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The Influence of Aryl Substitution on the Photophysics of 1-Aryl-Fluorenones

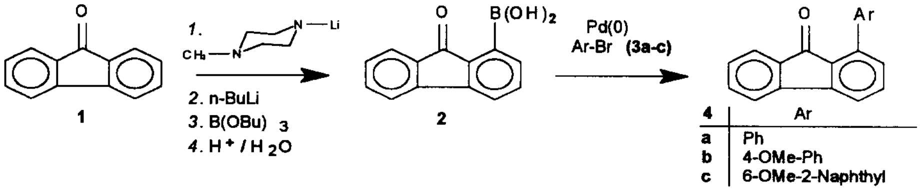
Attila Demeter[a], Géza Timári[a], András Kotschy[b] and Tibor Bérces[a]
a, Central Research Institute for Chemistry, H-1025 Budapest, Pusztaszeri u. 59-67, Hungary
b, Eötvös Loránd University, Dept. of General and Inorg. Chem., H-1518 Budapest 112, P.O.Box 32, Hungary

Abstract: 1-aryl-fluorenone derivatives were prepared from fluorenone via 9-fluorenone-1-boronic acid by coupling with the corresponding aryl-halides. The photophysical properties of these derivatives were found to be strongly influenced by a new CT transition, resulting in some cases in dual luminescence.

Different types of molecules were found to show dual luminescence. Well known examples are for instance the intramolecular monomer-eximers[1], donor-acceptor substituted aromatics[2], bianthryl analogons[3] and N-aryl-naphthalimides[4]. For the N-aryl-naphthalimides, it is suggested[4] that solvent and geometrical relaxation occurring subsequently to light absorption yields two excited states which emit short-wavelength and long-wavelength fluorescence respectively. The geometry of the short-wavelength emitting (locally excited) $^1A_2$ state is similar to that of the ground state (i.e. the plans of the phenyl and the naphthalimide moieties are close to orthogonal), while twisting of the phenyl group toward a coplanar geometry results in an extended conjugation, comprising the phenyl and naphthalimide moieties, and subsequently in an extra stability of the long-wavelength emitting $^1B_1$ state. The presence of a phenyl ring in vicinity to an aromatic carbonyl group seems to be essential in the development of this type of dual luminescence.

In the course of our research we were looking for new ring systems which emit dual luminescence. Among the compounds considered were aromatics with an aryl substituent in the proximity of a carbonyl group. In order to examine their photophysical properties, we prepared a series of 1-substituted 9-fluorenones by extending the methods employed by Gronowitz[5] and Snieckus[6] for the synthesis of polyfused heteroaromatics. Fluorenone was chosen because it is known as a good electron acceptor.

Experimental: Fluorenones containing an aryl substituent in the 1-position can be prepared either by radical procedures[7] or via the ring closure of the appropriate biphenyls[8], however, the scope of these procedures is fairly limited. To overcome this problem we synthetised 9-fluorenone-1-boronic acid (**2**), via the ortho-lithiation of the aminoalkoxide derived from fluorenone (**1**)[9,10], which was then coupled with the appropriate aryl-bromides (**3**) in the presence of Pd(0) catalyst, using the excellent Suzuki protocol[11].



4	Ar
a	Ph
b	4-OMe-Ph
c	6-OMe-2-Naphthyl

e-mail: demeter@cric.chemres.hu or timari@cric.chemres.hu

General procedure for the synthesis of 1-aryl-9-fluorenones (**4a-c**):

The solution of tetrakis(triphenylphosphine)palladium(0) (0.09 mmol) in 2 ml ethylene glycol dimethyl ether (DME) was added to a solution of the appropriate aryl bromide (3mmol) in DME. After stirring the mixture for 10 minutes under nitrogen, 9-fluorenone-1-boronic acid (3.3 mmol) was transferred to the flask with the help of another 2 ml of DME, and this was immediately followed by adding 9 mmol of sodium bicarbonate dissolved in 8 ml of water. The reaction mixture was refluxed for 4 hours under nitrogen. The resulting mixture was treated with 20 ml of water and extracted with diethyl ether. The organic layer was evaporated to dryness and subjected to flash chromatography and then to thin-layer chromatography (silica gel/$CHCl_3$).

1-phenyl-9-fluorenone (**4a**), yield: 72%, mp.: 119-120°C (lit. 119-121°C)[8].

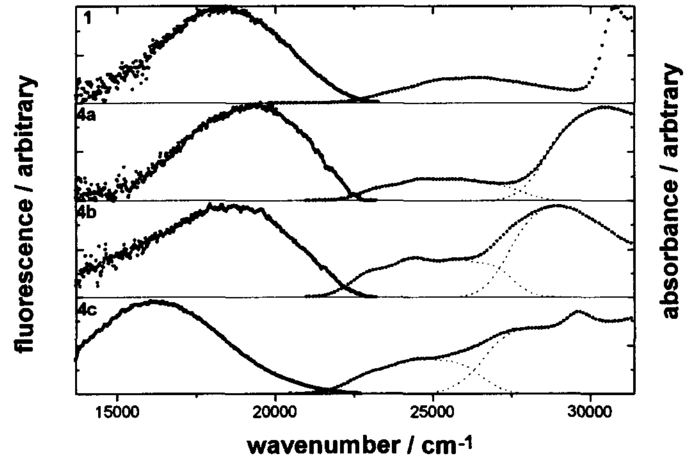
1-(4'-methoxyphenyl)-9-fluorenone (**4b**), yield: 82%, mp.: 140-141°C, H^1-NMR(acetone-d_6), 7.78(d, 1H, &Hz, H-5), 7.719(dd, 1H, 7Hz,1Hz, H-4), 7.59(t, 1H, 7Hz, H-6), 7.58(t, 1H, 7Hz, H-3), 7.55(d, 1H, 7Hz, H-8), 7.38(t, 1H, 7Hz, H-7), 7.26(dd, 1H, 7Hz, 1Hz, H-2), 7.51-6.98(m, 4H, AA'BB', Ar), 3.86(s, 3H, OCH_3)

1-(2'-methoxy-naphth-6-yl)-9-fluorenone (**4c**), yield: 75%, mp.: 172-173°C, H^1-NMR(acetone-d_6), 8.02(d, 1H, 2Hz, H-1'), 7.88(d, 1H, 9Hz, H-8'), 7.87(d, 1H, 9Hz, H-4'), 7.82(d, 1H, 7Hz, H-8), 7.79(d, 1H, 7Hz, H-4), 7.68(t, 1H, 7Hz, H-3), 7.67(dd, 1H, 9Hz, 2Hz, H-3'), 7.62(t, 1H, 7Hz, H-6), 7.57(d, 1H, 7Hz, H-5), 7.41(d, 1H, 7Hz, H-2), 7.38(d, 1H, 2Hz, H-5'), 7.20(dd, 1H, 9Hz, 2Hz, H-7), 3.96(s, 3H, OCH_3).

The technique used in spectroscopic and photophysical measurements were described elsewhere[4]. For excitation in the spectrofluorescence measurements, the 404 nm radiation of a high pressure mercury arc was applied.

Results and Discussion:

Figure 1. Absorption and fluorescence spectra of **1**, **4a**, **4b** and **4c** in acetonitrile.



The absorption and fluorescence spectra of **1**, **4a**, **4b** and **4c** measured in acetonitrile are shown in Figure 1. A comparison of the absorption spectrum of **1** with those of **4a**, **4b** and **4c** shows that substitution of fluorenone in the 1-position by an aromatic moiety results in the appearance of a new band. Data derived from fitting of the absorption spectra measured in hexane and acetonitrile are summarized in the Table 1. The fluorescence of the examined fluorenone derivatives was very week and was in most cases mirror symmetric to the absorption spectrum, but showing no well developed structure. The emission of **4c** in solvents of medium and strong polarity shows different features. In the most polar solvents, the emission of **4c** is (i) structureless with a considerable Stokes shift, and (ii) the fluorescence quantum yields are higher by two orders of magnitude

than in the case of the two other derivatives. The lifetime of the singlet excited state is short for all compounds, it was estimated by single photon counting to be 80 ps for 4c in acetonitrile. In medium polar solvents the emission of 4c (as well as 4b in polar solvents) is much weaker than in acetonitrile. Furthermore both show dual luminescence: the spectra are broad and their shapes are quite different from the emission spectra of 4a.

Table 1. Spectroscopic and photophysical properties of **1**, **4a**, **4b** and **4c.**

compound:	**1**		**4a**		**4b**		**4c**	
solvent:	hexane	ACN	hexane	ACN	hexane	ACN	hexane	ACN
E (S_1 0/0) / cm^{-1}	23930	23390	23130	23250	22900	23030	22350	22520
E (CT 0/0) / cm^{-1}	---	---	29270	29160	27745	27910	26840	26290
E_{ox}-E_{red} / cm^{-1}	---	---	---	28830	---	24480	---	22540
ν_f^{max} / cm^{-1}	19364	18380	20950	19540	20500	19200	20800	15570
ϕ^f	0.0005[12]	0.033	0.000012	0.000024	0.00004	0.000069	0.000016	0.0045
ϕ^{isc}	0.95±0.05	0.52	0.13	0.08	0.09	0.08	0.005	0.01
ϕ^{ic}	0.05	0.45	0.87	0.92	0.91	0.92	0.99	0.99

The triplet-triplet absorption spectra of the **4a** and **4b** are similar to that of **1**, the maximum is around 430 nm in hexane[12]. The ISC yield is small, and is decreasing with solvent polarity, similarly to that of the fluorenone[12]. Similar decrease of the triplet yield can be observed in the **1**, **4a**, **4b** and **4c** series.

The energy of the $S_1 \leftarrow S_0$ absorption band increases slightly with decreasing polarity indicating that this transition has $\pi\pi^*$ character. Furthermore, in the series of **1**, **4a**, **4b** and **4c**, a decrease of the $S_1(0/0) \leftarrow S_0(0/0)$ wavenumbers is observed together with an increase of the molar absorption coefficient (470, 640, 1700 and 1930 $mol^{-1}cm^{-1}$ in hexane). These facts suggest that the substitution in the 1-position effects the $S_1 \leftarrow S_0$ transition considerably. As a result of 1-aryl substitution, a new band appears in the absorption spectra (see Figure 1.). The energy of the transition which belongs to this band is strongly correlated with the oxidation potential, of the aryl substituent[13], implying the charge transfer (CT) character of this band.

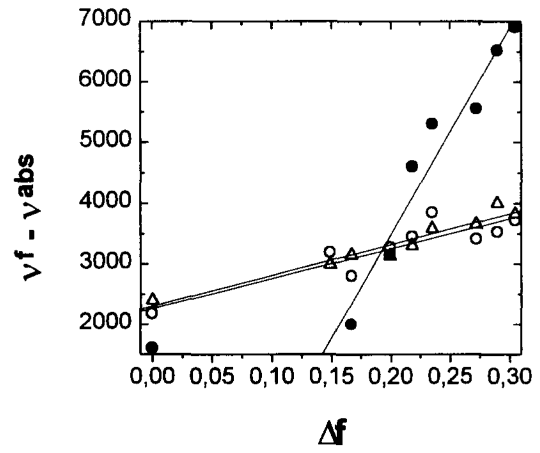


Figure 2. The horizontal Stokes-shift for **4a** (o), **4b** (Δ) and **4c** (•) as a function of the solvent polarity parameter Δf. (The solvents in order of increasing Δf are: n-hexane, chloroform, ethylether, ethyl acetate, dichloromethane, benzonitrile, butironitrile, propionitrile and acetonitrile.)

From the emission spectra one can conclude that **4a** and **4b** as well as **4c** emit from the $\pi\pi^*$ (LE) state in hexane, while the large Stokes shift of the fluorescence of **4c** in polar solvent suggests that for **4c** mainly the CT state is responsible for the emission in acetonitrile. The same conclusion can be drown from the polarity dependence of the emission maxima: from the slope of the fitted lines of Figure 2., the 5.1, 5.5 and 15.5 D transition dipole moments can be derived for **4a**, **4b** and **4c**, respectively. Extrapolation of the energy of the CT emission maximum of **4c** to n-hexane (where the solvent relaxation is negligible) results in a value of

(25700±900) cm^{-1}. Comparing this value with the 26840 cm^{-1} energy of the CT state obtained from the absorption spectra, and considering the halfwidth of the emission (aprox. 3700 cm^{-1} in chloroform), or the separation of the S_1 absorption and the LE emission of **4a** and **4b** in hexane (aprox 1300 cm^{-1}), one concludes that in case of 1-aryl-fluorenone derivatives there is not much room for phenyl rotational relaxation. This is not the case for the N-phenyl-2,3-naphthalimide derivatives[4], where the absorption and emission maxima of the S_2 bands differ by 9800 cm^{-1} in hexane. The appearance of the CT emission for **4c** is due to the smaller difference between the energy of the LE and CT states, and the higher solvent relaxation energy of the CT excited state.

The high internal conversion (IC) yields show that the CT transition influences the photophysical properties. The efficient internal conversion might be explained as follows: The aryl substitution in the 1-position of fluorenone results in a CT state which may interact with the $\pi\pi^*$ (LE) state. The vibronic coupling between the two states leads to efficient IC (which is also known as the proximity effect[14]). The decrease of the triplet yields in the sequence of **1**, **4a**, **4b** and **4c** might be caused by (i) the increasing difference between the energy of the LE and the low lying $n\pi^*$ state (responsible for a triplet quantum yield as high as 1)[12], and by (ii) the increasing competition between the IC and ISC processes.

Finally we can conclude that the photophysics of these molecules show significant differences from the naphthalimides, and exhibit some similarities to the features of the bianthryl analogons.[3]

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10. 2 Mmol (0.36 g) fluorenone in 2 ml dry benzene was added to the solution of 2.2. mmol lithium-N-methyl-piperazide (prepared by the addition of 1.4 ml 1.6 M n-butyllithium (2.2. mmol) to 2.2.mmol (0.22 g) N-methyl-piperazine in 4 ml dry benzene) and stirred at room temperature for 30 minutes under nitrogen. 4 ml of 1.6 M n-butyllithium (6.4 mmol) was added to the solution and the mixture was refluxed for 10 hours. After cooling to room temperature and the adding of 7 ml of dry THF, the mixture was cooled to -78 °C and 1.47 g (6.4 mmol) tributylborate was added droppwise. The stirred mixture was allowed to warm up to room temperature overnight. After acidic workup, the crude boronic acid was isolated and recrystallised from toluene. Yield 0.33 g (74%) H^1-NMR ($CDCl_3$ and DMSO-d_6) 8.7(s,2H, $B(OH)_2$), 7.94 (dd, 1H, 7Hz, 2Hz, H-8), 7.5-7.55(m, 2H, H-6, H-7), 7.63(d, 1H, 7Hz, H-4), 7.61(dd, 1H, 7Hz, 2Hz, H-5), 7.5(t, 1H, 7Hz, H-3), 7.29(m, 1H, H-2)
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