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Luminescent materials incorporating pyrazine or quinoxaline moieties.

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Abstract:
Though the past few decades, the development of new luminescent materials has received a lot of attention due to their applications as fluorescent sensors, in biological microscopy and in optoelectronic devices. Most of these applications are relied on intramolecular charge transfer (ICT). Presence of electron withdrawing N-heterocycles such as pyrazine and quinoxaline rings appeared therefore particularly interesting to be used as electron-attracting part in π-conjugated structures. Moreover, presence of nitrogen atoms with lone electron pairs allows to the pyrazine and the quinoxaline ring to act as effective and stable complexing agent or as base that can be protonated. This review reports luminescent small molecules and oligomers including a pyrazine or quinoxaline ring in their scaffold highlighting their applications related to photoluminescence and electroluminescence.

Keywords: pyrazine, quinoxaline, fluorescence, OLEDs, π-conjugated molecules, sensors

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1. Introduction
Diazines which belong to the most important heterocycles containing nitrogen are six-membered aromatics with two nitrogen atoms. Three different structures can be distinguished according to the relative position from the nitrogen atoms: pyridazine (1,2-diazine) [1], pyrimidine (1,3-diazine) [2] and pyrazine (1,4-diazine) [3]. Quinoxaline, also called benzopyrazine is a heterocyclic compound containing a ring complex made up of a benzene ring and a pyrazine ring [4]. Pyrazine and quinoxaline derivatives have been intensively studied because the 1,4-diazine core is found in many natural and man-made compounds [5]. Alkylpyrazines, produced from proteins by fermentation are for example the constituents of the aroma of coffee [6], some cheeses [7] or roasted meat [8]. The more complex imidazopyrazine moiety is found in the scaffold of the Coelenterazine, a bioluminescent compound isolated from the jellyfish Aequorea Vistoria [9]. Moreover numerous pyrazine and quinoxaline derivatives exhibit a large range of biological activities and are used for pharmaceuticals or phytosanitary applications [10]. Besides their medicinal uses, pyrazine and quinoxaline derivatives have found technical applications as dyes, electroluminescent materials, organic semi-conductors and as suitable ligands in coordination chemistry. We report herein the main results dealing with this kind of applications during the last two decades.

The elaboration of electro-optical (EO) and nonlinear optical (NLO) materials has attracted considerable attention because of their wide range of potential applications in optical data processing technologies. The synthesis of extended π-conjugated systems has been the key to provide organic materials with such properties. These compounds are often based on a push-pull system, which is constituted by an electron-donating group (D) and an electron-withdrawing group (A) linked through a π-conjugated spacer. The molecular properties of the chromophores depend on the strength of the “push-pull” effects which are function of the ability of the donor to provide electrons and the acceptor to withdraw electrons.
Pyrazine and quinoxaline, which are highly \( \pi \)-deficient aromatic heterocycles, can be used as electron withdrawing part in push-pull structures for intramolecular charge transfer (ICT). Such important ICT along the backbone of the molecule can induce luminescence properties. The ability of protonation, hydrogen bond formation and chelation of the nitrogen atoms of the 1,4-diazine ring are also of great importance: such derivatives could be therefore used for the formation of supramolecular assemblies and used as sensors.

Two general methods for the synthesis of \( \pi \)-conjugated pyrazine derivatives are described in the literature. The first method consists of the construction of the pyrazine ring by condensation reactions of \( \alpha \)-diketones with vicinal diamines [11] but these methods disappoint in the preparation of unsymmetrical substituted pyrazines. The second one involves the functionalization of the 1,4-diazine ring [12]. The advantages of the latter one are a greater versatility and the use of easily available starting materials. Indeed, a large variety of halogeno (more particularly chloro), amino and methyl derivatives are commercially available and can be used as building blocks to elaborate \( \pi \)-conjugated scaffolds. Among the synthetic strategies, the cross-coupling reactions involving halogenated pyrazines and / or quinoxalines constitute a method of choice to access such structures. It should be noted that the \( \pi \)-electron-deficient character of the 1,4-diazine ring makes easier the oxidative addition of palladium to a chlorine–carbon bond without the use of specific and expensive ligands [13]. Therefore, a wide range of cross-coupling reactions (Suzuki [14], Stille [15], Negishi [16], Sonogashira [17], Heck [18] and Corriu-Kumada [19]) have been carried out with halogenated pyrazine or quinoxaline building blocks. Another synthetic way to access to vinylpyrazines or vinylquinoxalines is the condensation reaction of various aldehydes with methyl derivatives [20].

Recently we have reviewed the use of pyrimidine and pyridazine as building blocks for the synthesis of \( \pi \)-conjugated materials [21]. This article is the last part of this series of
papers and has for aim to review the use of pyrazine and quinoxaline moieties in the synthesis of fluorescent materials. Only small molecules and oligomers will be described here, this review will not treat polymer materials. The first part of this review deals with pyrazine derivatives while the second part is dedicated to quinoxaline compounds. Each part will be organized by molecule classes.

2. Pyrazine derivatives

Because the 2,3-dicyanopyrazine ring has specific properties resulting from the two strong withdrawing cyano groups, this moiety has been introduced in the scaffold of a wide range of fluorophores.

2.1. Diamino and dicyanopyrazines

A first family of 2,5-diamino-3,6-dicyanopyrazines was synthesized and studied in 1998 by Matsuoka and coworkers [22]. The 2,5-diamino-3,6-dicyanopyrazine 1 absorbs at $\lambda_{\text{abs}} = 458$ nm and emits at $\lambda_{\text{em}} = 538$ nm with a quantum yield $\Phi_F = 0.3$. This compound is an interesting intermediate to access other fluorescent dyes. Alkylation of the amino groups leads to compounds 2 which present a bathochromic shift of $\lambda_{\text{abs}} = 449–522$ nm and a red fluorescence $\lambda_{\text{em}} = 532–603$ nm. On the contrary, acylation of the amino groups (compounds 3) induces a hypsochromic shift of $\lambda_{\text{abs}} (378–403$ nm) and of $\lambda_{\text{em}} (432–488$ nm). It is noteworthy that the imine 4 has similar $\lambda_{\text{abs}} (452$ nm) and $\lambda_{\text{em}} (527$ nm) than 1 but a higher quantum yield ($\Phi_F = 0.8$) (Scheme 1).

![Scheme 1. Structure and photophysical data of compounds 1–4.](image-url)
A series of mono- and diazomethines dyes derived from 1 were also developed by Matsuoka and coworkers and have proved to be red light emitters for electroluminescence devices (Scheme 2) [23].

More recently a comparative study of the photophysical properties of the 2,5-diamino-3,6-dicyanopyrazine 1 with other diaminodicyanopyrazines was performed in acetonitrile by Angulo et al [24]. The compound 1 exhibits red shifted absorption and emission in comparison with those of 6. These results could be explained by a more important ICT between the nitrile and amino groups due to their opposite position in the symmetrical compound 1 (Scheme 3).
2.2. **Diamino and dicarboxypyrazine derivatives**

Using the 2,5-diamino-3,6-dicarboxypyrazine 7 as starting material, various thioester and carbamoyl derivatives 8 and 9 were synthesized and their photophysical properties established in CHCl₃ (Scheme 4) [25].

![Scheme 4. Structure and photophysical data of compounds 7–9.](image)

The solid state spectra of compounds 8 and 9 were evaluated with respect to their molecular staking. In the case of the 2,5-diamino-3,6-bis(butoxycarbonyl)pyrazine, the X-ray crystal analysis has shown space-filling intermolecular interactions of diaminopyrazines making possible the construction of strong three dimensional molecular staking in single crystals, which affects their solid state absorption spectra.

Starting from chromophores 10, easily obtained by reductive amination reaction, Poreddy and coworkers have developed hydrophilic red fluorescent N,N’-dialkylated aminopyrazines 11 and 12 [26]. These compounds absorb and emit at higher wavelengths (~ 50 nm) than their corresponding aminopyrazines and could found potential applications in medical diagnostic (Scheme 5).
More recently, the same team has described similar hydrophilic pyrazine dyes 13 and 14 that have neutral and anionic groups [27]. These molecules have emission wavelengths $\lambda_{em}$ ranging between 557–600 nm and quantum yield around 0.4 in DMSO for the enantiomer of 13a (Scheme 6). Besides their interesting photophysical properties, some of these compounds could be used as fluorescent glomerular filtration rate (GFR) tracer agents.
Chromophoric crosslinkers constituted by tetra-functionalized 3,6-diaminopyrazines 15–17 bearing a set of terminal aliphatic and anilino amine groups were recently synthesized (Scheme 7). With these molecules, Wooley et al, have developed dual-emitting photonic nano-objects that can sense changes in the environmental pH [28].

Scheme 7. Structure and photophysical data of compounds 15–17.

Compounds 15–17 have demonstrated a morphology-dependent reactivity towards physical or chemical change leading to fine tuning of dual-emission over ca. 60 nm (496 to 560 nm) in a physiologically relevant pH range.

Teramae and coworkers have described the selective binding of Amiloride 18 (Scheme 8), a 2,6-diaminopyrazine derivative, to abasic (AP) site in RNA [29]. A dramatic increase of the fluorescence of amiloride at 415 nm was observed selectively in the presence of AP-RNA, making such a response applicable to microRNA detection.
2.3. **Arylvinyl and aryldicyanopyrazines**

2,3-dicyanopyrazines which are powerful electron acceptors were used as building blocks to synthesize chalcone analogues and styryldicyanopyrazines. The chalcone derivatives 20 were obtained by the Knoevenagel condensation of 2-acetyl-4-methyl-5,6-dicyanopyrazine 19 with various arylaldehydes whereas the styrylpyrazines 21 and 22 have resulted from a similar condensation reaction of the methyl group with arylaldehydes (Scheme 9). These compounds are highly fluorescent ($\lambda_{em}$ comprised between 479 and 610 nm in CHCl$_3$), showed solvatochromism depending from polarity of the solvents and an intramolecular charge transfer confirmed by semi-empirical calculations (MOPAC PM3 method) [30]. When the pyrazine is substituted by a hydroxyl group, a large negative solvatochromism is observed due to tautomerism between the hydroxypyrazine and the pyrazinone forms.
Di-(arylvinyl)dicyanopyrazines 23 and 24 and V-shaped structures 25 with a benzene or a pyridine as central core were also synthesized (Scheme 10) [31]. The physical properties of these fluorophores were determined and a reasonable correlation was found between calculated (PPP MO) and experimental data.
Scheme 10. Structure and photophysical data of compounds 23–25.

The 2,3-bis(phenylethenyl)-5,6-dicyanopyrazine 26 was studied as fluorescent material in solid state [32]. The single crystals of this compound underwent a morphological phase transformation (at 174°C) from a yellow crystal to an orange one via a thermal phase transition without the crystal state collapsing (Scheme 11). The crystal lattice transformation was explained in terms of the lattice contraction and the intermolecular π-π interaction in the solid state.

Scheme 11. Structure of compound 26 and color change of crystal via a thermal phase transition.
Matsumoto and coworkers have described the J-aggregate structure of a chloroform solvate of the 5-t-butyl-2,3-dicyano-6-[4-(dimethylamino)styryl]pyrazine 27a (Scheme 12) [34]. The dye was found to form a two-dimensional brick-wall structure, separated by chloroform molecules in the solvated crystals, which emits intense red fluorescence.

Moreover, other 2,3-dicyanopyrazine derivatives 27 with ester linkers were designed (Scheme 13) [35]. These molecules have a similar V-shaped geometry, confirmed by the X-ray structure of the central core, with lack of planarity between the two arms. The optical and thermal properties of these compounds were evaluated highlighting a blue fluorescence in solution ($\lambda_{em}$ 437–445 nm) with low to moderate quantum fluorescence yields ($\Phi_F$) from 0.003 to 0.1 and Stokes shifts of around 6000 cm$^{-1}$. 
The [2+2] photocycloaddition of 2,3-dicyanopyrazine derivatives 28 were achieved by irradiation at 365 nm under a high-pressure Hg lamp, leading to the photodimers 29 (Scheme 14) [36]. Spectral changes of UV-visible absorption and fluorescence intensity were examined at specific exposure intervals. While the cyclobutane ring of dimers induced a discrete π-conjugation with aryl substituents showing a hypsochromic shift of absorption and emission spectra. For example, change of fluorescence spectra of 28 with R = t-Bu in a thin film under irradiation became brighter and was blue shifted from 478 nm to 467 nm.
Lee and coworkers have developed dicyanopyrazine dyes 30 containing spiropyran groups [37]. These compounds have emission at 484 nm in CHCl₃ as well as photochromic properties under UV irradiation. The spiropyran part is used due to its ability to exhibit two forms: a colorless closed spiro form 30a and a colored open merocyanine form 30b (Scheme 15). Such derivatives have potential applications for data storage, electronic devices and optical filters.
A compound with ICT properties: the 5,6-bis-[4-(naphthalene-1-yl-phenyl-amino)-phenyl]-pyrazine-2,3-dicarbonitrile 31 (BNPPC) was synthesized by Chew et al (Scheme 16) [38].

![BNPPDC](image)


This compound was strongly fluorescent in non-polar and moderately polar solvents, as well as in thin solid film. The absorption and emission maxima shifted to longer wavelength with increasing solvent polarity. The fluorescence quantum yield also was also improved with increasing solvent polarity from non-polar to moderately polar solvents, then decreased with further increase of solvent polarity. This indicates that both “positive” and “negative” solvatokinetic effects co-exist. Using this material as hole-transporting emitter and host emitter has allowed elaboration of green-yellow electroluminescent (EL) devices.

Condensation reaction of pyrrole and a bis-styryl derivative containing the 2,3-dicyanopyrazine moiety has allowed Jaung to synthesize pyrazine-linked porphyrins 32 (Scheme 17) [39]. These systems with a strong ICT revealed specific spectral properties such as emission of red fluorescence with a large Stokes Shift (over 7300 cm\(^{-1}\)). The protonation/deprotonation were shown to affect the spectral properties of the compounds.
Starting from the 2,3-dicyanopyrazine derivative 33, Hill and coworkers have described a tetrapyrazinoporphyrinate 34 substituted at its periphery with eight antioxidant 3,5-di-t-butyl-4-hydroxyphenyl groups which behave as a turn-on fluorescent sensor for fluoride anions (Scheme 18) [40].
Scheme 18. Structure and photophysical data of compounds 33 and 34.

Two series of new stable V-shaped push-pull chromophores 35 with two dimethylamino as the donor, a pyrazine-2,3-dicarbonitrile moiety as the acceptor and with systematically extended and varied π-linkers were reported by Burês et al. (Scheme 19) [41].

Scheme 19. Structure and photophysical data of compounds 35.
The nature and the length of π-linkers were investigated and the UV/Vis spectra, electrochemical data and 2nd order nonlinear optical (NLO) properties of these CT chromophores were studied. Compounds 35b with an additional triple bound to separate the π-linker from the pyrazine-2,3-dicarbonitrile moiety, are the most planar and exhibit the best D-A conjugation and the best NLO properties ($\beta_{av} = 3.1$ pm $V^{-1}$).

2.4. **Arylvinyl and arylethynylpyrazines**

Synthesis, absorbance and fluorescence properties of the 2-(4′-hydroxystyryl)pyrazine 36a was reported (Scheme 20) [42]. The spectral data of 36a are better than those of the pyridine analogous and have exhibited a strong dependence on solvent polarity and pH. Recently, other 2-(4′aminostyryl)pyrazines 36b and 36c were synthesized. Their optical absorption and emission properties have highlighted strong emission in dichloromethane ($\lambda_{em} = 511$ and 532 nm respectively) with high Stokes shift (6137 and 6534 cm$^{-1}$), they have also exhibited an important positive emission solvatochromism and presented halochromism properties [43]. The second order NLO properties of compound 36b were also reported and compared with those of other diazine derivatives. With a value of $\mu\beta = 220$ 10$^{-48}$ esu, the pyrazine derivative 36b exhibits a better value than the pyridazine derivative but a lower value than the pyrimidine derivative.

![Scheme 20. Structure and photophysical data of compounds 36.](image-url)
Vinylpyrazine triphenylamine derivative 37 and its dimethylated salt 38 (Scheme 21) were described by Aranda and coworkers [44]. The neutral compound 37 revealed strong fluorescence in dichloromethane solution ($\lambda_{em} = 569$ nm, $\Phi_F = 0.94$), whereas the dimethylated salt 38 is non-luminescent. Nevertheless, this last compound exhibits a strong selective interaction for duplex DNA.

![Scheme 21. Structure and photophysical data of compounds 37 and 38.](image)

Linear and angular distyrylpyrazines 39 and 40 with a donor-acceptor-donor electronic structure were synthesized and their fluorescence studied by Schmitt et al (Scheme 22) [45]. The materials display a strong solvatochromism of the emission that is reflected by large red shifts of their fluorescence emission maxima on increasing the solvent polarity. This behavior suggests a highly polar emitting state, which is characteristic of compounds that undergo an internal charge transfer upon excitation. Under acidic conditions, the UV-vis spectra are altered, and the fluorescence intensity of the neutral compound vanishes. These molecules can be used as colorimetric and luminescence polarity and pH sensors.
Electrooptical and theoretical studies of various oligophenylenevinylene 41-43 with a pyrazine central core were carried out (Scheme 23) [46]. The dipole moments of these quadrupolar dyes in the ground state are not equal zero, which means that one of the functional end groups of these molecules is not on the axis or on the plane with the central part of the molecule. The localized excitation effect causes a large change of the dipole moments of quadrupolar molecules upon excitation to the Franck–Condon excited state. Due to an efficient ICT, the authors claimed that these pyrazine derivatives must have significant non-linear optical properties.
Other divinylpyrazine derivative 44 and 45 were described by Al-Hazmy et al (Scheme 24) [47]. The compound 44 with $\lambda_{\text{em}} = 463$ nm in DMF acts as a laser dye upon pumping with nitrogen laser ($\lambda_{\text{ex}} = 337$ nm).

The cross-shaped chromophore 46 with four arms constituted by a phenyl group substituted by a donor and linked to the pyrazine core through a vinyl bridge were synthesized and compared with its linear analogue 47 with only two branches (Scheme 25) [48]. Their one-photon and two-photon absorption (TPA) properties were investigated. Compounds 46 and 47 are fluorescent respectively at 563 nm ($\Phi_F = 0.67$) and 518 nm ($\Phi_F = 0.77$). The TPA
spectrum in toluene of 46 is quite similar to that of the two-branch analogue 47 ($\delta_{\max} = 1250$ GM, $\lambda_{\max} = 790$ nm). The spectral features observed for these chromophores suggest that electronic coupling between the branches is effective but does not lead to significant enhancement of the two-photon cross section when the branches extend is in more than one dimension. In particular, the type of coupling effective in the four-branch compound 46 should result in a subadditivity of the two-photon cross section of 47.

![Scheme 25. Structure and photophysical data of compounds 46 and 47.](image)

Detert et al. have described di($p$-aminostyryl)pyrazines 48 with bulky substituents on the nitrogen of external amino groups and in the adjacent positions (Scheme 26) [49]. Steric congestion around the amino groups modulates the ICT in these fluorophores because the orbital overlap between nitrogen and $\pi$-system is modulated by the steric hindrance. Strong solvatochromism of the fluorescence and huge Stokes shifts results from amplified donor–acceptor interaction in the excited state. Protonation occurs at the terminal amino groups first, followed by protonation of the central pyrazine only in very strongly acidic media. With
increasing strength of acid, absorption and emission spectra are first shifted to the blue followed by a red shift.


Synthesis and fluorescent properties of various bis(arylvinyl)pyrazines were reported by Schmidt et al. (Scheme 27) [50]. These compounds were tested as fluorescent probes for in vitro and in vivo detection of AD-associated protein deposits in human brain tissue by fluorescence microscopy.

Scheme 27. Structure and photophysical data of compounds 49.

A series of pyrazine derivatives was reported by Collette et al, where the number and substitution pattern of p-dimethylaminostyryl branches on the pyrazine core were systematically studied (Scheme 28) [51]. These fluorophores were designed to exhibit large changes in emission in response to changes in solvent composition or addition of various analyte species. These molecules shared the structural and electronic features common to quadupolar two-photon chromophores. Calculations of their second hyperpolarizabilities
(γ(−ω;ω,−ω,ω)) and comparison to known two-photon molecules showed that these molecules were expected to be good two-photon active molecules.

Scheme 28. Structure of compounds 36b, 49a and 50–53.

A four-branched quaternary ammonium pyrazine 54 (TASPI) was reported by Yan et al. [52]. This compound can be used for selective thrombin detection. In this detection system, the fluorescence of compound is almost eliminated by the DNA aptamer TBA (turn-off). However, in the presence of thrombin, it specifically binds to TBA by folding unrestricted TBA into an anti-parallel G-quadruplex structure and then releasing the pyrazine derivative, resulting in fluorescence recovery (turn-on) (Scheme 29).
A fluorescent sensor 55 containing a pyrazine central core and bis(2-pyridylmethyl)amine groups as a binding moiety for Pb²⁺ was developed (Scheme 30) [53]. Compound 55 shows selective response to Pb²⁺ over other metal ions in pH 7.0 HEPES buffer solution. The fluorescence intensity enhancement was ascribed to the complex formation between Pb²⁺ and 55 which blocked the photo-induced electron transfer process.

Wu and coworkers have explored the nature of binding interaction of a fluorescent pyrazine-Zn probe 56 with calf thymus deoxyribonucleic acid (ct-DNA) (Scheme 31) [54]. Absorption titration of DNA with 56 was performed by fluorescence polarization measurements. All
results showed that the interaction mode between the complex Zn-56 and the (ct-DNA) was electrostatic interaction.

Scheme 31. Structure and photophysical data of compound 56.

The synthesis of various push–pull molecules with a central pyrazine unit connected to a hexatriene chain terminated by various 4-substituted phenyl groups were reported (Scheme 32) [55]. These push–pull compounds 57-59 have interesting light-emitting properties ($\lambda_{em}$ ranging from 536 to 780 nm with fluorescence quantum yield up to 0.20 in chloroform) and high Stokes shifts. Compounds 57a and 57b were tested for their 2nd order NLO properties and promising results were observed ($\mu\beta = 1048 \times 10^{-48}$ esu) for compound 57b.
The synthesis of a wide range of other rod-like conjugated molecules 60-64 was also described. These compounds incorporate a pyrazine or a bipyrazine core connected to electron acceptor (A) or donor (D) groups through π-conjugated linkers as transmitters for the internal charge transfer (Scheme 33) [56]. Generally, these derivatives exhibit fluorescence in the red region of the spectra. Incorporation of a double bond or a hexatriene chain as linker and a bipyrazine unit as an electron-withdrawing central core improves the spectroscopic properties.
A series of 2,5-di(aryleneethynyl)pyrazine derivatives 65 was synthesized by Zhao et al (Scheme 34) [57]. The structure, electrochemical and photophysical properties of derivative 65a have been compared with those of di(phenylethynyl)benzene 66. The presence of the pyrazine ring leads to a significant enhancement of electron-accepting properties, as revealed by cyclic voltammetry data and was confirmed by quantum chemical calculations. Experiments have established the potential for compound 65b to act as an electron-transporting material as a blend with MEH-PPV in single layer OLEDs.
2.5. **Other pyrazine structures**

Phenylene–2,5-dimethylpyrazinyl co-oligomers 67, 68 and the dipyridylpyrazine derivative 69 were synthesized by Türksoy *et al* (Scheme 35) [58]. The absorption spectra in ethanol show the lowest energy band at wavelengths characteristic of twisted oligoaryl structures with a dihedral angle $\alpha$ determined by X-Ray crystallography. Blue electroluminescence, $\lambda_{\text{max}}$ 444 nm, is observed for the device structure ITO/PEDOT/68/Ca with no long-wavelength emission from $\pi$-aggregates or exciton states.
Fugisawa et al have reported the complexation of 2,3,5,6-tetra(2'-pyridyl)pyrazine (tppz) 70 and 1-octadecanol with Eu$^{3+}$ ions through formation of luminescent Langmuir films at the air/liquid interface (Scheme 36) [59].

Saito and coworkers have reported that 2,5-bis(benzimidazol-2-yl)pyrazine (BBPIP) 71 exhibited extremely intensive blue-fluorescence with maximum emission at 444 nm and a fluorescence quantum yield of 0.90 in DMSO [60]. In order to improve the solubility, derivatives 72 with two alkyl chains at the N-1 and N-1’ positions of the two benzimidazole moieties were synthesized (Scheme 37) [61]. Compounds 72 exhibit similar blue fluorescence with a positive solvatochromism. Compound 72c (n = 3) was used as a microenvironment
polarity probe to indicate the variation in polarity around the backbone of the temperature-sensitive poly(N-isopropylacrylamide) by measuring the spectral change caused by the thermal phase transition of the polymer.

Various 5,6-bisarylvinyl-3-pyrazine-1,2,4-triazine derivatives 73 were synthesized by Thirumurugan et al and have highlighted good sensor property with Fe(III) ions even in micro level concentrations (Scheme 38) [62].

New fluorescent sensors for Zn$^{2+}$ utilizing fluorescein as a reporting group and including pyridine moieties ZP 74 were first reported (Scheme 38)[63]. More recently, substitution of a
pyridine ring by a pyrazine one at each dipicolylamine (DPA) unit led to new ditopic fluorescent sensors ZPP 75 (Scheme 39) [64].

Scheme 39. Structure and photophysical data of compounds 74 and 75.

These sensors exhibit a novel two-step fluorescence response toward zinc binding that can be applied to quantify chelatable zinc in biological samples (Scheme 40). The authors claim that the advantages of incorporating pyrazine into the metal-binding units in this kind of sensor can be generally applied to detect zinc, and other metals such as mercury.

A novel series of fluorescence dyes based on pyrazine-boron complexes 76 bearing a β-iminoketone ligand were prepared from methylpyrazine and benzoate derivatives (Scheme
All synthesized complexes exhibited fluorescence in dichloromethane ($\lambda_{\text{max}}$: 472–604 nm) and in the solid state ($\lambda_{\text{max}}$: 496–624 nm). Unlike common fluorescent boron complexes such as BODIPY dyes which have generally low Stokes shifts (400–600 cm$^{-1}$, in most cases), these pyrazine-boron complexes exhibited large Stokes shifts (3690–4900 cm$^{-1}$). This difference could be explained by the flexibility of the scaffold of 76, owing to the molecular rotation of the aryl group.

The synthesis and luminescence of two iridium (III) pyrazine complexes 77 and 78 were investigated by Ge et al. (Scheme 42) [66]. Yellow OLEDs were obtained with these phosphorescent complexes. The iridium pyrazine complex 77 emits yellow light ($\lambda_{\text{max}}$ = 575 nm). Efficient OLEDs using the complex 77 as phosphorescent dopant were demonstrated.
Coe and coworkers have synthesized nonlinear optical (NLO) chromophores 79-81 with pyrazinyl-pyridinium electron acceptors complexing a known pro-ligand with electron-donating \{Ru^{II}(NH_3)_5\}^{2+} or trans-{Ru^{II}(NH_3)_4(py)}^{2+} (py = pyridine) centers (Scheme 43) [67]. These cationic complexes were characterized as their PF_6 salts. Molecular first hyperpolarizability $\beta$ were determined by using hyper-Rayleigh scattering (HRS) with a 1064 nm laser exhibiting relatively large $\beta$ values. Depolarization measurements confirm the strongly 2D nature of the NLO responses for the symmetric complexes. The $\beta_0$ value increases on moving from 79 to bimetallic species 80.

\[
\begin{align*}
79a (\text{Ru}) &= \text{Ru}^{II}(\text{NH}_3)_5 \\
79b (\text{Ru}) &= \text{trans-Ru}^{II}(\text{NH}_3)_4(\text{py}) \\
80a (\text{Ru}) &= \text{Ru}^{II}(\text{NH}_3)_5 \\
80b (\text{Ru}) &= \text{trans-Ru}^{II}(\text{NH}_3)_4(\text{py}) \\
81a (\text{Ru}) &= \text{Ru}^{II}(\text{NH}_3)_5 \\
81b (\text{Ru}) &= \text{trans-Ru}^{II}(\text{NH}_3)_4(\text{py})
\end{align*}
\]

$\lambda_{\text{abs}} = 665 - 713$ nm in CH_2Cl_2

Scheme 43. Structure and photophysical data of compounds 79–81.

Synthesis, electronic properties, and second-order nonlinear optical (NLO) response of asymmetric heteronuclear push-pull bimetallic complexes were reported by Pizzotti et al. [68]. The pyrazine moiety was used as polarizable linker, connecting the “W(CO)_5” fragment
(acting as donor group) and “cis-Rh(CO)2Cl”, “cis-Re(CO)4Cl”, and BF3 fragments (acting as acceptor groups) leading to structures 82-86 (Scheme 44). In this case, the asymmetrical pyrazine bimetallic complexes can be considered as organometallic counterparts of classical push-pull aromatic chromophores. These derivatives exhibit higher NLO response (assessed by EFISH technique and solvatochromic studies) than the related push-pull benzenic chromophores, but it is strongly dependent as sign and absolute value on the electronic structure of the pull inorganic and in particular organometallic group. So, an opposite sign of the response is observed when “cis-Rh(CO)2Cl” (86) is used as acceptor group.

![Scheme 44. Structure and photophysical data of compounds 82–86.](image)

3. **Quinoxalines derivatives**

3.1. **Arylvinylquinoxalines**

The push-pull molecule PQX 87 with a quinoxaline as π-deficient moiety, linked to a pyrrole ring through an ethenyl linker was designed by Kudo and coworkers (Scheme 45) [69]. This compound, soluble in many common solvents, exhibits a full-color solvatochromic
fluorescence ($\lambda_{em} = 430-607$ nm) and was described as a promising fluorescent sensor for binding sites in proteins or other host molecules, especially in aqueous solution.

Some of us have also described a series of arylvinylquinoxaline compounds (Scheme 46) [43]. In addition to fluorescence solvatochromism and halochromism, these structures exhibit second order NLO properties assessed by EFISH measurements. With a value of $\mu\beta = 300 \times 10^{-48}$ esu, the quinoxaline derivative 88d exhibits a better value than the pyrimidine, pyrazine and pyridazine derivative.

Other fluorescent arylvinylquinoxalines 89 were reported by Bachowska et al. and are described as pale blue luminescent structures (Scheme 47) [70].
A series of 2,3-bis(arylvinyl)quinoxaline 90 and 2,3-bis(arylvinyl)pyridopyrazine 91 derivatives have been synthesized by Thirumugan and coworkers (Scheme 48) [71]. Quinoxaline derivatives show two absorption maxima and three ones for the pyridopyrazines. All these compounds present good photophysical properties, stable fluorescence ($\lambda_{em} = 431 – 558$ nm) as well as very good fluorescence lifetimes. Moreover, the pyridopyrazine derivatives exhibit halochromism.

Various 6,7-bis-(3-methylbutoxyl)quinoxaline derivatives 92 (Scheme 49), with different electron-donating arylvinyl moieties were described and studied by Jaung [72] These
compounds are fluorescent ($\lambda_{em} = 470$-567 nm in CHCl$_3$/MeOH 10/1 mixture) with a red-shifted emission in acidic media.

A series of quinoxalines derivatives 93 with a 2,2',6',2''-terpyridine moiety in one arm have also been synthesized and studied (Scheme 50) [73]. The absorption and fluorescence maximum of these compounds were observed at 398–443 nm and 484–586 nm, respectively. These compounds were used as fluorescence probes for transition metal ions such as Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Fe$^{3+}$.
3.2. **Azomethine Quinoxalines**

The synthesis of a new Schiff base 94, derived from 3-hydroxyquinoxaline-2-carboxaldehyde and 2,3-diaminomaleonitrile was reported by Arun et al. and studied as a fluorescent bisazomethine dye (Scheme 51) [74]. Like other 2-hydroxyquinoxaline derivatives, it exhibits prototropic tautomerism. Compound 94 presents positive absorption and emission solvatochromism and a large Stokes shift, making it as a suitable candidate for application as fluorescent and charge transport dyes.

![Diagram of tautomer equilibrium of compound 94.](image)

Another Schiff base, the 3-hydroxyquinoxaline-2-carboxalidine-4-aminoantipyrine 95, was prepared by the same team (Scheme 52) [75]. Spectroscopic studies have revealed that 95 exists predominantly in the amide tautomeric form and exhibits both absorption and fluorescence solvatochromism with a large Stokes shift. Otherwise, the values of third-order non-linear absorption coefficient: $\beta$ ($1.48 \times 10^{-6}$ cmW$^{-1}$), imaginary part of the third-order non-linear optical susceptibility: $\text{Im } \chi^{(3)}$ ($3.36 \times 10^{-10}$ esu) and its optical limiting threshold (340 MW cm$^{-2}$), make that 95 could be used for applications in photonic age.
If substitution of the quinoxaline core with arylinyl or arylimine moities gave generally good fluorescent compounds, other quinoxaline structures bearing aryl moieties with different electronic characters have also intensively reported.

### 3.3. Arylquinoxalines

A series of dipolar quinoxaline derivatives substituted with electron-rich terminal N-hexylcarbazole or triphenylamine moieties **96-98** were synthesized and fully characterized (Scheme 53) [76]. As expected, these compounds exhibit excellent blue-green fluorescence ($\lambda_{em} = 493–560$ nm) and are presented as potential emissive and electron-transport materials for organic light-emitting diodes.
Cao et al. have developed ethoxyphenyl and triphenylamine-modified quinoxaline 99 and benzoquinoxaline 100 (Scheme 54) [77]. Their linear spectroscopy and two-photon absorption properties were investigated. The quinoxaline-type compounds 99 exhibited significantly higher fluorescence quantum yields than the benzoquinoxalines-type ones 100. The triphenylamine species presented 2PA cross sections values ($\delta_{2PA}$) around 160 GM in the laser light wavelength range of 780–820 nm.

Scheme 54. Structure and photophysical data of compounds 99 and 100.
A series of dipolar compounds featuring quinoxaline 101 or pyridopyrazine 102 cores as acceptors and various triarylamines as donors were synthesized by Thomas et al. (Scheme 55) [78]. The emission colors of these compounds can be easily tuned from bluish green to orange by independent suitable modifications of the amine or quinoxaline units.

More recently, the same authors have synthesized a series of electroluminescent materials 103 comprising quinoxaline, triarylamine, and bulky and rigid aromatic fluorophores such as carbazole, pyrene, and fluorene (Scheme 56) [79]. These products exhibit a strong green fluorescence in film and devices were fabricated using these materials as hole-transporters and emitters with intense light emission.
A series of multi-branched fluorophores with a quinoxaline or with a di- or a tetraquinoxalineethylene as the core and diphenylaminofluorene units incorporated at the peripheral positions was synthesized by Lin and coworkers (Scheme 57) [80]. These derivatives (104-106) possess good fluorescence quantum yields ($\Phi_F > 0.5$ in THF and toluene) and a strong solvent effect on emission and life-time behaviors. These compounds exhibit two-photon activities and effective optical power limiting properties in the near-IR region under the irradiation of nanosecond laser pulses.

Scheme 57. Structure and photophysical data of compounds 104–106.

The synthesis and photophysical properties of a series of bipolar compounds 107, 108 including a quinoxaline unit and substituted triarylamine groups were reported by Burrows
and coworkers (Scheme 58) [81]. Incorporation of the bulky dehydroabietic methyl ester group in the scaffold of compounds 108 was achieved to improve solubility and to prevent crystallization, without affecting their photophysical behaviors. These compounds exhibited relatively strong fluorescence, their emission maximum are dependent from the nature of the substituents present on the stilbene group. These molecules were evaluated as electroluminescent materials: the devices prepared with these materials and with magnesium cathodes show efficiencies up to 0.03 cd/A. This result is about one order of magnitude higher than the efficiency obtained with the related diphenylstilbeneamines [82].

Scheme 58. Structure and photophysical data of compounds 107 and 108.

The photophysical properties of two polyphenylphenyl compounds CPQ 109 and MPQ 110 with a quinoxaline core were investigated in aqueous solutions (Scheme 59) [83]. For these compounds, the abnormal photoluminescent phenomena observed in THF-water mixtures could be explained by combinational effects of intramolecular rotation, intermolecular hydrogen bonds, solvent viscosity, hydration and formation of nanoparticles. Based on detection of the fluorescence observed during formation of nanoparticles, when CPQ or MPQ
and nucleobases are present in aqueous medium, an application as nucleobase sensing was reported with a sensitivity of guanine > adenine > thymine ≥ cytosine.

Scheme 59. Structure of compounds 109 and 110.

Various 5,8-dithienyl quinoxaline derivatives 111 substituted on the thienyl ring were described by Hemgesberg and coworkers (Scheme 60) [84]. Compound 111a is fluorescent with high Stokes shift (λ_{abs} = 273 nm and λ_{em} = 542 nm) and could be used to access fluorescent sol-gel precursors.

Scheme 60. Structure and photophysical data of compounds 111.

The 2,3-dipyrrrole-2’-ylquinoxaline (DPQ) 112 [85] and its derivatives with substituents either on the pyrrole ring 113-115 or on the phenyl ring of the quinoxaline moiety, leading to extended chromophores 116-119 (Scheme 61), are described as sensors for inorganic anions.
such as fluoride and pyrophosphate [86]. The quinoxaline derivatives bearing dipyrromethane or tripyrromethane substituents 114 and 115 act as better anion receptors than the unsubstituted dipyrrolylquinoxaline (DPQ) 111 from which they are derived. The extension of the conjugation provides an enhancement of the fluorescence affinity and an increased affinity for inorganic anions with a stronger selectivity.

Scheme 61. Structure of compounds 112–119.

Quinoxaline-bridged porphyrinoids 120, macrocycles containing dipyrrolylquinoxaline (DPQ) subunits, were also reported with the same sensing applications as well as encapsulation of CHCl₃ in solid state (Scheme 62) [87].
Wang and coworkers have described a series of dipyrroloquinoloxaline-bridged Schiff bases 121 as fluorescent sensors for Hg$^{2+}$ ion [88]. More recently, other Schiff bases 122, synthesized and studied by Hu et al. were reported as fluorescent ON/OFF switching system (Scheme 63) [89]. These compounds displayed good sensitivity toward transition metal ions with Cd(II), Zn(II) turn-on and Cu(II), Hg(II) turn-off in fluorescence.

3.4. **Micellaneous substituted Quinoxalines**

Synthesis of the 2-(quinoxalin-2-yl)-2,3-dihydro-1H-perimidine 123 was performed by Varsha and coworkers (Scheme 64) [90]. The fluorescent compound 123 ($\lambda_{em} = 386$ nm, $\Phi_F = 0.81$ in ethyl acetate), exhibits a negative fluorosolvatochromism in polar solvents, and presents interesting antibacterial activities.
Katoh and coworkers have described the strong fluorescence of the 2,3-dimorpholino-6-aminoquinoxaline (Qx) 124 [91]. Two other fluorescent monomers 125 and 126 incorporating the quinoxaline skeleton Qx in their scaffold were described by the same group (Scheme 65) [92]. Compounds 125 and 126 showed intense solvatochromism in their fluorescence. Thermo-responsive copolymers of N-isopropylacrylamide (NIPAM) and a small amount of these fluorescent monomers were synthesized and their fluorescence properties investigated. Contrary to Qx 124, both compounds 125 and 126 having double bond on their structure can thus sense and report microenvironmental changes in thermo-responsive polymers and could be applicable as new intramolecular fluorescent probes.

Touzani and coworkers have described two 2,3-functionalized quinoxalines 127 (Scheme 66) [93]. These compounds exist as the keto-enamine form in both solution and solid state. These
structures are slightly fluorescent (λ_{em} = 488-523 nm, Φ_F = 0.06-0.14 in dichloromethane solution) and are presented as interesting ligand for metallo-organic NLO-phores.

![Scheme 66. Structure and photophysical data of compounds 127.](image)

With the aim of forming a pre-organized molecular cleft, the quinoxaline derivative 128, possessing a 2,6-pyridyl-based amidothiourea moiety, was developed by Duke et al. and was studied as a fluorescent anion sensor (Scheme 67) [94]. The anion-sensing occurs most likely via deprotonation of the amidothiourea receptor, adjacent to the quinoxaline fluorophore. In this case, significant changes are observed with a red-shift in the absorption spectra, and in the emission spectra with a significative quench due to interaction of 128 with anions such as AcO⁻ and OH⁻.

![Scheme 67. Structure and photophysical data of compound 128.](image)
3.5. **Fused Quinoxalines**

Two quinoxaline derivatives reported by Benzeid *et al.* (Scheme 68) have proved their ability to stain amyloid fibers, such as aggregated lysozyme and Aβ(1-40)-peptide by a fluorescence “turn on” mechanism [95]. Thienoquinoxaline 129 allowed the detection of lysozyme and Aβ(1-40) fibers at λ = 555 and 532 nm, respectively, with excitation at λ = 450 nm. Styryl-quinoxaline 130 stained lysozyme and Aβ(1-40) fibers with fluorescence at λ = 579 and 567 nm, respectively, upon excitation at λ = 453 nm. The apparent Kₐ values for Aβ(1-40) fibers were 77 and 294 nM for 129 and 130, respectively. Due to their unique fluorescence properties compared to other dyes reported in the field, they can be considered as additional staining tools for the detection and studies of peptide/protein aggregation.

![Scheme 68. Structure and photophysical data of compounds 129 and 130.](image)

A series of 6H-indolo[2,3-b]quinoxaline compounds 131-136, containing triarylamines with aromatic units such as phenyl, naphthyl, pyrene, anthracene, or fluorene were synthesized by Thomas *et al.* (Scheme 69) [96].

For the derivatives 131-134, in which the amines were directly anchored on the 6H-indolo[2,3-b]quinoxaline nucleus, the absorption data are significantly influenced by the
nature of the diarylamine segment and they displayed green or yellow emission ($\lambda_{em} = 544$ – 586 nm, $\Phi_F = 0.01$–0.08). For the derivatives 135 and 136, with an insertion of a conjugating aromatic linker between the amine and the indoloquinoxaline unit, a hyperchromism and a bathochromic shift of the absorption values are observed, due to an extended conjugation.

Gemma and coworkers have studied a class of pyrroloquinoxaline and imidazoquinoxaline hydrazones 137 and 138 as fluorescent probes for $\text{A} \beta_{1-42}$ fibrils (Scheme 70) [97]. All these compounds were able to bind amyloid fibrils formed in vitro and some of them displayed an increase of their fluorescence upon binding, allowing the stain of amyloid structures. The
described pyrrolo(imidazo)quinoxalines could be useful for studying amyloid structures *in vitro*. Moreover, their experimentally proven ability to cross the blood–brain barrier in mouse opens the possibility of developing these compounds as potential amyloid imaging agents for *in vivo* applications.

![Scheme 70](image)

**Scheme 70.** Structure of compounds 137 and 138.

Diimidazo[1,2-a:2′,1′-c]quinoxalines 139 were described by Matsumoto *et al.* (Scheme 71) [98]. These derivatives exhibit blue fluorescence with high quantum yield ($\lambda_{em} = 415–454$ nm, $\Phi_F = 0.47-0.93$). They were also applied to organic light-emitting devices (OLED) as emitters, in which the diphenyl derivative emits a nearly pure blue light.

![Scheme 71](image)

**Scheme 71.** Structure and photophysical data of compounds 139.

A series of substituted 2-phenylbenzo[g]quinoxalines 140 with a rotatable para-substituted phenyl moiety were synthesized and used as fluorophore for viscosity-sensitive probes (Scheme 72) [99]. The fluorescence properties of these compounds were investigated in the media of the ethylene glycol–glycerol mixture with varied viscosity. Compounds bearing the
stronger electron-donating groups show more sensitive fluorescence response to viscosity, revealing their potential use in viscosity detection and the key role of the substituted groups. These compounds exhibit also solvatochromism and halochromism.

Several new 1H-pyrazolo[3,4-b]quinoxaline derivatives 141, 142 with N,N-dialkylamino as the electron-donating group were reported (Scheme 73) [100]. Their electroluminescence and photoluminescence were investigated. In solution, these compounds show emission at about 520–540 nm with a fluorescence quantum yield close to unity. EL devices fabricated, using these compounds as dopants, highlight green emission with efficiencies of 7.5–9.7 cd.A⁻¹ and a narrow bandwidth of 65–70 nm peaking at 530–545 nm.
A series of compounds based on the 8-halogeno-5,12-dihydroquinoxalino[2,3-b]quinoxaline skeleton 143, were synthesized and studied by Podsiadly and coworkers (Scheme 74) [101]. These new dyes emit blue light with fluorescence quantum yield ranging from 0.24 to 0.90. When combined with pyridinium or iodonium salts, these compounds may have practical applications as visible-light photo-initiators for free radical and/or cationic polymerization. Their chemical structure is determinant to use these compounds as photoinitiator. Their quantum yields of singlet oxygen generation $[\Phi(1{O}_2)]$ have been measured, in accordance with the “heavy atom effects” the much greater $[\Phi(1{O}_2)]$ values was determined for the 6-bromo-2,3-dichloroquinoxaline.

![Scheme 74. Structure and photophysical data of compounds 143.](image)

Bolligarla et al. have synthesized new acceptor–donor–acceptor (A–D–A) compounds 144, 145 incorporating the electron donor tetrathiafulvalene (TTF) as central unit, which is fused with acceptors such as quinoxaline and dipyrido[3,2-a:2’,3’-c]phenazine (dppz) moities (Scheme 75) [102]. These compounds exhibit good emission in visible region at room temperature with a large dependence on the polarity of the solvent, which indicates that the excited state is stabilized in more polar solvents due to the intramolecular charge transfer.
Another π-conjugated donor-acceptor based on tetrathiafulvalene (TTF) functionalized with quinoxaline was synthesized by Jia et al. (Scheme 76) [103]. Spectroscopic and electrochemical behaviors of compound 146 demonstrate that the donor (TTF) unit strongly interacts with the electron-accepting pyridine groups through the quinoxaline bridge giving weak fluorescence. The interaction of compound 146 with metallic ions induces a progressive decrease of its fluorescence.

4. Conclusion and outlooks

The research efforts in the field of synthesis and use of luminescent materials have strongly increased within the last few years. The considerable interest for these compounds is due to their wide range applications in various fields. They can be used as fluorescent sensors
(polarity, pH, metal cations, or more particularly to detect explosives), as stain for microscopy
and diagnostic in medicine, for lighting in organic light-emitting devices (OLEDs) and NLO
materials.

The research efforts in the field of pyrazine and quinoxaline luminescent molecules have
strongly increased during the past decade. Indeed, due to their π-deficient character, incorporation of a N-heterocycle such as pyrazine or quinoxaline in the backbone of luminescent molecules leads to significant modifications of the photophysical properties of π-conjugated materials. The electron-deficiency of the pyrazine or the quinoxaline ring can be used as a dipolar moiety, which favors the internal charge transfer. As largely illustrated in this review, this kind of molecules exhibits important fluorescence solvatochromism and good NLO properties. Quadrupolar (D-π-A-π-D) and octopolar structures with a pyrazine central core exhibit also 3rd order NLO properties such as two photon absorptions with high cross sections.

Moreover, presence of nitrogen atoms with lone electron pairs allows to the pyrazine and the quinoxaline rings to act as effective and stable complexing agents making of them good cation sensors. For the same reasons, pyrazine and quinoxaline derivatives can be protonated exhibiting halochromism, that has been illustrated by numerous examples given in this review. Specific interactions of some pyrazine compounds with particular forms of DNA and specific proteins lead to anticipate their use as promising tools for medical diagnosis of diseases such as cancer or Alzheimer disease.

Another aspect of the luminescence of pyrazine and quinoxaline is the electroluminescence properties leading to OLEDs. Some examples are details along the reviews.

This review emphasizes the great interest to incorporate pyrazine or quinoxaline moieties in π-extended conjugated systems, owing to their applications in various fields. The elaboration
of new efficient structures with such a target is always topical and constitutes an interesting challenge.


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