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ABOUT FDCD (Fluorescence Detected Circular Dichroism)

FDCD (the difference in fluorescence intensity for left and right circularly polarized excitation) has been proposed in 1974[1] as a simple extension to existing CD spectropolarimeters. The Tinoco article is very short, actually it's a note, but very informative and documented.

In FDCD we measure: $\mathbf{\Delta F = F_L - F_R}$ instead of $\mathbf{\Delta\varepsilon = \varepsilon_L - \varepsilon_R}$ we measure in normal CD mode

Instrument manufacturers soon implemented dedicated accessories based on this idea. It's indeed a simple job: it's basically enough to place the PM tube at 90° and to collect, as efficiently as possible by a lens system, the total fluorescence rather than the transmitted radiation. A suitable high pass filter should be placed in the collection path in order to remove elastic scattering. An additional facility may allow to change freely the detection wavelength using a proper high aperture monochromators.
In FDCD raw data must be corrected to compensate for total fluorescence, in order to measure:

$$\mathbf{(F_L - F_R) / (F_L + F_R)}$$

this is achieved using dynode feedback or more elegantly, in modern systems as the Jasco J-810, collecting FDCD/DC and DC separately at fixed applied photomultiplier tube high voltage.
In this mode you obtain simultaneously also the total fluorescence signal. In addition if a second PM tube is used in the transmission path *corrected* excitation spectra may be obtained.
The technique is appealing for two main reasons:
-selectivity: since fluorophores in a chiral environment can be detected also in systems containing nonfluorescent chromophores
-sensitivity: when in presence of a fluorophore with proper quantum yield

Well, why technique didn't expand? Published references are indeed not so many, in contrast to the fact that a fair number of FDCD accessories were delivered in the years. This is not easy to explain; probably many groups purchased the accessory with the basic instrument forecasting a future use it never took place. In contrast to this trend today many instruments are supplied with a second photomultiplier tube for simultaneous fluorescence detection, so ready also to perform FDCD, simply exchanging the PM tubes.

More recently however a few articles appeared using FDCD coupled with the powerful exciton chirality methods[2 3].
FDCD coupled with exciton chirality methods can be used for absolute configuration of small molecules.
The choice of proper fluorophores is a challenging job since they should have high absorbance, high fluorescence quantum yield, but very low polarization of fluorescence.
As the conventional CD technique is valid for isotropic samples, in case of FDCD this is equivalent to low polarization of fluorescence.

FDCD and exciton coupling combined (as developed at Columbia University) seem indeed able to provide a new promising expansion for chiro-optical measurements.
For more understanding on exciton-coupled circular dichroism, the Harada & Nakanishi text[4] is the proper starting point.

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[1] Turner D. H., Tinoco I., Maestre M. *J. Am. Chem. Soc.* 1974, 96, 4340
[2] Dong J.G., Wada A., Takakuwa T., Nakanishi K., Berova N. *J. Am. Chem. Soc.* 1997, 119, 12024
[3] Nehira T., Parish C.A., Jockusch S., Turro N.J., Nakanishi K., Berova N. *J. Am. Chem. Soc.* 1999, 121, 8681
[4] Harada N., Nakanishi K. *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Chemistry*, University Science Books, Mill Valley, CA, 1983

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