Fluoranthocyanine: A New Member of the Phthalocyanine Family

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(Received February 3, 1998; CL-980077)

Fluoranthocyanine, a phthalocyanine analog fused by four five-membered rings and four 1,8-naphthalene units, has been synthesized and characterized by electronic absorption, magnetic circular dichroism, and fluorescence spectroscopy.

Among various types of tetraazaporphyrins (TAPs),[1] phthalocyanines (Pcs) and naphthalocyanines (Ncs) have been used in practical fields, and quite often the position of the main absorption band which is controlled by the shape and size of π-conjugated systems has been important.[2] However, those including both 1,8-naphthalene and five membered aromatic rings have not been reported to date because of, plausibly, preparative difficulty and low solubility of the precursors. We herein present the first example of such a compound, *i.e.* **1**, which may be named dilithium fluoranthocyanine (Li$_2$Fluc) (inset in Figure 1).

The precursor, fluoranthene dinitrile, was prepared by a methodology similar to that reported by Campbell and Gow.[3] The sequence began with the preparation of a mixture of *cis* and *trans* 7,8-dimethylacenaphthene-7,8-diols by reaction of two equivalents of methyl magnesium iodide with acenaphthenequinone.[4] Reaction of a mixture of the resultant *cis* and *trans* dimethyl glycols (1 eqv.), fumaronitrile (1.5 eqv.), and acetic anhydride (3 eqv.) in refluxing toluene for 17 h afforded yellow powder of tetrahydrofluoranthene dinitrile in 51% yield (unoptimized).[5] Dehydrogenation of the dinitrile (0.125 moles) by dichlorodicyanobenzoquinone (0.255 moles, a 2% excess) in refluxing dioxane (500 ml) for 17 h produced the desired fluoranthenedinitrile in 91% yield. Cyclization of the dinitrile was performed in refluxing hexanol (1 h) in the presence of a catalytic amount of lithium.[2] After cooling, the solution was filtered, and the residue washed many times with methanol, acetone, and chloroform. A portion of the residue was taken, dissolved in DMF containing a amall amount of LiOEt and passed through a column of deactivated basic alumina using the same solvent as an eluent. The eluent was removed to some extent by using a vacuum evaporator, heated to dissolve the materials which precipitated out, and cooled. The precipitates were collected by filtration to obtain the 1st crop and chloroform was added to the filtrate to cause further precipitation of the desired compound. After filtration and drying, the desired com-pound was obtained as a dilithium derivative, *i.e.* Li$_2$Fluc[5b] in *ca.* 19% yield.

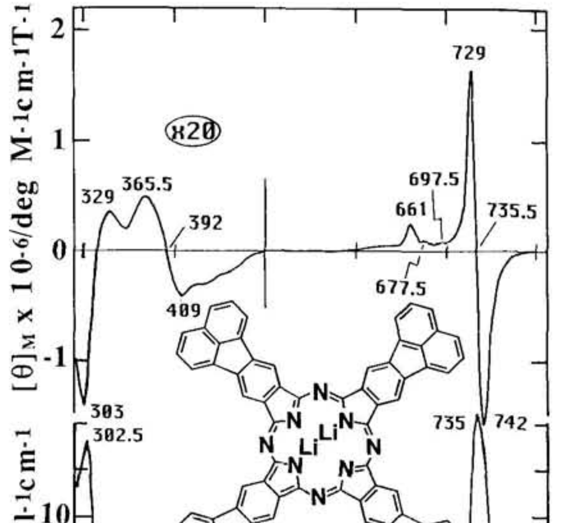

Figure 1. Electronic absorption (bottom) and magnetic circular dichroism spectra (top) of Li$_2$Fluc in DMF. The inset shows the structure of Li$_2$Fluc.

Figure 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of Li$_2$Fluc in DMF. The absorption spectrum has characteristics typical of Pcs,[6] although each peak shifts to a longer wavelength by *ca.* 50-60 nm. This shift is a reflection of the expansion of the π-systems in a radial direction looking from the molecular center.[7] The 1,8-naphthalene units contribute only a less degree to the shift, because two centers of each benzene ring in 1,8-naphthalene units are on "inclined" sites, not on the line radiating from the center of Li$_2$Fluc. Thus, the main contribution to the shift is due to the presence of the five membered rings between the benzene and 1,8-naphthalene rings. In the TAP analogues, the extent of the red-shift is roughly proportional to the sizes of aromatic molecules fused to the TAP skeleton, and these fused molecules must be in the radial direction looking from the center.[2] For example, cobalt complexes of *tert*-butylated TAP, Pc, 2,3-Nc, and 2,3-anthracocyanine (Ac) show the Q bands at 570, 660, 752, and 832 nm, respectively, in pyridine.[8] In accord with the above arguments, the Q band position of Li$_2$Fluc (735 nm) is slightly shorter than that of metal Ncs without substituent groups (for example, ZnNc shows a $Q_{0\text{-}0}$ band at 756 nm in THF[9]), due to the smaller size of five membered rings compared to six membered benzene rings. The unsplit Q band is due to the near degeneracy of the Q_x and Q_y states as seen in metal-free Ncs and -Acs.[2,7] In metal-free TAP derivatives with D_{2h} symmetry, the splitting of the lowest unoccupied e_g molecular orbitals in compounds with D_{4h} symmetry becomes smaller the larger the derivatives looking from their center, and approaches almost zero in metal-free Ncs. Thus, it is considered that the $Qx_{(0\text{-}0)}$ and $Qy_{(0\text{-}0)}$ states are very close in energy in Li_2Fluc, whose size is larger than Ncs. Accordingly, the dispersion type, Faraday *A*-term-like MCD curve at *ca.* 700-770 nm appears a superimposition of two closely lying Faraday *B*-terms.[10] Indeed, a negative envelope between 735.5 and 800 nm is "fatter" than the positive envelope between *ca.* 700 and 735.5 nm, although the MCD magnitudes at 742 and 729 nm are, apart from their sign, seemingly the same. The so-called Soret band is detected at *ca.* 388 nm, which is longer than that of general Pcs and Ncs by 50-60 nm. This is a unique property of this compound, because generally the Soret band does not shift as much on expansion of the π-systems. For example, the Soret band of the above mentioned cobalt complexes of *tert*-butylated TAP, Pc, 2,3-Nc, and 2,3-Ac appear at 313, 332, 340, and 364 nm, respectively.[8] Several small MCD curvatures in 409-500 nm suggest that there are indeed some transitions in this region (in the cases of several MtPcs, a transition to a degenerate state is known to the red of the Soret band, and sometimes the corresponding band is called the B1 band).[6]

Figures 2 A and B show the time-resolved S_1 and S_2 emission spectra of Li_2Fluc in DMF. The S_1 emission was detected when excited at both 337-350 and 645-670 nm. As seen, both the S_1 and S_2 emission decay monotonously with time without changing their shape. Although not shown, their excitation spectra have mirror-image relationships with the emission spectra and are close in shape to the absorption spectra, particularly in the Soret region. Namely, peaks in the excitation spectra were found at 735, 389, and 332 nm with a shoulder around 360-370 nm. The Stokes shift of the S_1 emission is small (~15 nm, 270 cm^{-1}) but larger than that in usual Pcs (*ca.* 3-4 nm), while that of the S_2 emission was much larger (~60 nm, 3490 cm^{-1}) as in Pcs (*ca.* 7000-7800 cm^{-1}).[11] The quantum yield of the S_1 emission ($\Phi_F(S_1) = 0.0863$) is much smaller than that of Pcs (very roughly 0.2-0.8)[12] but is close to that of Ncs (roughly *ca.* 0.07-0.15).[12] While the value of S_2 emission ($\Phi_F(S_2) = 0.0987$) is the largest among the Pc derivatives known to date and one order of magnitude larger.[11] The lifetimes (τ) of S_1 and S_2 emissions were *ca.* 3.6 and 8.8 ns, respectively. The former value is approximately the same as that of *tert*-butylated H_2Nc ($\tau = 3.2$ ns in $CHCl_3$), which has the $Q_{0\text{-}0}$ band at 784 nm in pyridine.[2] In addition to the above unexpectedly large $\Phi_F(S_2)$ value, another important characteristic on S_2 emission is that its decay curves could be fitted by a monoexponential curve. This shows a marked contrast to the usual Pc systems which require a biexponential fit.[11]

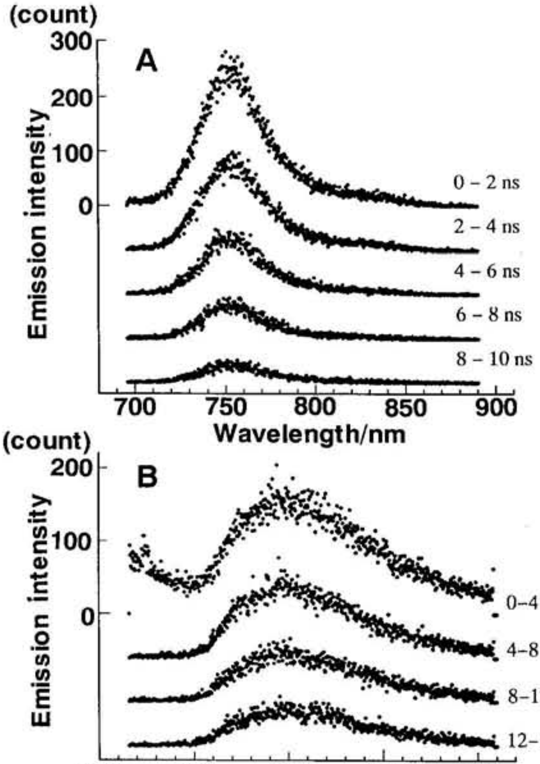

Figure 2. Time-resolved fluorescence (A) S_1 and (B) S_2 spectra of Li_2Fluc in deaerated DMF. The excitation was at 646 and 337 nm for the S_1 and S_2 emission, respectively.

In conclusion, we have reported the synthesis and some spectroscopic properties of a new Pc-like compound, fluoranthocyanine. Although we succeeded in obtaining cobalt complex also by cobalt insertion reaction to Li_2Fluc in DMF, it did not give a monomer-like absorption spectrum even in a coordinating solvent such as pyridine (absorption maxima at 382 and 672 nm with absorbance ratio of *ca.* 3:1), suggesting a strong tendency toward aggregation.[13]

We thank the Asahi Glass foundation for financial support.

References and Notes

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