

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

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INTRODUCTION

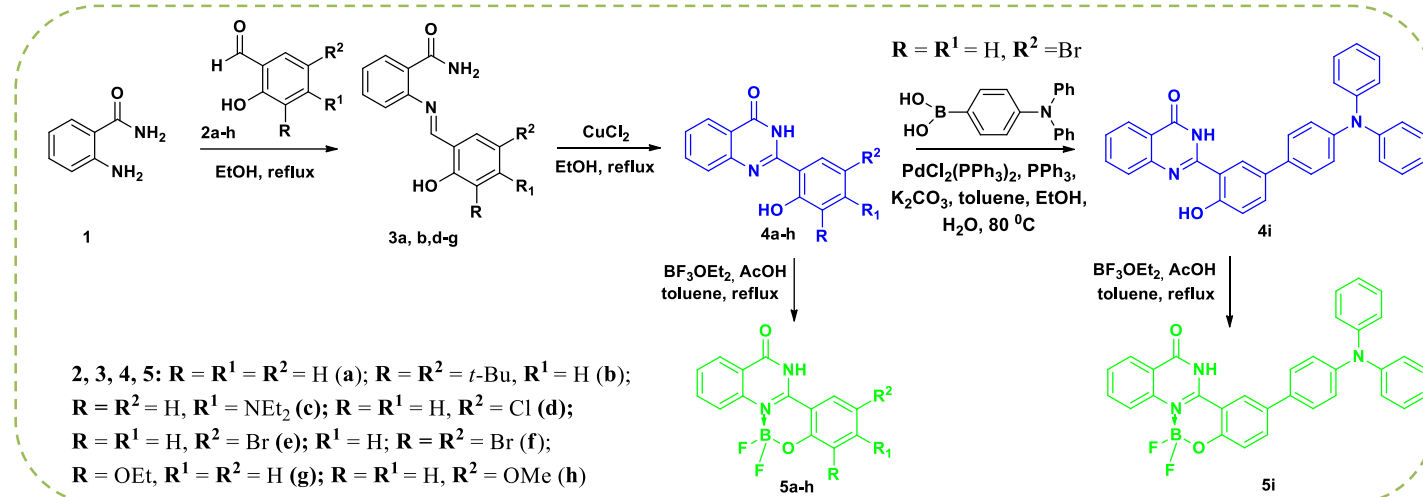
Benzazines are widely used as electron withdrawing part in light sensitive materials for electronic devices. 2-(2-Hydroxyphenyl)-3H-quinazolin-4-ones as one of the type of benzazines attract significant attention. Such molecules display excited state intramolecular proton transfer (ESIPT) effect and can serve as N,O-ligand for BF₂ complexes. Moreover, the numerous modifications of the 2-(2-hydroxyphenyl)-3H-quinazolin-4-ones structure allow tuning photophysical properties of target chromophores.

SYNTHESIS

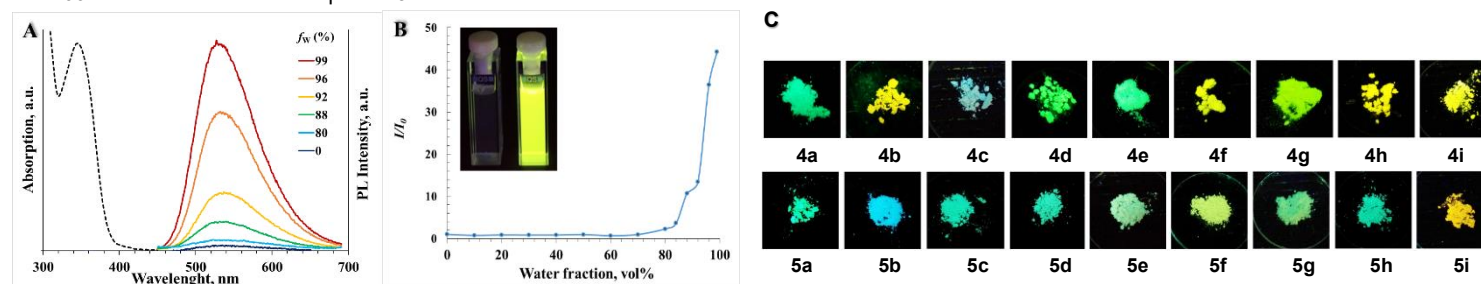
The preparation of 2-(2-hydroxyphenyl)-3H-quinazolin-4-ones **4a-h** was achieved similar to previously described method. Stirring of 2-aminobenzamide **1** and the corresponding 2-hydroxybenzaldehyde **2a-h** in ethanol at room temperature for 5 hours and subsequent boiling of mixture with CuCl₂ led to ligands **4a-h**. Modification of 2-(2-hydroxy-5-bromophenyl)-3H-quinazolin-4-one **4e** by Pd-catalyzed cross coupling reaction gave quinazolinone **4i**. All target difluoroboron complexes **5a-i** were prepared by treatment of corresponding ligands **4a-i** with BF₃·OEt₂ in the mixture of toluene and glacial acetic acid under refluxing.

PHOTOPHYSICAL PROPERTIES

	Solvent	λ_{Absr} [nm]	λ_{em} [nm]	Φ , [%]		λ_{Absr} [nm]	λ_{em} [nm]	Φ , [%]
4a	THF	346	506 sh	< 1	5a	347 sh	417	16
	Toluene	351	505 sh	1		354 sh	423	24
	Powder	-	495	29		-	500	19
4b	THF	345	530	< 1	5b	362	445	43
	Toluene	342	532	< 1		366	441	42
	Powder	-	544	3		-	469	66
4c	THF	375	404	< 1	5c	379	422	11
	Toluene	379	487	< 1		392	412	62
	Powder	-	446	< 1		-	504	2
4d	THF	355 sh	514	< 1	5d	358	427	11
	Toluene	359 sh	517	2.0		362	434	18
	Powder	-	511	15		-	505	11
4e	THF	355 sh	513	< 1	5e	357	428	1
	Toluene	360 sh	512	3		367	433	2
	Powder	-	502	15		-	506	2
4f	THF	346	527	2	5f	360	435	< 1
	Toluene	352	524	5		370	432	< 1
	Powder	-	529	6		-	503	< 1
4g	THF	342	-	0	5g	370	468	3
	Toluene	343	-	0		350	466	5
	Powder	-	518	11		-	509	1
4h	THF	362	542	< 1	5h	374	470	22
	Toluene	367	557	< 1		385	474	70
	Powder	-	546	10		-	489	4
4i	THF	380	562	1	5i	400	591	2
	Toluene	380	563	3		405	538	22
	Powder	-	530	2		-	563	1



We studied photophysical properties in solution and the solid state for all compounds **4, 5**. Obtained data demonstrate that the emission color both the ligands and boron complexes can be tuned by the substituent effect. It was shown that the introduction of methoxy group at *para*-position of phenol ring (compound **5h**) leads to increase in quantum yield compared to parent quinazolinone **5a** (from 24% to 70%, respectively). The solvents have slightly effect on the absorption and emission spectra of both ligands **4a-i** and complexes **5a-h**. Only 2-(2-hydroxy-5-(4-diphenylaminophenyl)-3H-quinazolin-4-onatoboron difluoride **5i** is characterized by short-wave shift in emission band when going from THF to toluene due to intermolecular charge transfer. All substituted quinazolinones demonstrated AIE/AIEE characteristics caused by the synergistic effect of excited state intramolecular proton transfer (ESIPT) and restriction of intramolecular motion (RIM) mechanisms. As an example, spectra of quinazolinone **4b** in THF/water mixture with different water fractions are shown on Figures **A, B**. Emission of **4, 5** in solid state was studied (Figure C), the emission quantum yield in powder reached 29 % for the ligands **4** and 66 % for difluoroboron complexes **5**.



(A) UV-VIS absorption spectra (dashed line) of compound **4b** in THF. PL spectra in THF and THF/water mixtures with different water fraction (f_w); C = 10 μ M; λ_{ex} = 345 nm. (B) Plot of relative PL intensity (I/I_0) of **4b** at $\lambda=532$ nm versus the solvent composition of THF/water mixture. T = 23 °C. Inset: photographs of **4b** in THF and THF/water mixture (98/1, v/v) taken under UV light $\lambda=365$ nm. (C) Emission of compounds **4** and **5** in solid state (powder).

CONCLUSION

We synthesized 2-(2-hydroxyphenyl)-3H-quinazolin-4-ones bearing various substituents in phenol ring and obtained N,O-coordinated BF₂ complexes based on them. The present study may be a significant step towards the development of new quinazolinone-based fluorophores.

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