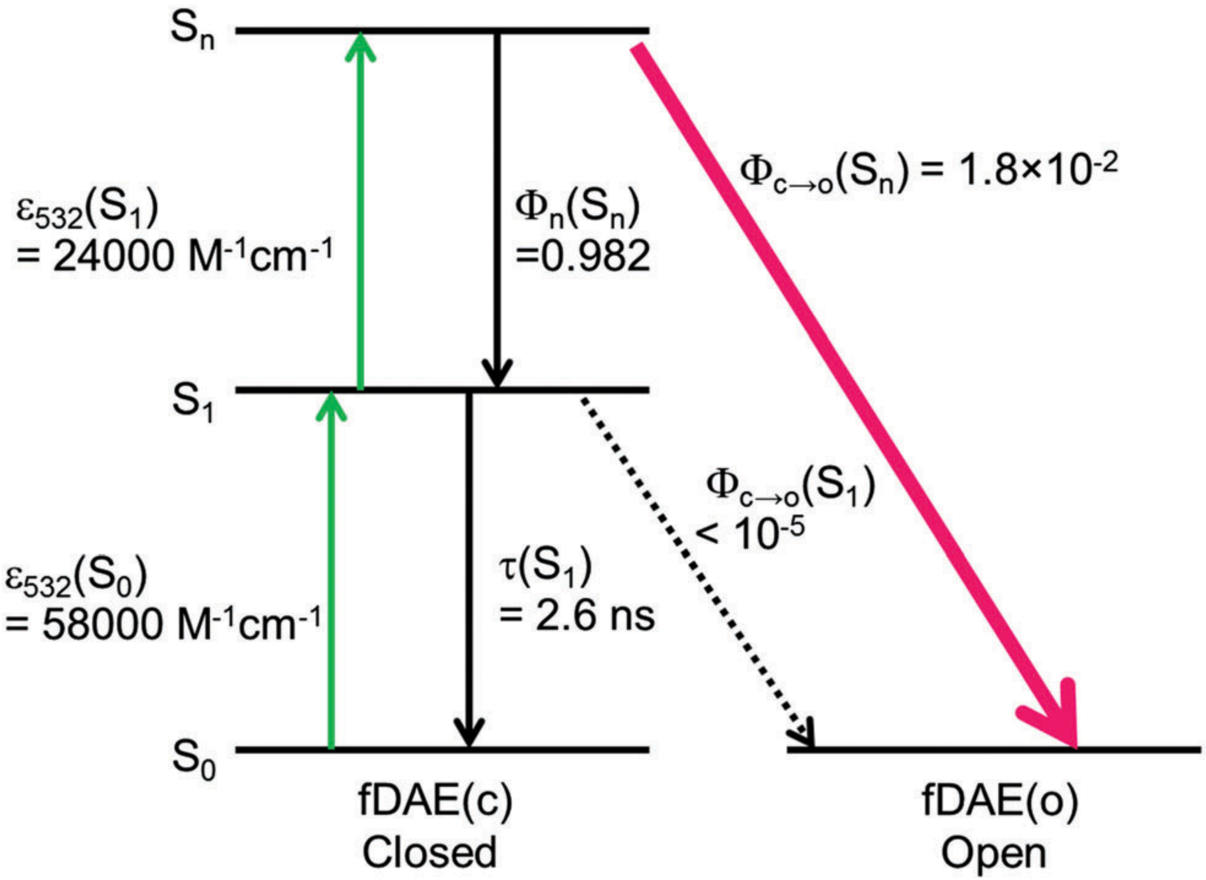
The background index as a function of full-width-at-half-maximum energy resolution for selected past, current and future experiments with 76Ge, 100Mo, 130Te, and 136Xe as target. Note that large homogeneous detectors like SNO+, KamLAND-Zen, and nEXO are not well characterized by a single background index.

Michelle J Dolinski, Alan WP Poon, and Werner Rodejohann. Neutrinoless doublebeta decay: status and prospects. Annual Review of Nuclear and Particle Science, 69:219–251, 2019.

Sofia Andringa, SNO+ collaboration, et al. Sno+ present status and prospects. In Journal of Physics: Conference Series, volume 1137, page 012053. IOP Publishing, 2019

Multiphoton Cycloreversion





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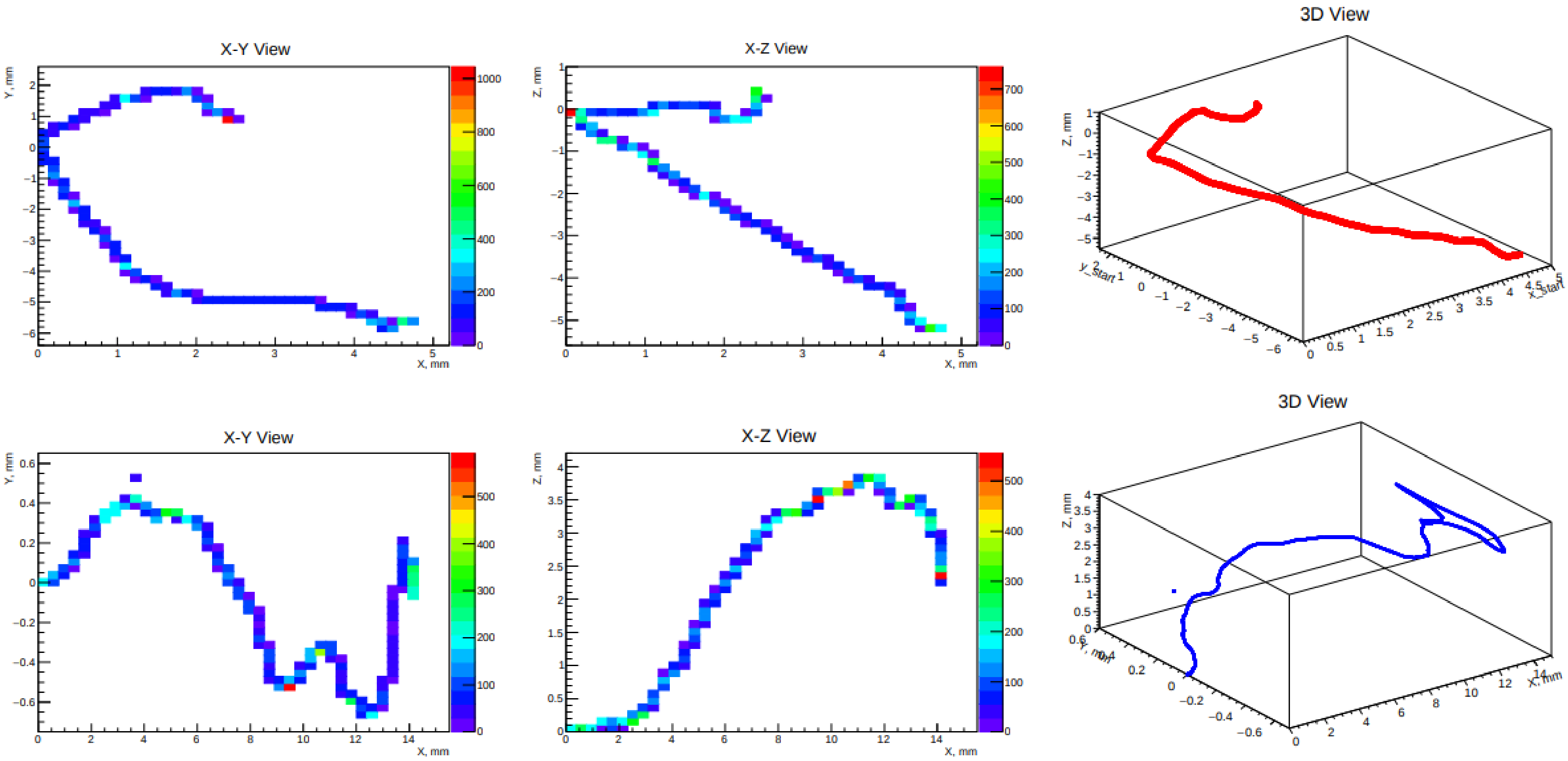
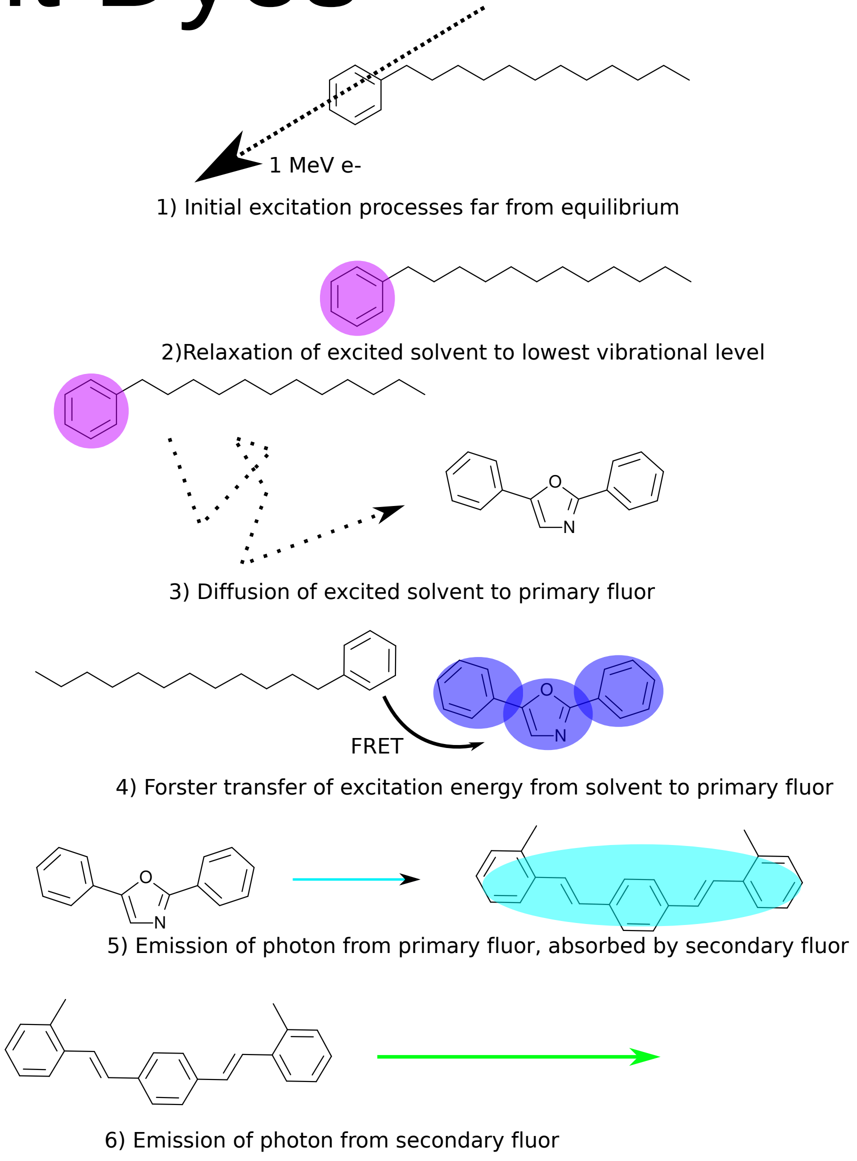
More Detail on That Simulation Image



- Comparison between 0νββ-decay and 8B solar neutrino events. [Top panel]: An event display of a randomly selected 130Te 0νββ-decay. An electron with energy of 1/2·Q(130Te) = 1.26 MeV travels a total path lenght of 7.1±0.9 mm in a liquid scintillator [Bottom panel]: An event display of a randomly selected 8B solar background event. An electron with energy of Q(130Te) = 2.53 MeV (energy of an electron from solar neutrino that would mimic 0νββdecay) travels a total path length of 15.5±2.0 mm. [Left]: X-Y plane. [Middle]: X-Z plane. [Right]: 3D view.

Organic Scintillators Run on Fluorescent Dyes

- A liquid scintillator is a fluorescent liquid solvent with small admixtures of fluorescent dyes
- An ionizing particle excites the fluorescent transition of the solvent, among many other interactions
- Fluorescent molecules usually aren't very transparent to their own emissions, so usually two fluorescent dyes are added, each more dilute than the last, so that the solution is transparent to the emission of the last dye in the chain
- Depending on concentration, the energy transfer can either proceed by emission and absorption of a photon, or by the near-field (kR << 1) equivalent i.e. Forster Resonant Energy Transfer
- The near and far field versions both depend on overlap between the emission band of the emitter and the absorption band of the absorber



1) Initial excitation processes far from equilibrium

2)Relaxation of excited solvent to lowest vibrational level

3) Diffusion of excited solvent to primary fluor

4) Forster transfer of excitation energy from solvent to primary fluor

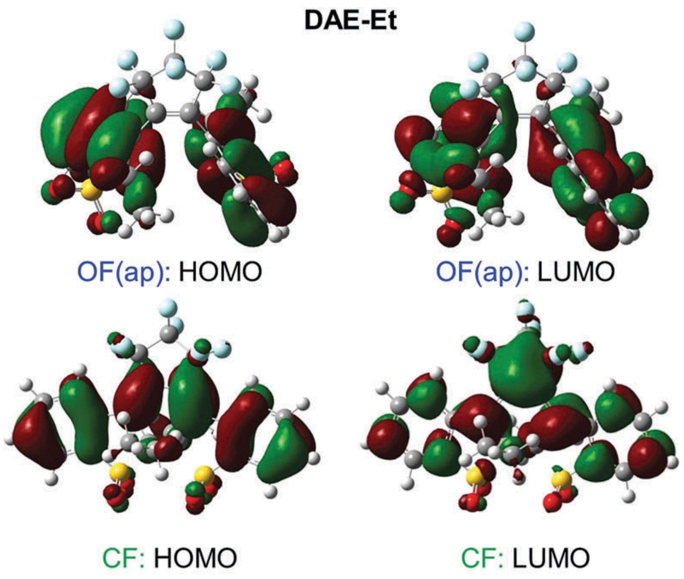
5) Emission of photon from primary fluor, absorbed by secondary fluor

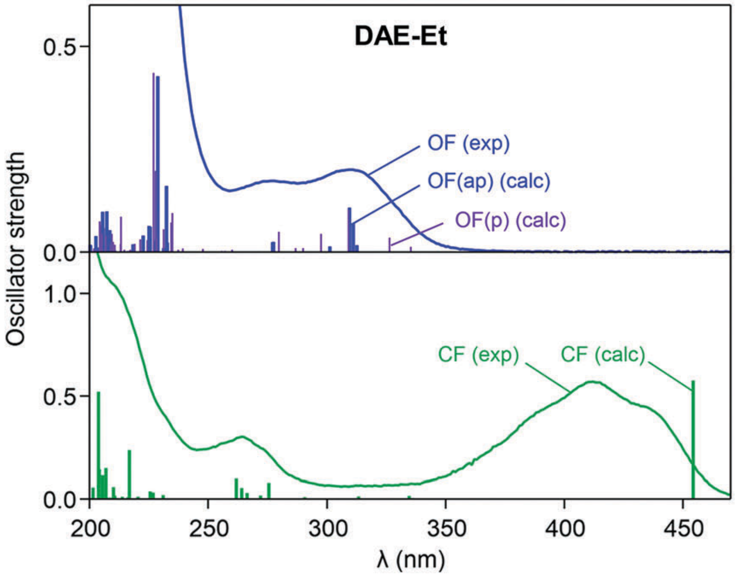
6) Emission of photon from secondary fluor

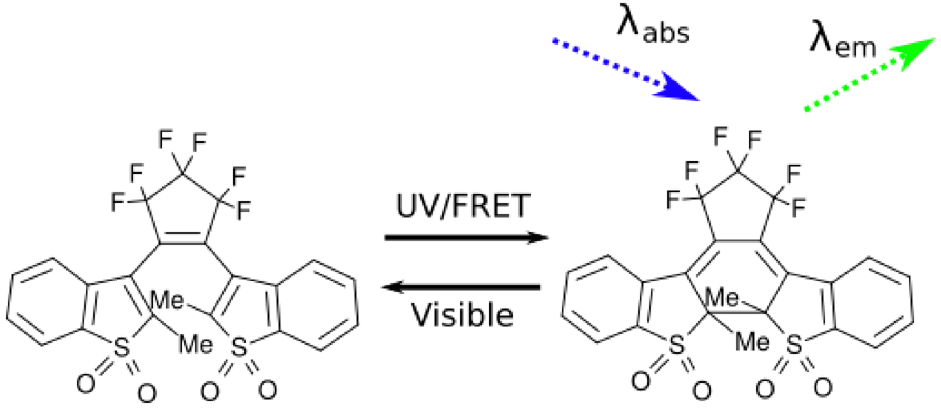
Christian Buck and Minfang Yeh. Metal-loaded organic scintillators for neutrino physics. Journal of Physics G: Nuclear and Particle Physics, 43(9):093001, 2016.

David L Andrews. Mechanistic principles and applications of resonance energy transfer. Canadian Journal of Chemistry, 86(9):855–870, 2008.

The Central Moiety





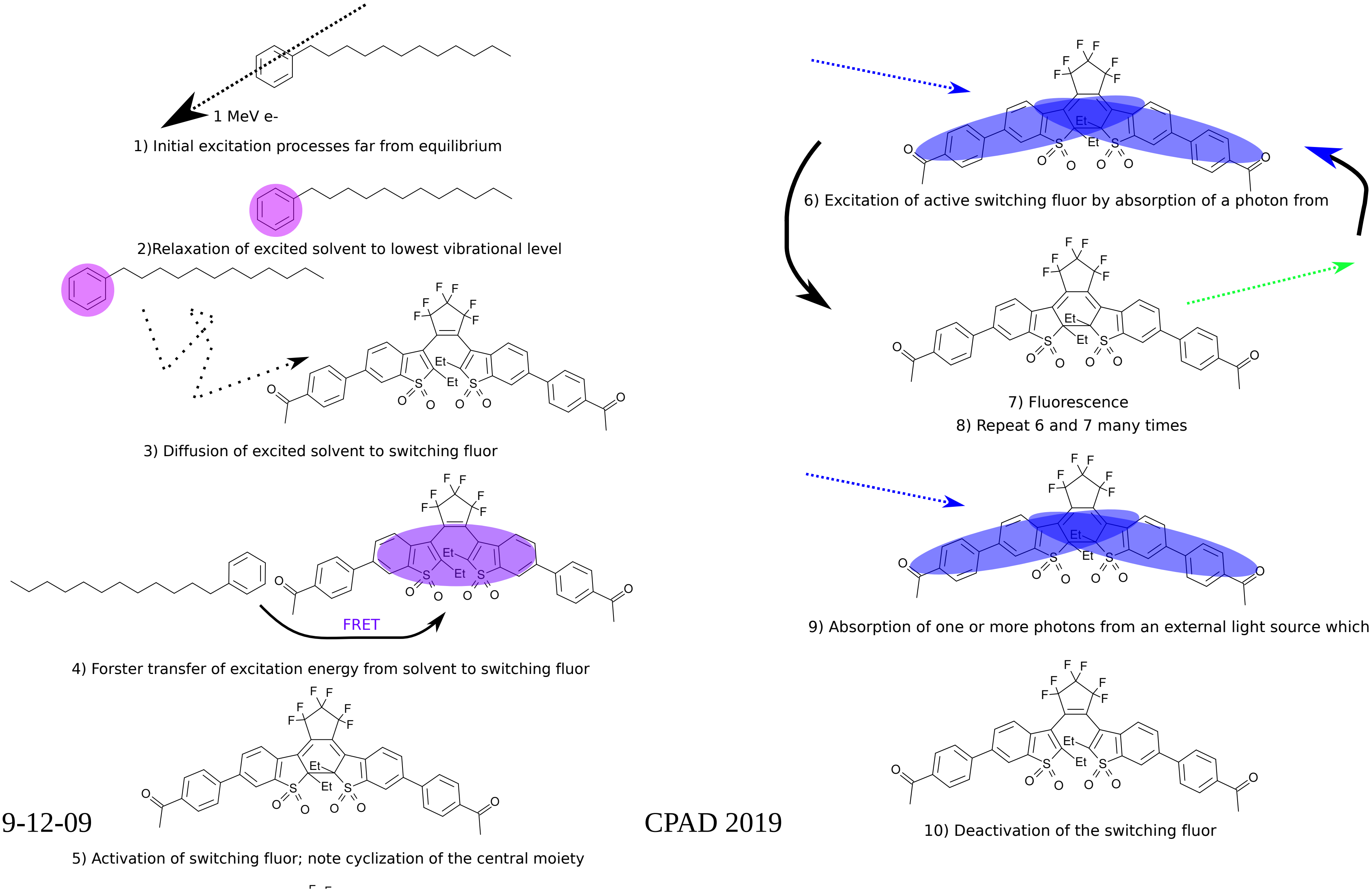


- Fulgides and diarylethenes can undergo 6pi cyclization photoreactions, sometimes with high efficiency
- The cyclization/cycloreversion can make or break an extended fluorescent orbital
- In the example, the open-ring isomer absorbs UV but not visible light; after UV excitation it can change to closed ring
- Closed ring isomer can repeatedly absorb a visible photon and fluoresce
- This one doesn’t work; the quantum yields of fluorescence and cyclization are too low, among other problems

E Barrez, G Laurent, C Pavageau, M Sliwa, and R M´etivier. Comparative photophysical investigation of doubly-emissive photochromic-fluorescent diarylethenes. Physical Chemistry Chemical Physics, 20(4):2470–2479, 2018.

Yong-Chul Jeong, Sung Ik Yang, Kwang-Hyun Ahn, and Eunkyoung Kim. Highly fluorescent photochromic diarylethene in the closed-ring form. Chemical Communications, (19):2503–2505, 2005.

A Photoswitching Fluor could Isomerize and be Efficiently Detected



1) Initial excitation processes far from equilibrium

2)Relaxation of excited solvent to lowest vibrational level

3) Diffusion of excited solvent to switching fluor

4) Forster transfer of excitation energy from solvent to switching fluor

5) Activation of switching fluor; note cyclization of the central moiety

6) Excitation of active switching fluor by absorption of a photon from

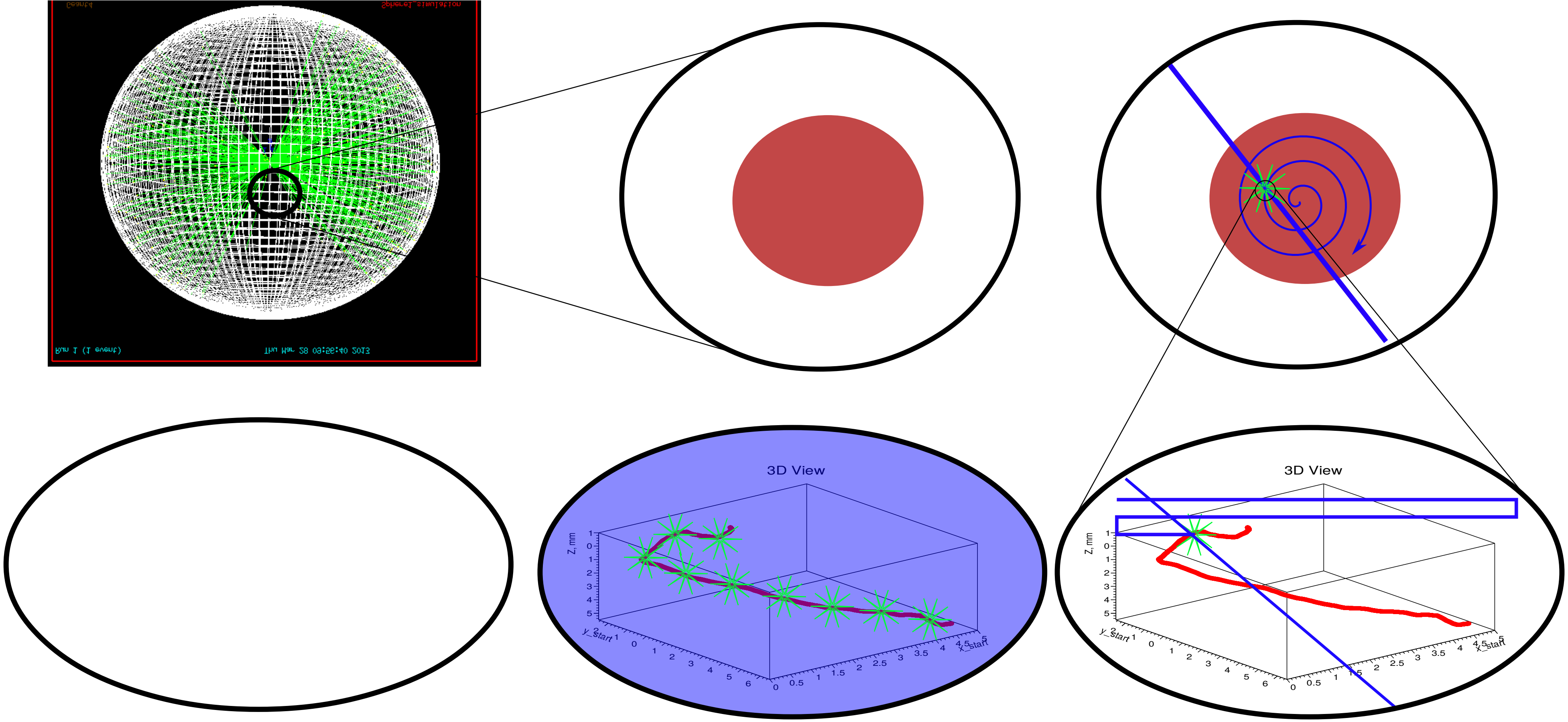
7) Fluorescence

8) Repeat 6 and 7 many times

9) Absorption of one or more photons from an external light source which

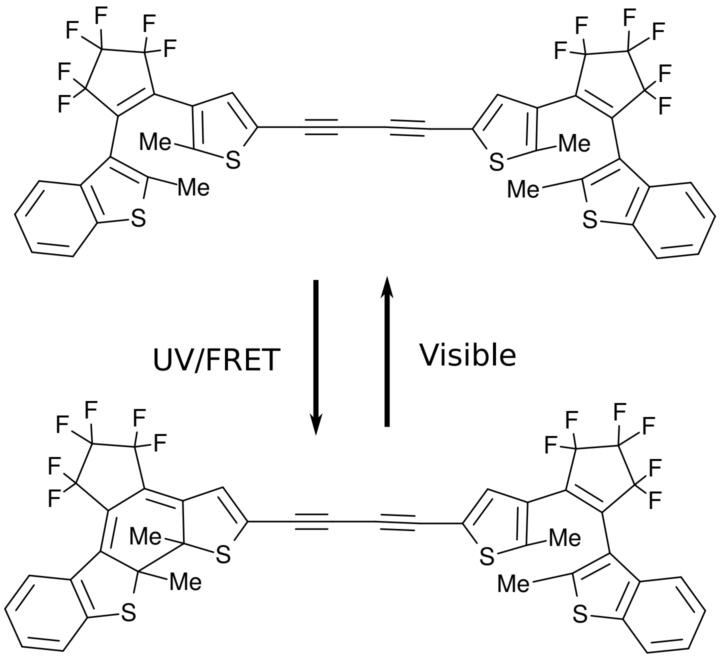
10) Deactivation of the switching fluor

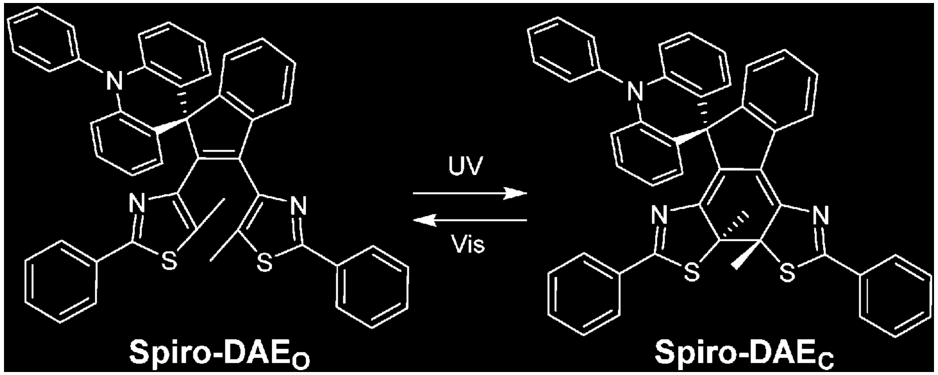
The Readout Sequence

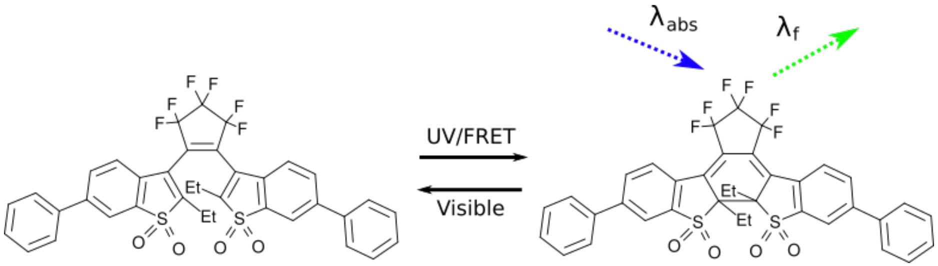


1) An event occurs
2) Detector detects Cherenkov light and triggers, promptly producing a ROI
3) A laser beam scans the ROI
4) Some fluorescence is detected, and a more accurate position is reconstructed
5) Further illumination according to some scheme until it is possible to count the fluors and reconstruct the full 3D event with adequate precision
6) The activated fluors are erased somehow. Possibilities include further illumination, pulsed illumination, passive deactivation etc.

A Few Promising Examples







- Upper left may have well-separated bands for activation, deactivation, fluorescence excitation and fluorescence emission, but the activation quantum yield is only 0.36 and the fluorescence quantum yield is low/not measured
- Upper right has an activation quantum yield of 0.98, but fluorescence quantum yield below .01 and deactivation comparable to fluorescence
- Lower left has high QY for activation and fluorescence, but the activation band has a long tail so it is easily activated by fluorescent excitation light

Tetsuya Nakagawa, Yosuke Miyasaka, and Yasushi Yokoyama. Photochromism of a spiro-functionalized diarylethene derivative: multi-colour fluorescence modulation with a photon-quantitative photocyclization reactivity. Chemical communications, 54(26):3207–3210, 2018.

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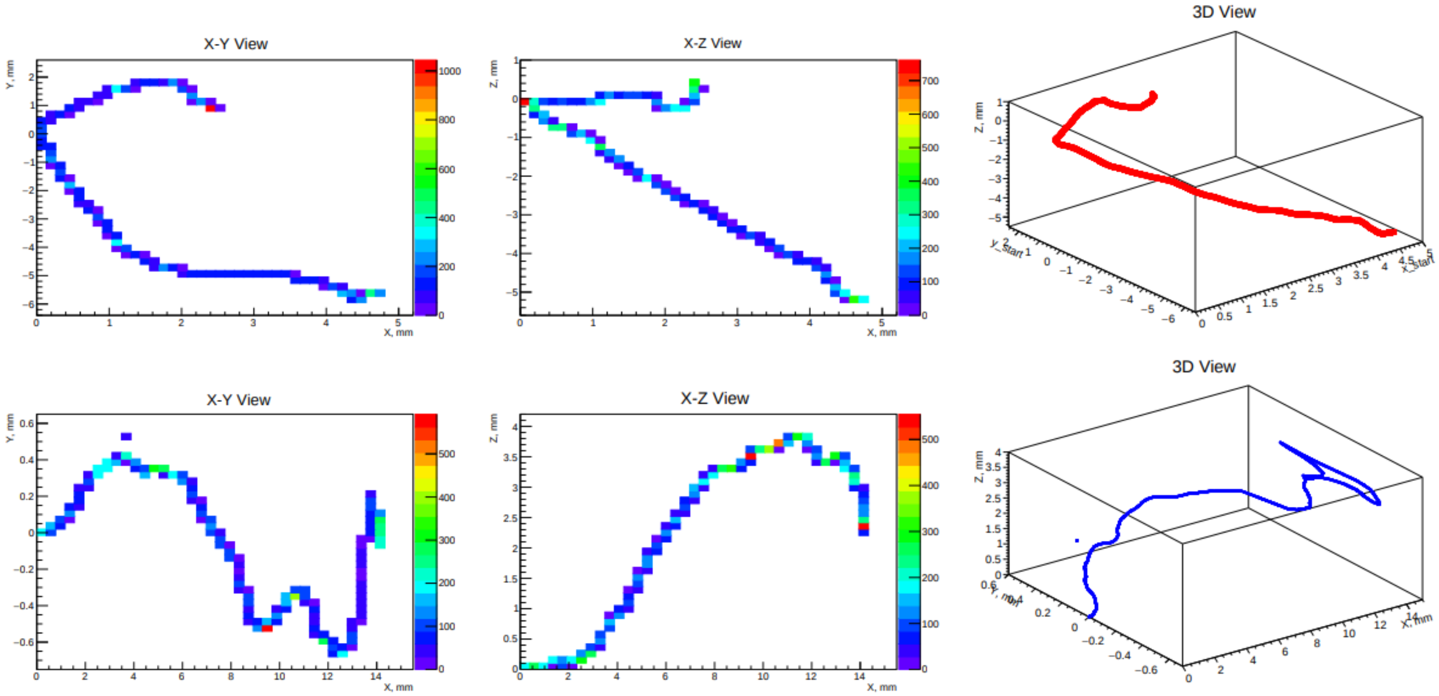
Tomographic Imaging



- The fluorescent excitation used to read out an event could be selective
- For example, one could scan a narrow beam across the region of interest
- When the beam intersects the track, it fluoresces
- Ideally one would reconstruct the event in real time so as to avoid wasting light where there’s nothing to see
- Each illumination source can generate a 2D projection, so with 2 or more sources the full 3D information is available
- 1 mm beam waist is probably all that is required
- Liquid diffusion is slow-- D << (0.1 mm)²/s in relevant solvents