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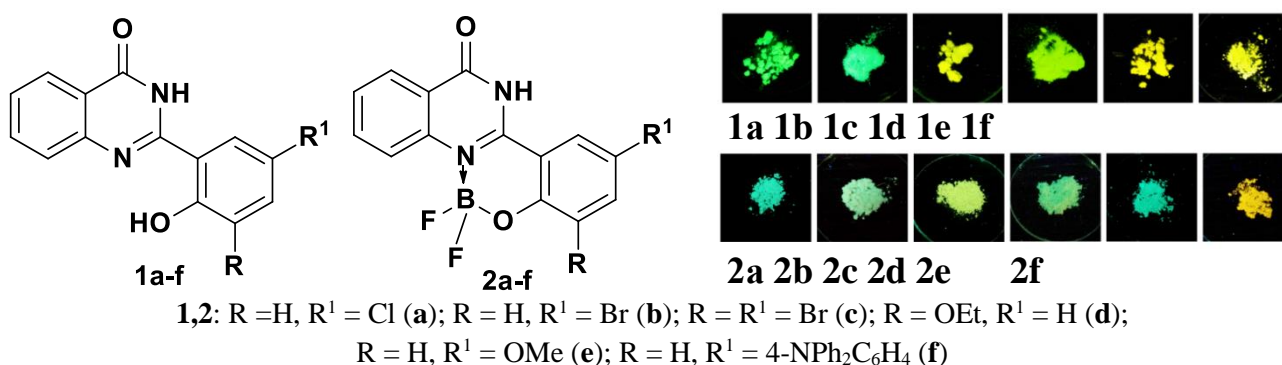
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## 2-(2-HYDROXYPHENYL)QUINAZOLINONE DYES AND THEIR DIFLUOROBORON COMPLEXES: SYNTHESIS AND PHOTOPHYSICAL PROPERTIES\*

**Keywords:** 2-(2-hydroxyphenyl)-3*H*-quinazolin-4-ones, BF<sub>2</sub> complexes, N,O-bidentate ligands, fluorescence.

Benzazines are widely used as electron withdrawing part in light sensitive materials for electronic devices [1]. 2-(2-Hydroxyphenyl)-3*H*-quinazolin-4-ones as one of the type of benzazines attract significant attention. Such molecules display excited state intramolecular proton transfer (ESIPT) effect [2, 3] and can serve as N,O-ligand for BF<sub>2</sub> complexes. Moreover, the numerous modifications of the 2-(2-hydroxyphenyl)-3*H*-quinazolin-4-ones structure allow tuning photophysical properties of target chromophores.

The preparation of 2-(2-hydroxyphenyl)-3*H*-quinazolin-4-ones **1a-e** was achieved similar to previously described method [4]. Stirring of 2-aminobenzamide and corresponding 2-hydroxybenzaldehyde in ethanol at room temperature for 5 hours and subsequent boiling mixture with CuCl<sub>2</sub> led to ligands **1a-e**.



Modification of 2-(2-hydroxy-5-bromophenyl)-3*H*-quinazolin-4-one **1b** by Pd-catalyzed cross coupling reaction [5] gave quinazolinone **1f**. All target difluoroboron

complexes **2a-f** were prepared by treatment of corresponding ligands **1a-f** with  $\text{BF}_3 \cdot \text{OEt}_2$  in mixture of toluene and glacial acetic acid under refluxing [4].

The UV/Vis and photoluminescence (PL) spectra of all compounds **1a-f**, **2a-f** were measured in THF and toluene solutions and are summarized in table 1.

Table 1

	Solvent	$\lambda_{\text{Abs}}$ , [nm]	$\lambda_{\text{em}}$ , [nm]	$\Phi^{[1]}$ [%]	$\Delta\nu_{\text{st}}$ [ $\text{cm}^{-1}$ ]		$\lambda_{\text{Abs}}$ , [nm]	$\lambda_{\text{em}}$ , [nm]	$\Phi^{[1]}$ [%]	$\Delta\nu_{\text{st}}$ [ $\text{cm}^{-1}$ ]
<b>1a</b>	THF	355	514	< 1	9785	<b>2a</b>	358	427	11	4514
	Toluene	359	517	2.0	9643		362	434	18	4583
<b>1b</b>	THF	355	513	< 1	9747	<b>2b</b>	357	428	1	4647
	Toluene	360	512	3	9370		367	433	2	4153
<b>1c</b>	THF	346	527	2	9926	<b>2c</b>	360	435	< 1	4789
	Toluene	352	524	5	9325		370	432	< 1	3879
<b>1d</b>	THF	342	-	0	-	<b>2d</b>	370	468	3	5660
	Toluene	343	-	0	-		350	466	5	5568
<b>1e</b>	THF	362	542	< 1	9174	<b>2e</b>	374	470	22	5461
	Toluene	367	557	< 1	9359		385	474	70	4877
<b>1f</b>	THF	380	562	1	12510	<b>2f</b>	400	591	2	8080
	Toluene	380	563	3	12000		405	538	22	6104

<sup>[1]</sup> Quantum yield was determined relative to quinine bisulfate in 0.1 N  $\text{H}_2\text{SO}_4$  as standard.

The solvents have slightly effect on the absorption and emission spectra of both ligands **1a-f** and complexes **2a-e**. Only 2-(2-hydroxy-5-(4-diphenylaminophenyl)-3H-quinazolin-4-onatoboron difluoride **2f** is characterized by short-wave shift in emission band when going from THF to toluene caused by charge transfer character. The absorption band of difluoroboron derivatives **2** is red-shifted up to 25 nm compare to ligands **1** due to the better-conjugated plane structure of  $\text{BF}_2$  complexes. The emission maxima of complexes **2** are shortwave-shifted in comparison with ligands **1** and appear in blue region for **2a-e** or in green-yellow for **2f**. The nature of substituent at phenol ring proved to have a significant influence on photophysical properties. Remarkably, the presence of chloro or methoxy substituent at position 4' of phenol ring of complexes **2** leads to increase of intensity (up to 18 % for **2a** and up to 70 % for **2e** in toluene). The incorporation of dithenylaminophenyl moiety at 4' position (compound **2f**) also strengthen the emission in toluene. Some ligands and difluoroboron complexes were found to be highly emissive in the solid state.

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## ACRYLIC ACID BASED CONVENIENT SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBON-CONTAINING COPOLYMERS\*

**Keywords:** polycyclic aromatic hydrocarbon (PAH), acrylic acid, copolymers, synthesis, fluorescence studies.

Polycyclic aromatic hydrocarbon (PAH) derivatives exhibit unique fluorescence properties including high quantum yield, long fluorescence lifetime and excellent photostability [1], and can be used in biological fluorescent probe, press-sensitive materials and organic light emitting diodes [2]. In the area of polymer materials, PAH is usually introduced into the polymer to label macromolecular chains, improve polymer fluorescence or modify carbon nanotubes [3]. Herein, we are pleased to report convenient approaches for the synthesis of few PAH containing copolymers (such as pyrene, anthracene and naphthalene) based on acrylic acid. First, we have carried out vinylation of the PAH for the synthesis of starting vinyl PAH. We used various proportion of acrylic acid with respect to the starting vinyl PAH.

