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Tunable Color of Aggregation-Induced Emission Enhancement in a Family of Hydrogen-Bonded Azines and Schiff Bases

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Abstract: A simple synthesis strategy afforded a family of hydrogen-bonded azines and Schiff-bases. Although in dilute solution these dyes are faint light emitters, all exhibit bright luminescence upon aggregation. Changing the peripheral substituents from electron donating to electron withdrawing allows emission fine-tuning in a range from bluish-green to orange-red. The crystal structure of the materials reveals the restriction of intramolecular rotations is the main mechanism for the aggregation-induced enhancement properties.

Keywords: Azine • Schiff base • Fluorescence • Aggregation Induced Emission • Crystal

Introduction

Aromatic imines usually absorb strongly in the visible region of the light spectrum, making them highly colored compounds. However, they are not known to be strong emitters, the absorbed energy being lost as heat through vibrational relaxation. To promote the emission process, stiffening of the backbone surrounding the imine is necessary. Introduction of a phenol group creates a *N*,*O* complexing pocket, which has been used to chelate transition metals such as zinc,¹ copper, nickel, platinum,² or semi metallic elements such as boron³ or aluminium. This has resulted in numerous luminescent complexes, with interesting emitting properties in solution,⁴ and in the solid state as crystals, amorphous powders or thin films.

Aggregation may also stiffen the backbone of Schiff bases of the salen type, turning them from non-emissive in solution to luminescent in the solid state. This phenomenon is the opposite of 'Aggregation Caused Quenching' usually observed with organic chromophores, and is known as 'Aggregation-Induced Emission Enhancement' (AIEE),⁵⁻⁸ which is different from the formation of *J*-aggregates^{9,10} or the observation of phosphorescence instead of fluorescence.^{11,12} This approach has been successfully applied to the synthesis of luminescent square tubes,¹³ and to the detection of small amounts of hydrazine in water.¹⁴ Salicylaldehyde azine derivatives, with AIEE properties, have also been used for cellular imaging^{15,16} and as

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molecular probes for the detection of thiols in live cells.¹⁷ The study of the solid-state organization of one benzophenone azine derivative provided insight into the importance of polymorphs, as a change in the crystal structure lead to a change in the emission wavelength, induced and controlled by the application of external stimuli.¹⁸ Salicylaldehyde azines and Schiff bases are also known to undergo excited-state intramolecular proton transfer process (ESIPT), which gives rise to larges Stokes shifts. The ESIPT process can be facilitated in the solid state, as the conformation is usually blocked and the intramolecular O-H…N hydrogen bond is adequately oriented. Thus, both ESIPT and AIEE processes can be found in salicylaldehyde azines and Schiff bases, leading to efficient emission and large Stokes shifts in the solid state.¹⁹ All these results make azines and Schiffbases promising compounds for biological imaging and luminescent devices. But to date, such studies have not been comprehensive and, in particular, no attempt to tune the emission wavelength has been reported.

Here, we wish to report the synthesis and characterization of hydrogen bonded azines and Schiff bases with tunable emission colors. To tune the emission properties of the Schiff bases, two strategies were adopted. The first one relies on the variation in conjugation of the aromatic system, using hydrazine or 1,4phenylenediamine as linking group. The second strategy takes advantage of the donating or withdrawing properties of the aromatic substituents. These two approaches aim at modifying the HOMO-LUMO energy difference and, hence, the absorption and emission wavelengths. The results show all dyes present AIEE and ESIPT properties, with larges Stokes shifts and good quantum yields in the solid state.

Results and Discussion

All compounds were obtained following a straightforward strategy (Scheme 1). The corresponding aldehyde or ketone was condensed with hydrazine in a two to one ratio, in refluxing methanol, and the product was collected by filtration or purified over silica gel flash

emission

column chromatography. When 1,4-phenylenediamine was used instead of hydrazine, the double condensation was readily obtained with the aldehyde derivatives. The double condensation with the ketones requested the use of longer reaction time or more concentrated solutions to obtain the product, noticing that the mono imine was also obtained in some cases. Compounds were characterized by NMR spectroscopy and HRMS (see Supporting Information).



Scheme 1. Synthesis of the fluorophores. Reagents and conditions: i) hydrazine hydrate, methanol, reflux; ii) 1,4-phenylenediamine, methanol, reflux.

The photophysical properties were first studied in dilute THF solution. The dyes present an absorption maximum between 351 and 391 nm, with molar extinction coefficients from 16,000 to 110,000 M⁻¹ cm⁻¹ (Table 1, Figure 1 and SI). There is no clear trend in the absorption properties but the introduction of electron donating or withdrawing substituents, and aromatic rings, red shifts the absorption maximum, and increases the absorption coefficient. All dyes emit faintly upon excitation at 400 nm (Figure 2 and SI), with quantum yields <0.1% in solution. Stokes shifts are large, *ca.* 9,000 cm⁻¹, indicating an ESIPT process.

Table 1. Absorption and emission properties in THF solution and in the solid state.

		THF solut		Solid state		
Dye	$\lambda_{abs}~(nm)$	$\epsilon (M^{-1} cm^{-1})^{[a]}$	$\lambda_{\rm em}~(nm)$	$\phi_{\rm f}(\%)^{[b]}$	$\lambda_{\rm em}(nm)$	ϕ_{f} (%) ^[c]
1a	357	16 300	560	< 0.1	541	40
2a	364	22 000	565	< 0.1	568	54
3a	391	40 900	n.a.	n.a.	620	4
4a	373	34 600	610	< 0.1	595	10
5a	377	86 100	603	< 0.1	620	13
6a	374	99 800	545	< 0.1	550	11
7a	360	57 200	n.a.	n.a.	523	19
1b	370	110 000	n.a.	n.a.	587	20
2b	341	45 400	n.a.	n.a.	525	1
3b	368	21 800	n.a.	n.a.	604	2
4b	384	44 800	595	< 0.1	610	3
5b	351	19 200	590	< 0.1	568	7
a	292	52 500	565	< 0.1	550	2

[a] Recorded at concentration of *ca*. 10^{-5} mol L⁻¹. [b] Determined by comparison with fluorescein,²⁰ quantum yield 95% in aqueous NaOH 0.1 mol L⁻¹. [c] Determined using an integrating sphere, with excitation at 300 nm.

1a-7a and **1b-6b** are almost non-emissive in dilute solution but exhibit bright emission in solid state, which can be ascribed to the formation of *J*-aggregates or to Aggregation-Induced Emission Enhancement. To decide which phenomenon is responsible for this behaviour, the emission spectra of solutions and suspensions of **1a-6b** in THF-water mixtures were recorded (Figure 3 and SI). All compounds present the same behavior: the solutions are almost non-emissive, but when the ratio of water reaches 60-70%, a precipitate forms and the suspension is brightly emissive.



Figure 1. Normalized absorption spectra of 1a-7a in THF solution.



Figure 2. Normalized emission spectra of 1a-7a in THF solution. Excitation at 400 nm. The spectra of the non-emissive dyes are not shown (3a, 7a).

The solid-state emission spectra were also recorded (Figure 4 and SI). **1a-6b** emit at similar wavelengths in the solid state and in solution, but the quantum yields are much higher in the former (Table 1). The absence of noteworthy shift between solution and solid-state emission rules out *J*-aggregates formation as the reason for the observed emission enhancement. Fehler! Textmarke nicht definiert. The restriction of intramolecular rotation (RIR) is, thus, the likely mechanism for such emission enhancement.

In the solid state, the emission maxima range from 523 nm to 620 nm, depending on the fluorophore substituents, and on the presence or absence of a phenyl ring between the two nitrogen atoms. Concerning the substituents, the addition of electron donating groups (OMe) at the periphery of the dyes induces an emission blue-shift, whereas the addition of electron withdrawing groups (Br) causes a red-shift. The change between hydrazine and 1,4-phenylenediamine linker induces

a shift in both absorption and emission maxima. Red shifts are observed for the compounds bearing an aldimine group CH=N ($1a \rightarrow 1b$, $4a \rightarrow 4b$, and $6a \rightarrow 6b$), and blue shifts are observed for the compounds bearing a ketimine group CR=N ($2a \rightarrow 2b$, $3a \rightarrow 3b$, and $5a \rightarrow 5b$). To better understand the structure-properties relationship, the crystalline structure of some compounds was studied.



Figure 3. Emission spectra in THF:water solutions or suspensions of dihydroxybenzalazine 1a (ca. 10^3 mol L⁻¹, $\lambda_{ex} = 400$ nm), and photograph of the solutions/suspensions under UV light (365 nm).



Figure 4. Normalized solid-state emission spectra of 1a-7a (excitation at 370 nm).

Single crystals suitable for X-ray diffraction were grown for compounds **1a**, **2a**, **3a**, **5a**, **1b**, **2b**, and **3b** (see SI for the CIF files). Bond lengths and angles are in normal range.²¹ As expected, all compounds present strong intra-molecular O-H…N hydrogen bonds, that are also present in solution, as witnessed by the NMR spectra exhibiting a OH proton resonance between 11 and 15 ppm.

Compound **1a** can adopt several crystal forms, but in this study only one polymorph was obtained, so the discussion is based on this form. The obtained crystal structure of **1a** is shown in figure 5.²² The two phenyl rings are coplanar with the two imino groups and, as a result, the π system is fully conjugated. The molecules pack in a herringbone fashion. In the layers, the molecules are linked by C-H···C contacts between an aromatic C-H and the C-C=N carbon atoms. The layers stack without significant interactions (no contact shorter than the sum of the Van der Waals radii). There are no π - π interactions. This organization could be described as an *H* or *J*-aggregate, but the distances between the adjacent dipoles are too large to allow a strong interaction, thus the exciton splitting is close to zero.²³ This is confirmed by the absorption and emission spectra: there is almost no shift in the maxima between the solution and solid-state emission spectra.



Figure 5. Crystal structure of 1a, a) asymmetric unit, b) packing. Hydrogen bonds and short contacts indicated as black dashed lines. Ellipsoids are drawn at the 50% level, hydrogen are shown as sphere of arbitrary radius of 0.30 Å. C, grey; H, white, O, red; N, blue.

The molecules of **2a** also arrange in a herring-bone fashion²⁴ (Figure 6), but the molecules stack in a staircase fashion with close contact. The angle between the dipole (represented by the $O \cdots O$ axis) and the line of molecular centers in the staircase alignment is 54.72°, which according to the exciton model gives a nearly zero band splitting. Fehler! Textmarke nicht definiert. The distance between adjacent molecules is too long to allow a strong interaction of the dipoles, in accord with the absence of shift observed between the solution and solid-state emission spectra.



Figure 6. Crystal structure of 2a. a) asymmetric unit, b) packing. Hydrogen bonds and short contacts indicated as black dashed lines. Ellipsoids are drawn at the 50% level, hydrogen are shown as sphere of arbitrary radius of 0.30 Å. C, grey; H, white, O, red; N, blue.

In the crystal of **3a** (Figure 7), the two phenol rings are coplanar but the phenyl rings are perpendicular to the imine bond. The molecules arrange in planes, into which the molecules are cross-linked through C-H…O hydrogen bond between an aromatic C-H and a hydroxyl group. There are no π - π interactions. The dipoles are too far away from each other to allow a significant interaction, and thus there is no exciton splitting. In solution, the phenol ring sees its motion restricted by the intramolecular O-H···N hydrogen bond, but the other phenyl ring is free to rotate. Similarly to the other compounds, the rotation around the N-N single bond is not restricted in solution, and as a consequence, the preferred relaxation pathway is through torsional vibrations and the molecule is non-emissive in solution. In the crystalline state, the torsional vibrations of the N-N single bond are restricted, and the phenyl ring is efficiently blocked by two intermolecular C-H···O hydrogen bonds, thus promoting fluorescence.



Figure 7. Crystal structure of 3a. a) asymmetric unit, b) packing. Hydrogen bonds and short contacts indicated as black dashed lines. Ellipsoids are drawn at the 50% level, hydrogen are shown as sphere of arbitrary radius of 0.30 Å. C, grey; H, white, O, red; N, blue.

Compound **5a**, bearing bromo substituents, also arranges in a herringbone fashion in the crystalline state (Figure 8). In the staircase organization along the b axis, the molecules stack through two Br···C=N contacts and one C···C contact between the C-OH, leading to parallel displaced π - π interactions. The angle between the dipole (represented by the O···O axis) and the line of molecular centers in the staircase alignment is 32.18°, which according to the exciton model categorizes the interaction as *J*-aggregates. The shift in the emission maxima in solution and in the solid state is small (*ca.* 20 nm), but the quantum yield is much higher in the solid state. Therefore, an additional stiffening of the structure in the solid state is the main reason for the observed increase in emission efficiency.



Figure 8. Crystal structure of 5a. a) asymmetric unit, b) packing. Hydrogen bonds and short contacts indicated as black dashed lines. Ellipsoids are drawn at the 50% level, hydrogen are shown as sphere of arbitrary radius of 0.30 Å. C, grey; H, white, O, red; N, blue; Br, brown.

The structure of **1b** in the solid state confirmed the planarity of the compound, and the co-planarity of the three phenyl rings (Figure 9). The compounds stack on top of each other along the b axis, at a distance of *ca*. 3.29 Å, the main axis of the molecules at an angle of 46.25° with the line of molecular centers. If the dipole of the molecule is viewed along the O-H…N axis, it is at an angle of 57.43° to the line of the molecular centers. This value does not allow the classification into *J* or *H*-aggregates, as it is close to the limit between the two.



Figure 9. Crystal structure of 1b. a) asymmetric unit, b) packing. Hydrogen bonds and short contacts indicated as black dashed lines. Ellipsoids are drawn at the 50% level, hydrogen are shown as sphere of arbitrary radius of 0.30 Å. C, grey; H, white, O, red; N, blue.

In contrast to compound **1b**, compound **2b** is not planar (Figure 10). The steric hindrance created by the methyl substituents forces the central phenyl rings to be close to perpendicular to the imine plane (dihedral angle of 80.38°), which in turn is co-planar with the phenol ring (dihedral angle of 2.00°). This torsion breaks the conjugation in the chromophore, and explains why its emission maximum is blue-shifted relatively to compound **1b**. It also prevents any π - π interactions, and forces the dipole to stay far from each other.



Figure 10. Crystal structure of 2b. a) asymmetric unit, b) packing. Hydrogen bonds and short contacts indicated as black dashed lines. Ellipsoids are drawn at the 50% level, hydrogen are shown as sphere of arbitrary radius of 0.30 Å. C, grey; H, white, O, red; N, blue

Compound **3b** crystallizes with two independent molecules in the asymmetric unit (Figure 11), arranged in a herring-bone fashion and cross linked through C-H···C and C-H···O interactions. The imine bond is coplanar with the phenol ring, and at a dihedral angle of 57.82° (or 59.87) with the central ring, and of 71.76° (or 69.62) with the other phenyl. These torsion angles prevent a stacking of the molecules and keep the dipoles far away from each other. These torsion angles also break the conjugation of the backbone, and explain why the emission is blue-shifted relatively to compound **3a**.



Figure 11. Crystal structure of 3b. a) asymmetric unit, b) packing. Hydrogen bonds and short contacts indicated as black dashed lines. Ellipsoids are drawn at the 50% level, hydrogen are shown as sphere of arbitrary radius of 0.30 Å. C, grey; H, white, O, red; N, blue.

In short, consideration of the crystal structures shows that the aggregates cannot be described as J or H-aggregates. The distances between the molecules are too large, preventing a significant interaction between the dipoles. Moreover, the emission wavelength does not change significantly between solution and solid state. The increase in the emission intensity observed when the molecules aggregate is therefore due to the restriction of molecular motion.

It has to be noticed that, in the solid state, the quantum yields of the compounds with 1,4-phenylenediamine linker are much lower than those with hydrazine linker. If the restriction of torsional vibrations around the N-N single bond is the main cause for the AIEE effect

observed, the introduction of the 1,4-phenylenediamine linker would add some extra torsional vibrations modes, around the two C-N single bonds. These may not be as efficiently blocked in the solid state, thus dissipating some of the energy in a non-radiative way, and lowering the quantum yields of the compounds.

Conclusion

A family of hydrogen-bonded azines and Schiff bases has been prepared and characterized. Although their emission intensity in dilute solution is very low, it increases dramatically in the solid-state. The study of the material's crystal structures demonstrated their Aggregation-Induced Emission Enhancement properties. By changing the substituents from electron donating to electron withdrawing, and by increasing or decreasing the conjugation of the aromatic backbone, the emission color could be tuned from bluegreen to orange-red.

Experimental Section

Experimental Details: All procedures and characterizations are included in the Supporting Information. CCDC-1843629-1843633 contain the supplementary crystallographic data this paper. These data can be obtained free of charge for www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: C44 1223 336 033. E-mail: deposit@ccdc.cam.ac.uk).

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Entry for the Table of Contents (Please choose one layout only)

Layout 1:

A rainbow of AIEEgens

Tunable Color of Aggregation-Induced Emission Enhancement in a Family of Hydrogen-Bonded Azines and Schiff Bases



Hydrogen bonded azines and Schiff bases are non-emissive in dilute solutions but exhibit bright luminescence upon aggregation, in a range from bluish-green to orange-red.