Microwave-Assisted Synthesis and Photophysical Studies of Novel Fluorescent N-acylhydrazone- and Semicarbazone-7-OH-Coumarin Dyes

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**Fig. S28.** IR spectra of 3h in KBr.
Fig. S29. EM spectra of 3h.

---- Shimadzu LCsolution Analysis Report ----

Acquired by : Admin
Sample Name : AK-5
Sample ID : 
Tray# : 1
Vial # : 64
Injection Volume : 40 µL
Data File Name : AK-5.lcd
Method File Name : MET_60AGN_40AGUA_T10.lcm
Batch File Name : tabla.lcb
Report File Name : Default.lcr
Data Processed : 4/26/2016 4:56:10 PM

<Chromatogram>
pKa determination:

The spectral change from pH 5 to pH 8 is ascribed to the deprotonation of the hydroxyl group in the coumarin nucleus, as typical for other hidroxycoumarins, and lead to a well-defined isosbestic point around 375 nm. By the relationship between the pH and \(\log[(A - A_f)/(A_0 - A)]\), the pKa constant for the deprotonation of the \(3b\) hydroxycoumarin was calculated to be 6.7.

Fig. S31. pH titrations of \(3b\). Absorption and emission spectrum.

Fig. S32. pKa determination of \(3b\) considering 412nm and 351nm wavelengths.

\[\text{pKa} \approx 6.7.\]
Table S1. Photophysical parameters in water (pH = 3.0) at 298 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>0.048</td>
</tr>
<tr>
<td>3b</td>
<td>0.068</td>
</tr>
<tr>
<td>3c</td>
<td>0.068</td>
</tr>
<tr>
<td>3d</td>
<td>0.066</td>
</tr>
<tr>
<td>3h</td>
<td>0.065</td>
</tr>
</tbody>
</table>

*Quantum yields were measured by the relative method against the standard compound ethyl-7-OH-coumarin-3-carboxylate ($\Phi = 0.83$ in water) [32].

Fig. S33. Proposition of protonated states of $N$-acylhydrazone- and Semicarbazone-7-OH-Coumarins