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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 Victoria* [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 π -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 π -conjugated pyrazine derivatives are described in the literature. The first method consists of the construction of the pyrazine ring by condensation reactions of α -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 π -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 π -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 π -conjugated materials [21]. This article is the last part of this series of

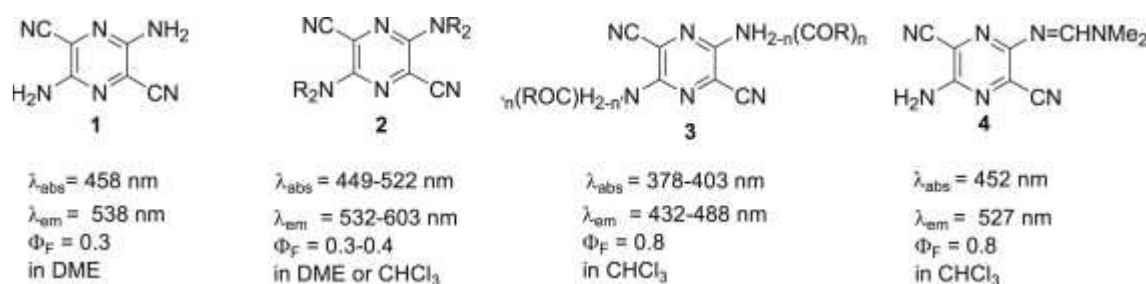
papers and has for aim to review the use of pyrazine and quinoxaline moieties in the synthesis of fluorescent materials. Only small molecules and oligomers will be described here, this review will not treat polymer materials. The first part of this review deals with pyrazine derivatives while the second 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.

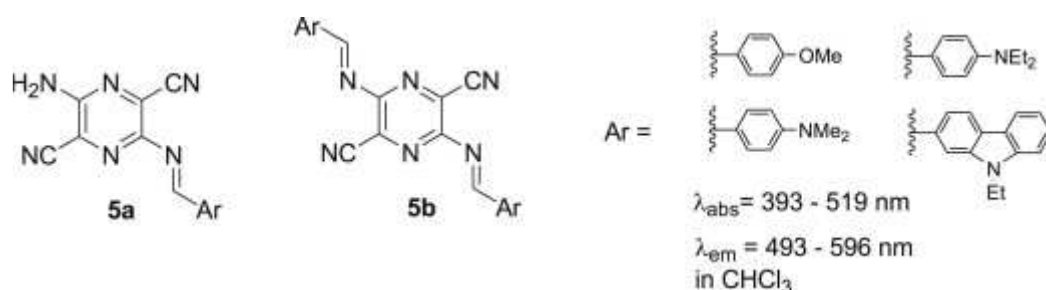
2.1. Diamino and dicyanopyrazines

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 $\lambda_{\text{abs}} = 449\text{--}522$ nm and a red fluorescence $\lambda_{\text{em}} = 532\text{--}603$ nm. On the contrary, acylation of the amino groups (compounds **3**) induces a hypsochromic shift of λ_{abs} (378–403 nm) and of λ_{em} (432–488 nm). It is noteworthy that the imine **4** has similar λ_{abs} (452 nm) and λ_{em} (527 nm) than **1** but a higher quantum yield ($\Phi_F = 0.8$) (Scheme 1).



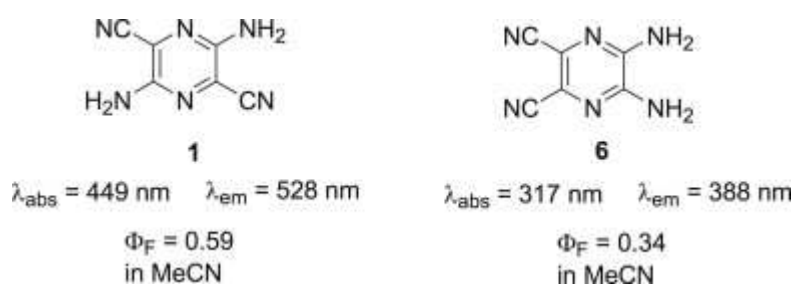
Scheme 1. Structure and photophysical data of compounds **1–4**.

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].



Scheme 2. Structure and photophysical data of compounds **5**.

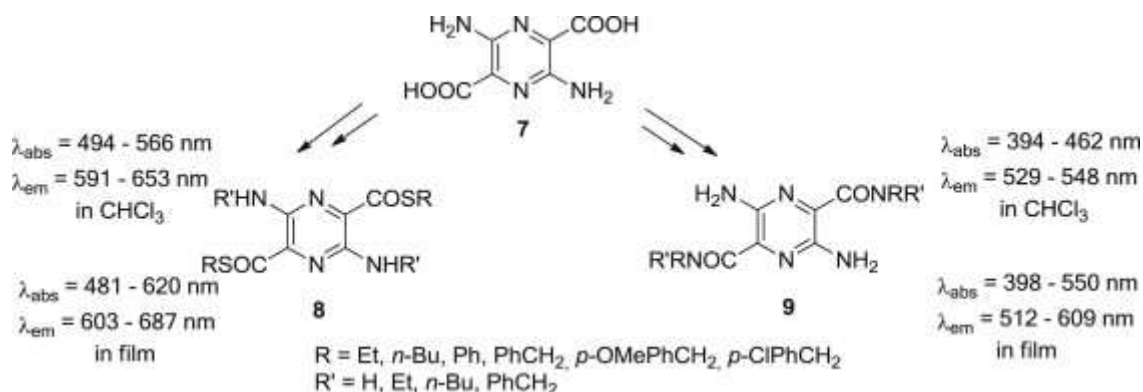
More recently a comparative study of the photophysical properties of the 2,5-diamino-3,6-dicyanopyrazine **1** with other diaminodicyanopyrazines was performed in acetonitrile by Angulo *et al* [24]. The compound **1** exhibits red shifted absorption and emission in comparison with those of **6**. These 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).



Scheme 3. Structure and photophysical data of compounds **1** and **6**.

2.2. Diamino and dicarboxypyrazine derivatives

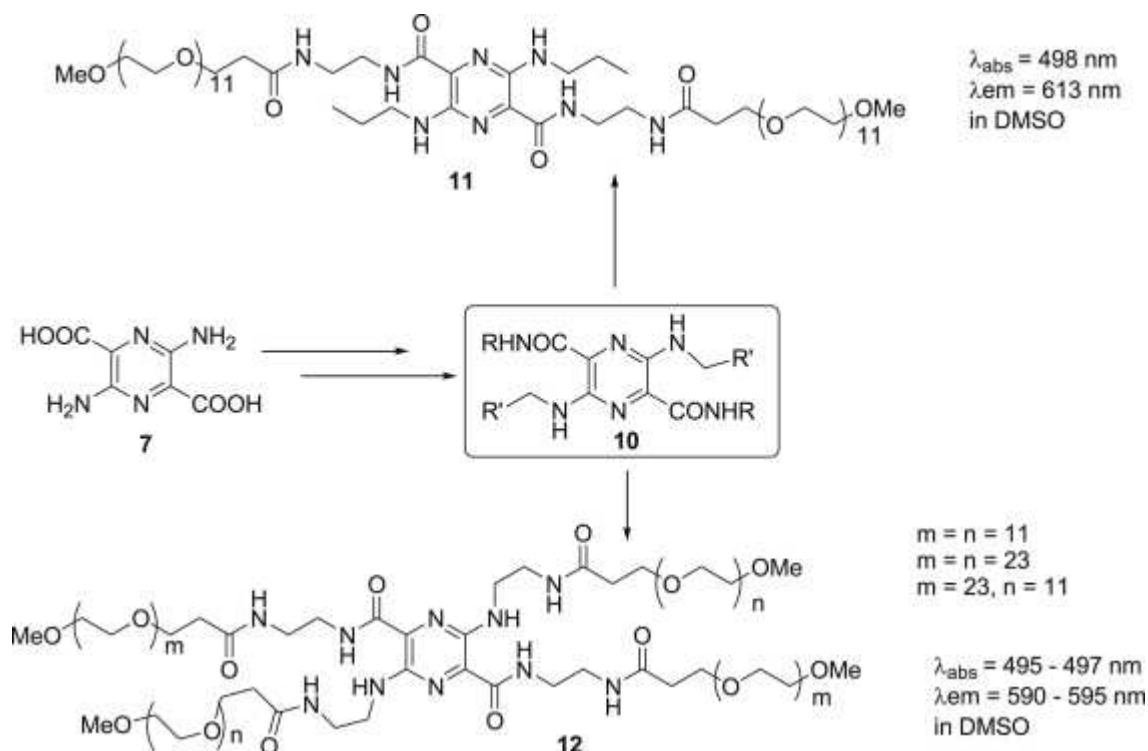
Using the 2,5-diamino-3,6-dicarboxypyrazine **7** as starting material, various thioester and carbamoyl derivatives **8** and **9** were synthesized and their photophysical properties established in CHCl_3 (Scheme 4) [25].



Scheme 4. Structure and photophysical data of compounds **7–9**.

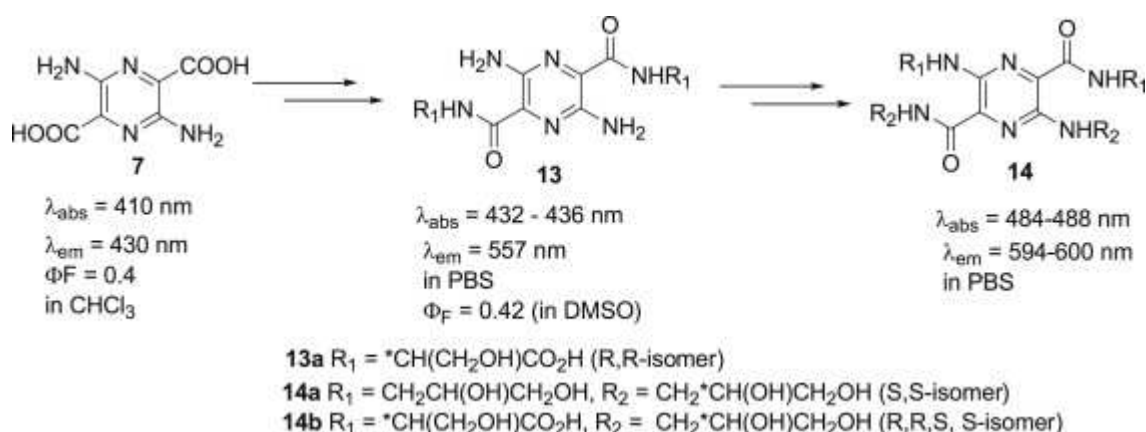
The solid state spectra of compounds **8** and **9** were evaluated with respect to their molecular staking. In the case of the 2,5-diamino-3,6-bis(butoxycarbonyl)pyrazine, the X-ray crystal analysis has shown space-filling intermolecular interactions of diaminopyrazines making possible the construction 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 ($\sim 50 \text{ nm}$) than their corresponding aminopyrazines and could found potential applications in medical diagnostic (Scheme 5).



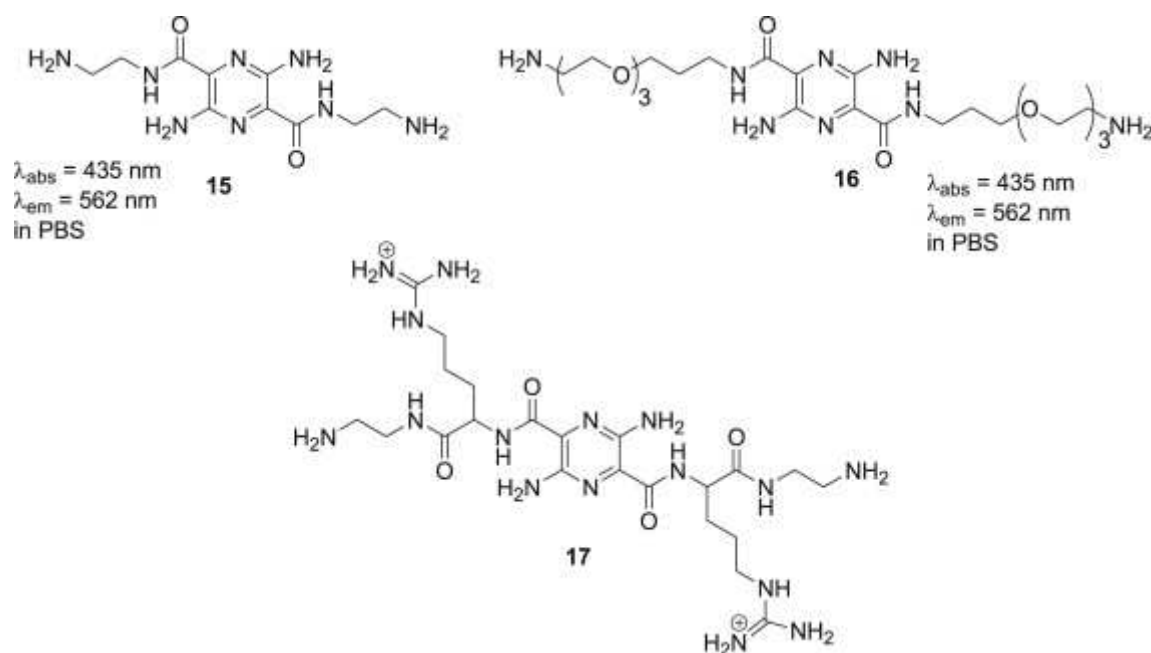
Scheme 5. Structure and photophysical data of compounds **10–12**.

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 λ_{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.



Scheme 6. Structure and photophysical data of compounds **7**, **13** and **14**.

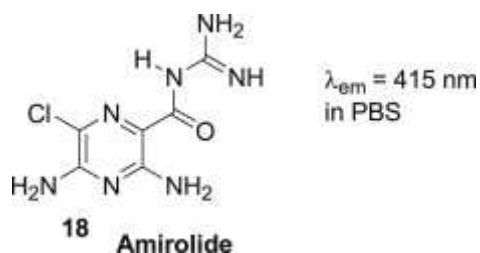
Chromophoric crosslinkers constituted by tetra-functionalized 3,6-diaminopyrazines **15–17** bearing a set of terminal aliphatic and anilino amine groups were recently synthesized (Scheme 7). With these molecules, Wooley *et al.*, have developed dual-emitting photonic nano-objects that can sense changes 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.

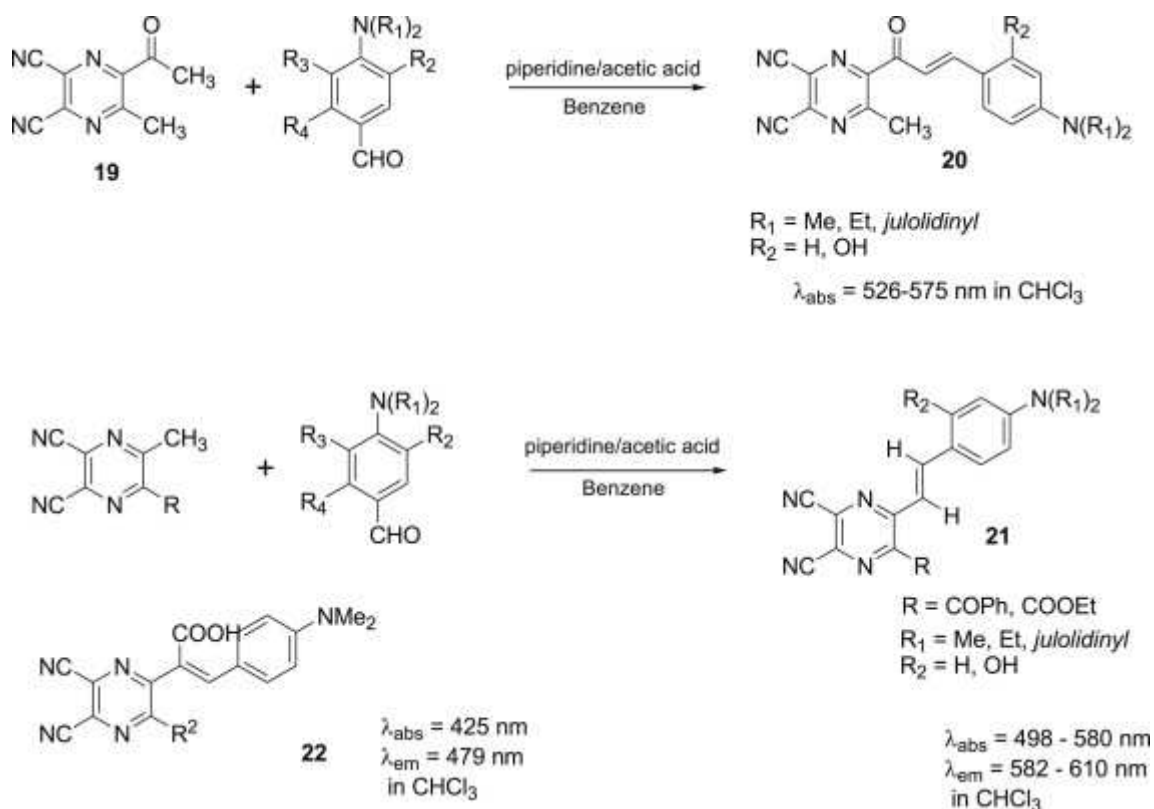
Teramae and coworkers have described the selective binding of Amiloride **18** (Scheme 8), a 2,6-diaminopyrazine derivative, to abasic (AP) site in RNA [29]. A dramatic increase of the fluorescence of amiloride at 415 nm was observed selectively in the presence of AP-RNA, making such a response applicable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



Scheme 8. Structure and photophysical data of compound **18**.

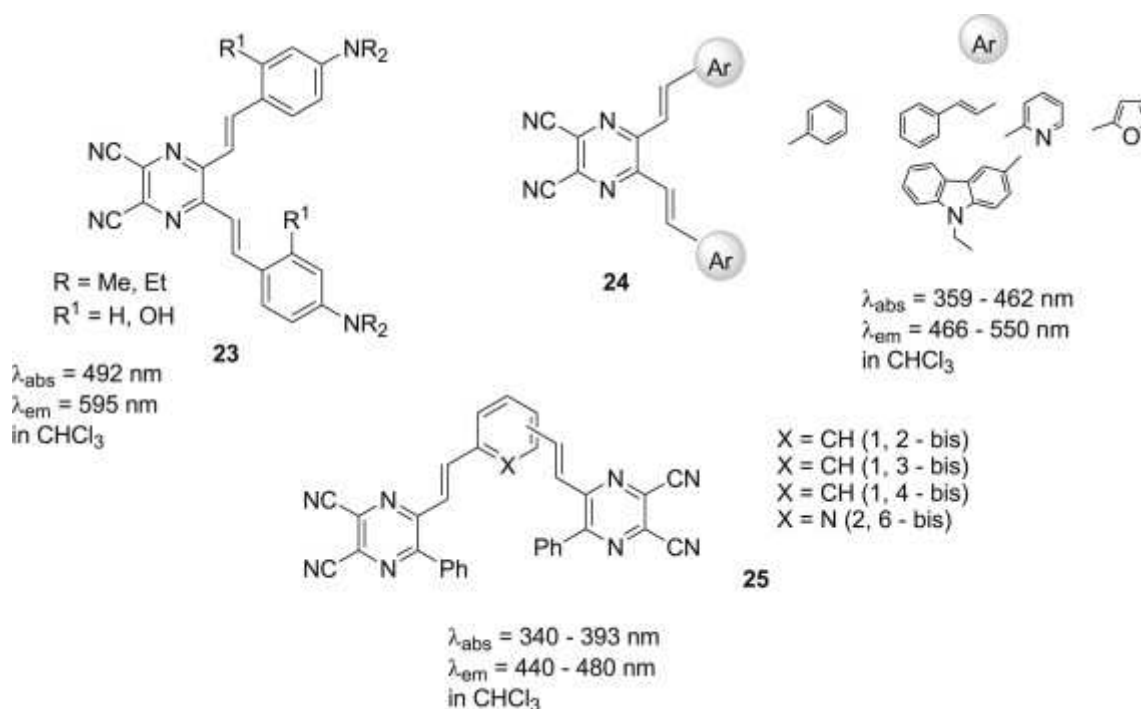
2.3. Arylvinyl and aryldicyanopyrazines

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 (λ_{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.



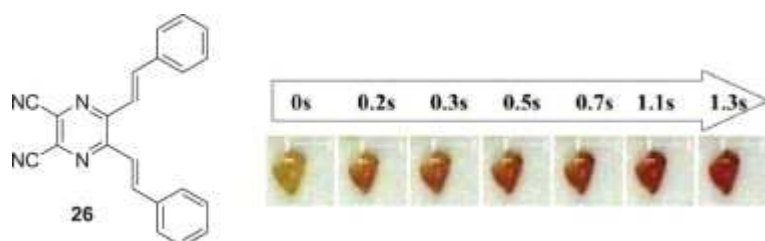
Scheme 9. Structure and photophysical data of compounds **19–22**.

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.



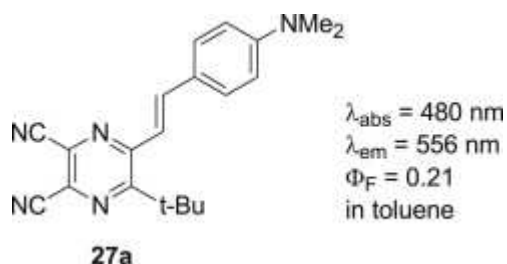
Scheme 10. Structure and photophysical data of compounds **23–25**.

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.



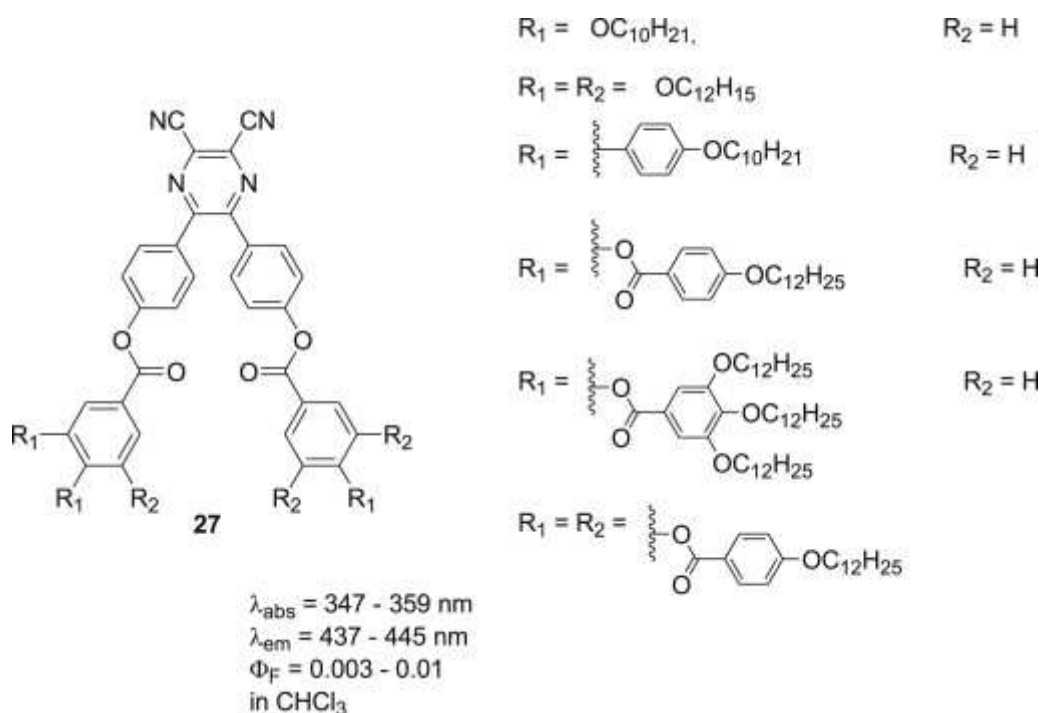
Scheme 11. Structure of compound **26** and color change of crystal via a thermal phase transition.

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.



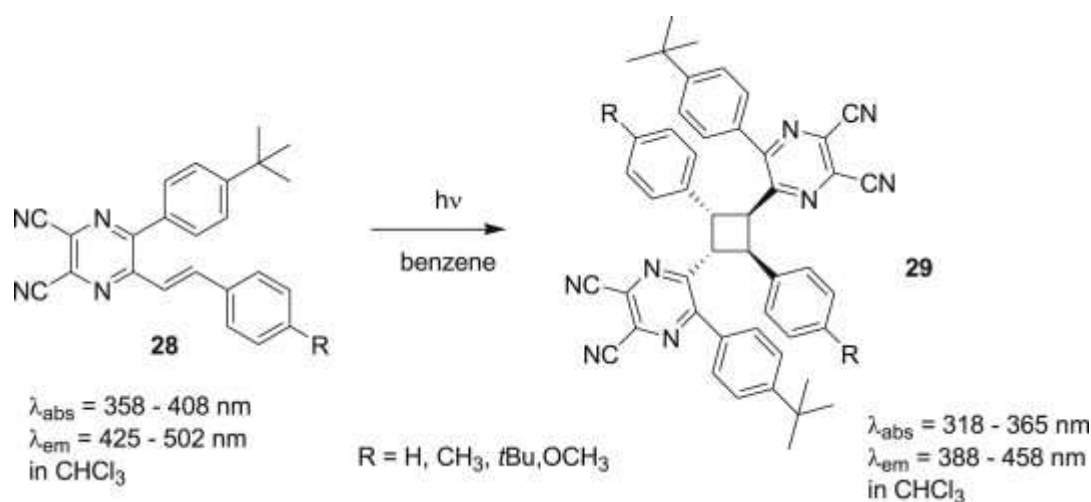
Scheme 12. Structure and photophysical data of compound **27a**.

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 (λ_{em} 437–445 nm) with low to moderate quantum fluorescence yields (Φ_F) from 0.003 to 0.1 and Stokes shifts of around 6000 cm^{-1} .



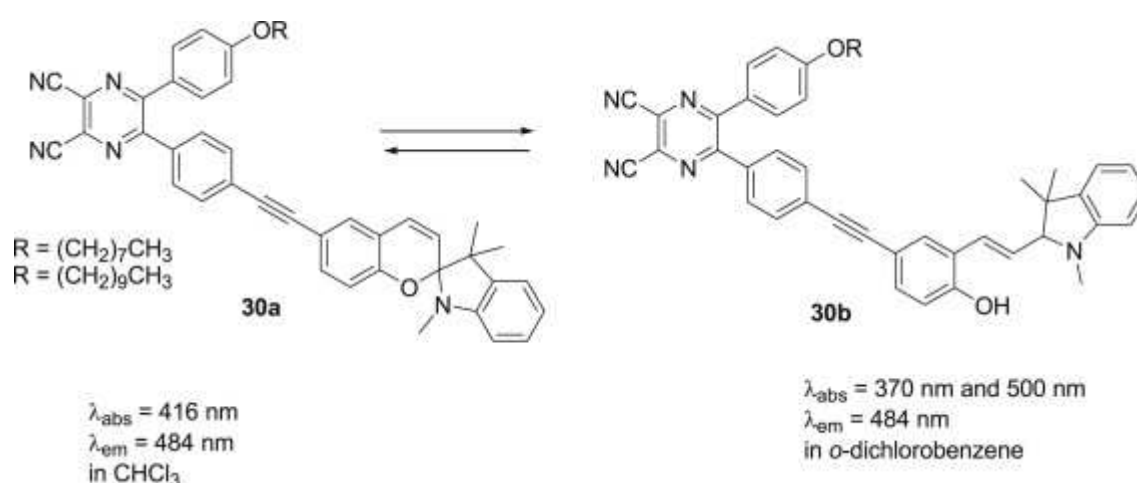
Scheme 13. Structure and photophysical data of compounds **27**.

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 $R = t\text{-Bu}$ in a thin film under irradiation became brighter and was blue shifted from 478 nm to 467 nm



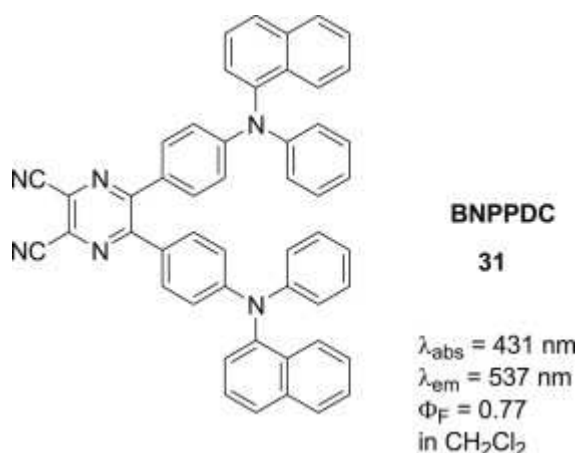
Scheme 14. Structure and photophysical data of compounds **28** and **29**.

Lee and coworkers have developed dicyanopyrazine dyes **30** containing spiropyran groups [37]. These compounds have emission at 484 nm in CHCl_3 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.



Scheme 15. Structure and photophysical data of compounds **30**.

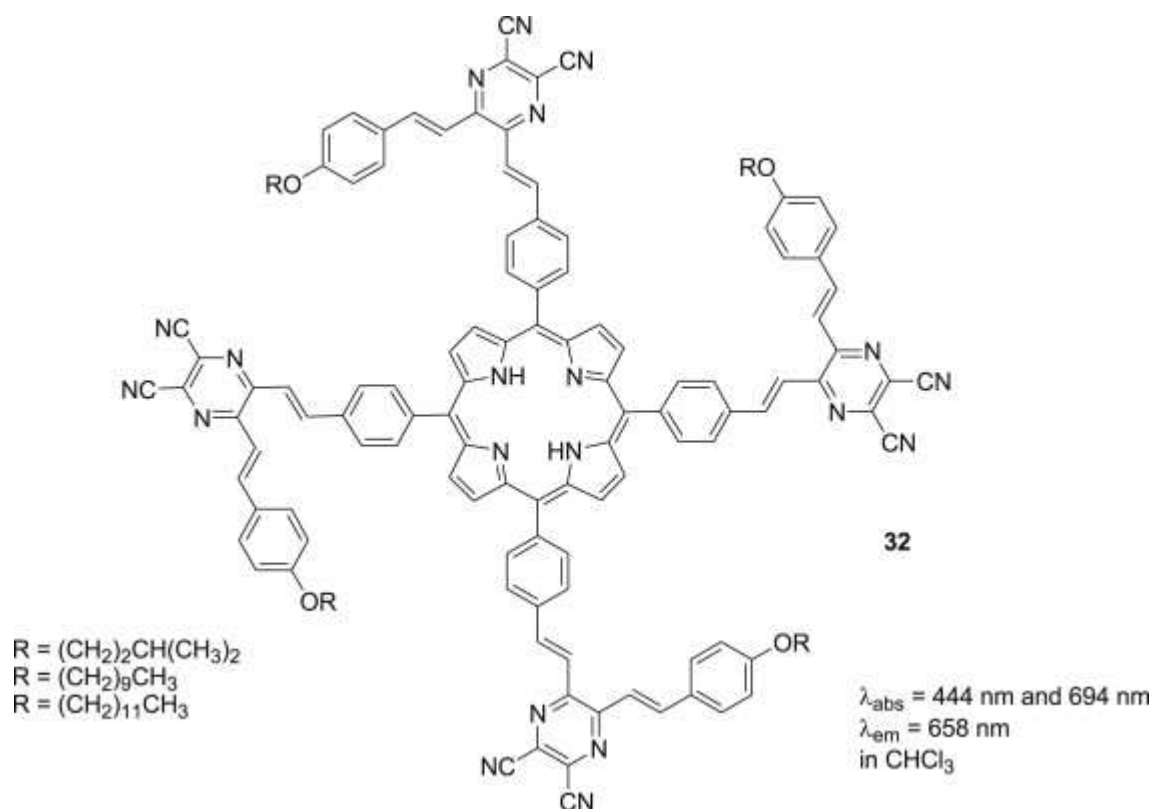
A compound with ICT properties: the 5,6-bis-[4-(naphthalene-1-yl-phenyl-amino)-phenyl]-pyrazine-2,3-dicarbonitrile **31** (BNPPC) was synthesized by Chew *et al* (Scheme 16) [38]



Scheme 16. Structure and photophysical data of compound **31**.

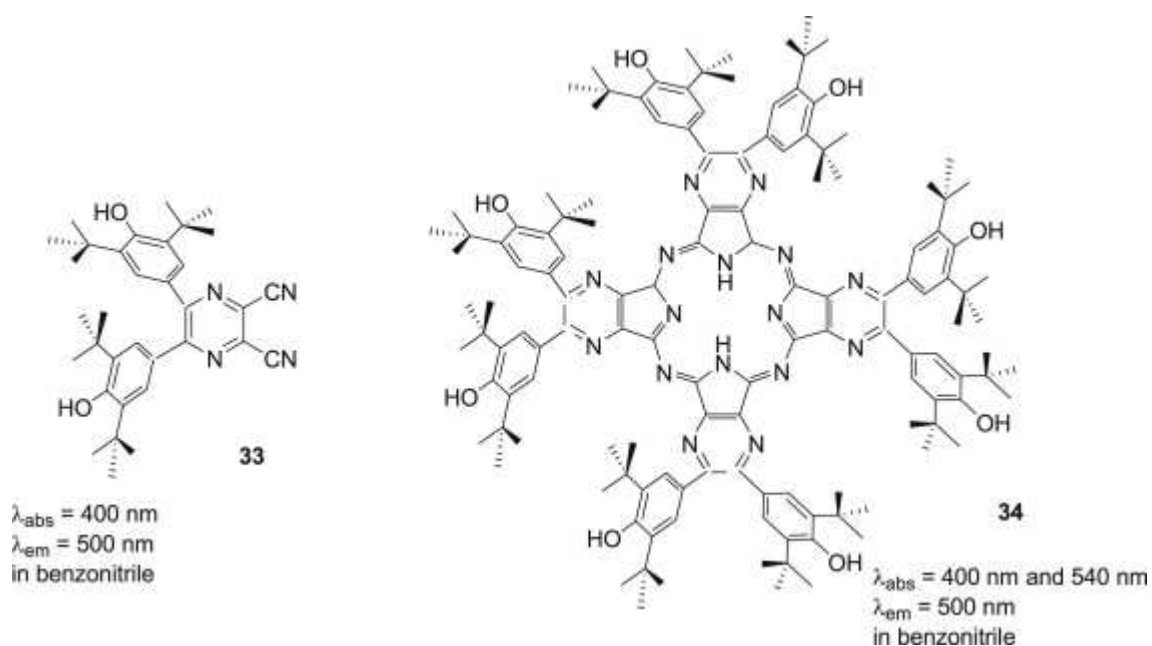
This compound was strongly fluorescent in non-polar and moderately polar solvents, as well as in thin solid film. The absorption and emission maxima shifted to longer wavelength with increasing solvent polarity. The fluorescence quantum yield also was also improved with increasing solvent polarity from 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.



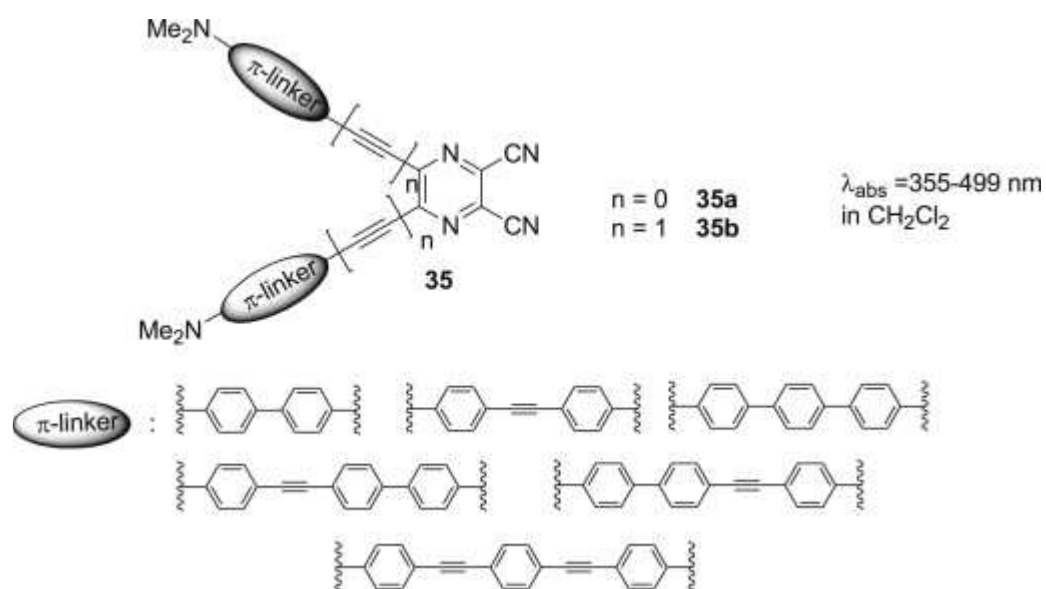
Scheme 17. Structure and photophysical data of compounds **32**.

Starting from the 2,3-dicyanopyrazine derivative **33**, Hill and coworkers have described a tetrapyrazinoporphyrazine **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 Burěš *et al.* (Scheme 19) [41].

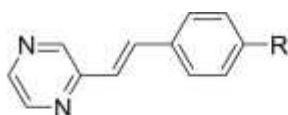


Scheme 19. Structure and photophysical data of compounds **35**.

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 bond 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 ($\beta_{av} = 3.1 \text{ pm V}^{-1}$).

2.4. Arylvinyl and arylethynylpyrazines

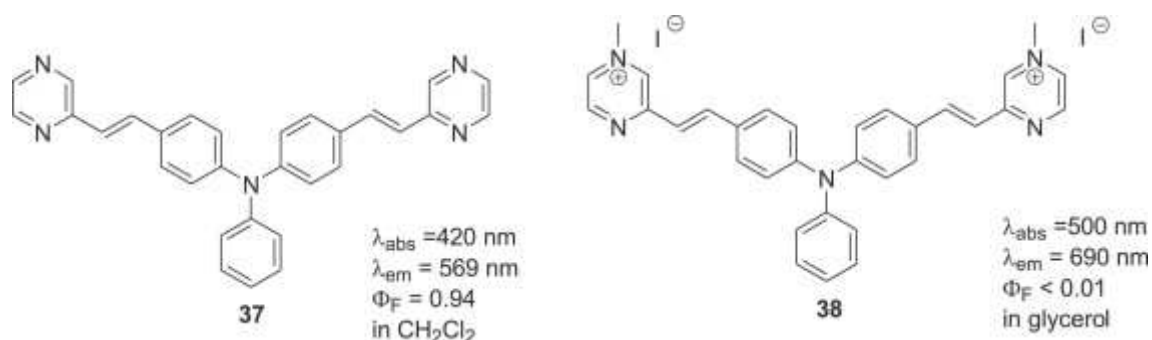
Synthesis, absorbance and fluorescence properties of the 2-(4'-hydroxystyryl)pyrazine **36a** was reported (Scheme 20) [42]. The spectral data of **36a** are better than those of the pyridine analogous and have exhibited a strong dependence on solvent polarity and pH. Recently, other 2-(4'-aminostyryl)pyrazines **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 $\mu\beta = 220 \cdot 10^{-48} \text{ esu}$, the pyrazine derivative **36b** exhibits a better value than the pyridazine derivative but a lower value than the pyrimidine derivative.



R = OH **36a** $\lambda_{abs} = 350 \text{ nm}$ $\lambda_{em} = 491 \text{ nm}$ in EtOH
 R = NMe₂ **36b** $\lambda_{abs} = 389 \text{ nm}$ $\lambda_{em} = 511 \text{ nm}$ $\Phi_F = 0.17$ in CH₂Cl₂
 R = NPh₂ **36c** $\lambda_{abs} = 394 \text{ nm}$ $\lambda_{em} = 532 \text{ nm}$ $\Phi_F = 0.41$ in CH₂Cl₂

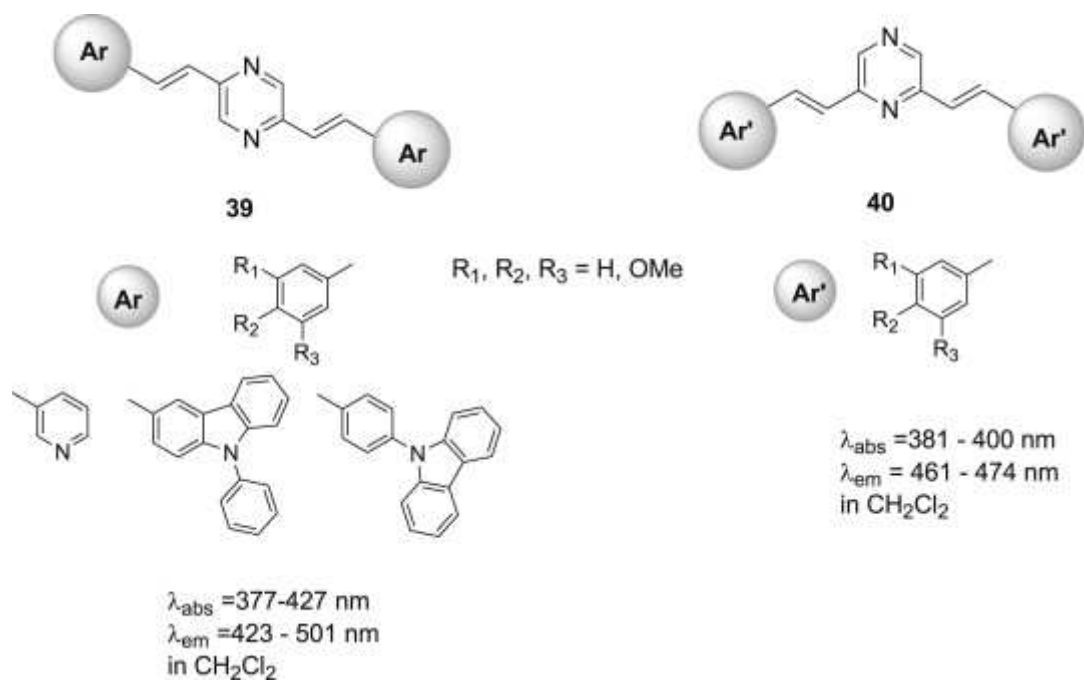
Scheme 20. Structure and photophysical data of compounds **36**.

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 ($\lambda_{\text{em}} = 569 \text{ nm}$, $\Phi_{\text{F}} = 0.94$), whereas the dimethylated salt **38** is non-luminescent. Nevertheless, this last compound exhibits a strong selective interaction for duplex DNA.



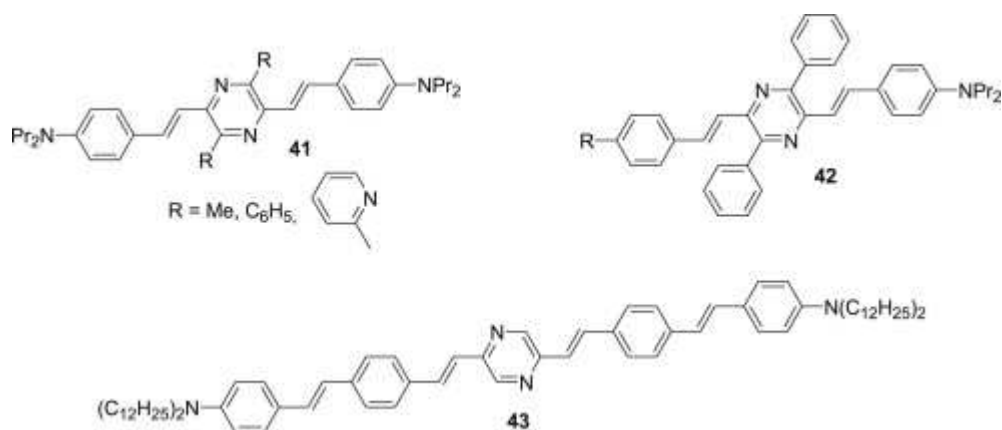
Scheme 21. Structure and photophysical data of compounds **37** and **38**.

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.



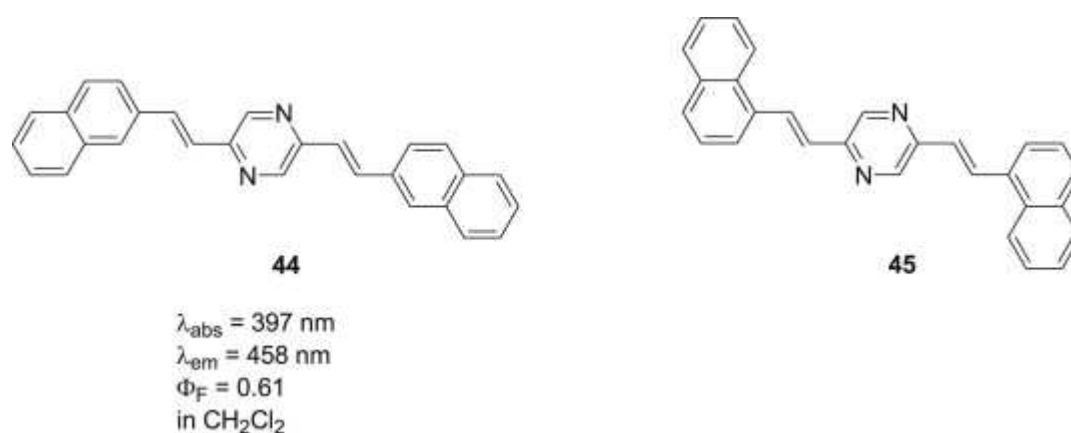
Scheme 22. Structure and photophysical data of compounds **39** and **40**.

Electrooptical and theoretical studies of various oligophenylenevinylenes **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.



Scheme 23. Structure and photophysical data of compounds **41–43**.

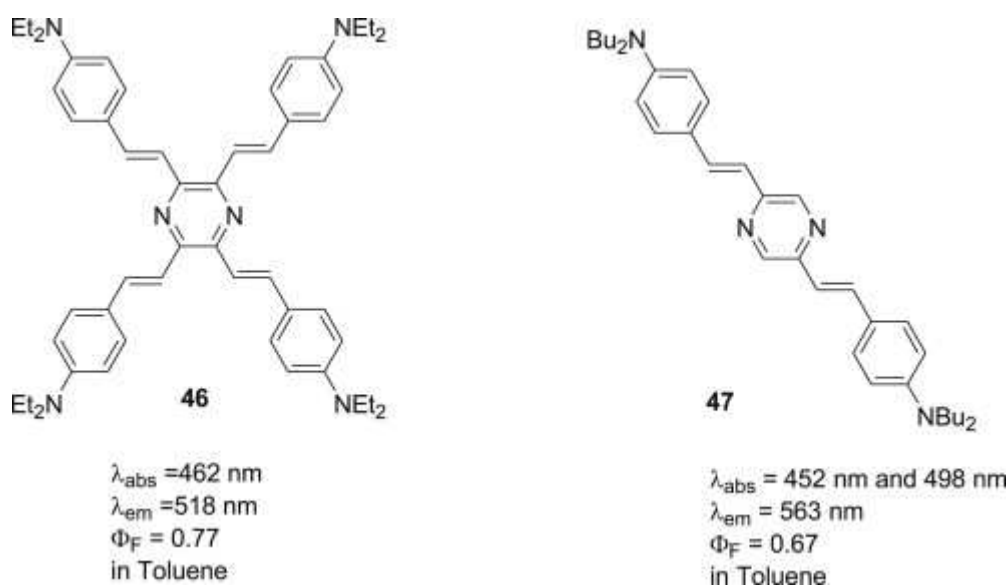
Other divinylpyrazine derivative **44** and **45** were described by Al-Hazmy *et al* (Scheme 24) [47]. The compound **44** with $\lambda_{\text{em}} = 463$ nm in DMF acts as a laser dye upon pumping with nitrogen laser ($\lambda_{\text{ex}} = 337$ nm).



Scheme 24. Structure and photophysical data of compounds **44** and **45**.

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 ($\Phi_{\text{F}} = 0.67$) and 518 nm ($\Phi_{\text{F}} = 0.77$). The TPA

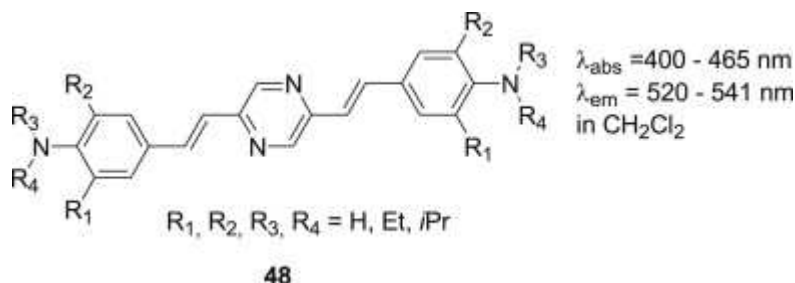
spectrum in toluene of **46** is quite similar to that of the two-branch analogue **47** ($\delta_{\text{max}} = 1250$ GM, $\lambda_{\text{max}} = 790$ nm). The spectral features observed for these chromophores suggest that electronic coupling between the branches is effective but does not lead to significant enhancement of the two-photon cross section when the branches extend 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**.

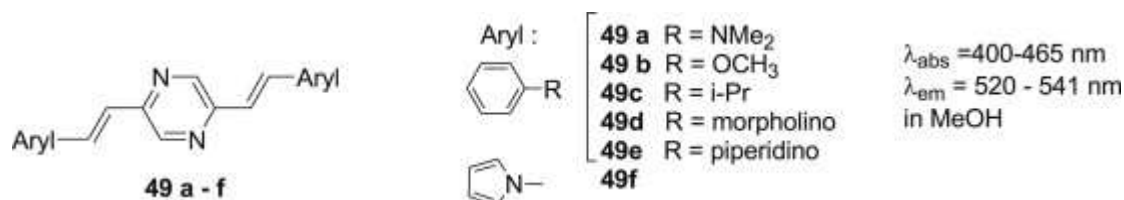
Detert *et al.* have described di(*p*-aminostyryl)pyrazines **48** with bulky substituents on the nitrogen of external amino groups and in the adjacent positions (Scheme 26) [49]. Steric congestion around the amino groups modulates the ICT in these fluorophores because the orbital overlap between nitrogen and π -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.



Scheme 26. Structure and photophysical data of compounds **48**.

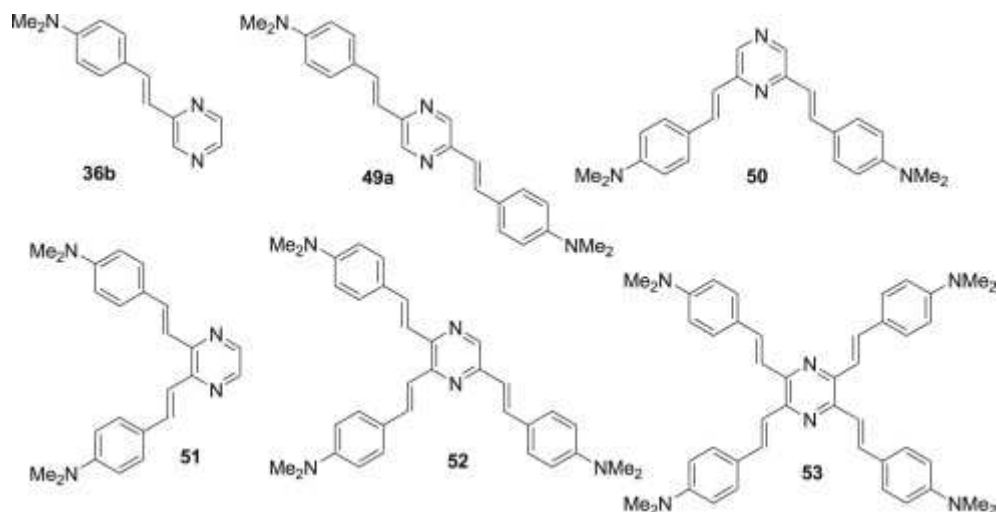
Synthesis and fluorescent properties of various bis(arylvinyl)pyrazines were reported by Schmidt *et al.* (Scheme 27) [50]. These compounds were tested as fluorescent probes for *in vitro* and *in vivo* detection of AD-associated protein deposits in human brain tissue by fluorescence microscopy.



Scheme 27. Structure and photophysical data of compounds **49**.

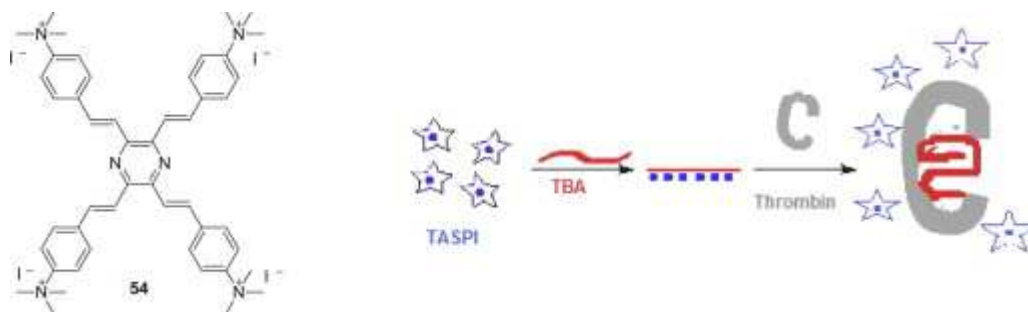
A series of pyrazine derivatives was reported by Collette *et al.*, where the number and substitution pattern of *p*-dimethylaminostyryl branches on the pyrazine core were systematically studied (Scheme 28) [51]. These fluorophores were designed to exhibit large changes in emission in response to changes 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

($\gamma(-\omega;\omega,-\omega,\omega)$) and comparison to known two-photon molecules showed that these molecules were expected to be good two-photon active molecules.



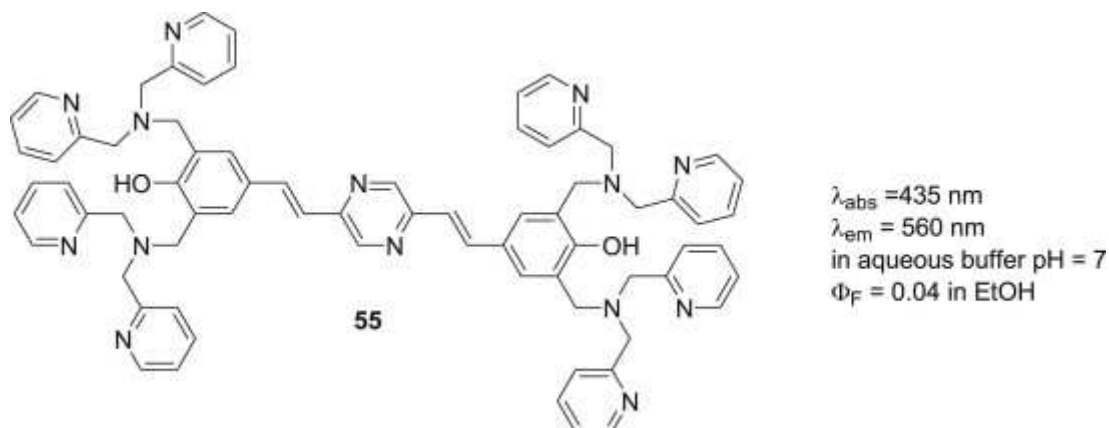
Scheme 28. Structure of compounds **36b**, **49a** and **50–53**.

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).



Scheme 29. Structure of compound **54**, Schematic representation of the binding of TBA DNA aptamer and thrombin.

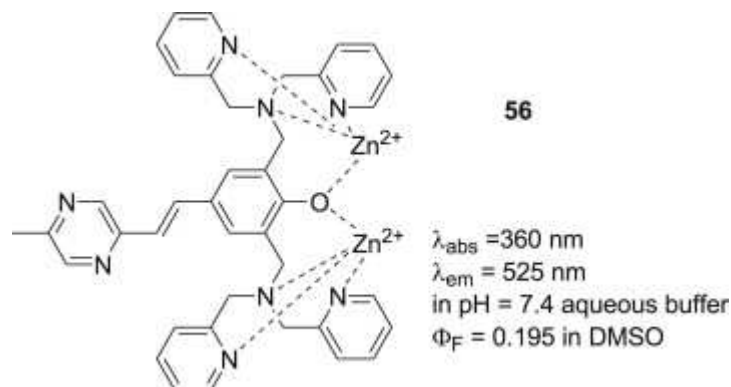
A fluorescent sensor **55** containing a pyrazine central core and bis(2-pyridylmethyl)amine groups as a binding moiety for Pb^{2+} was developed (Scheme 30) [53]. Compound **55** shows selective response to Pb^{2+} over other metal ions in pH 7.0 HEPES buffer solution. The fluorescence intensity enhancement was ascribed to the complex formation between Pb^{2+} and **55** which blocked the photo-induced electron transfer process.



Scheme 30. Structure and photophysical data of compound **55**.

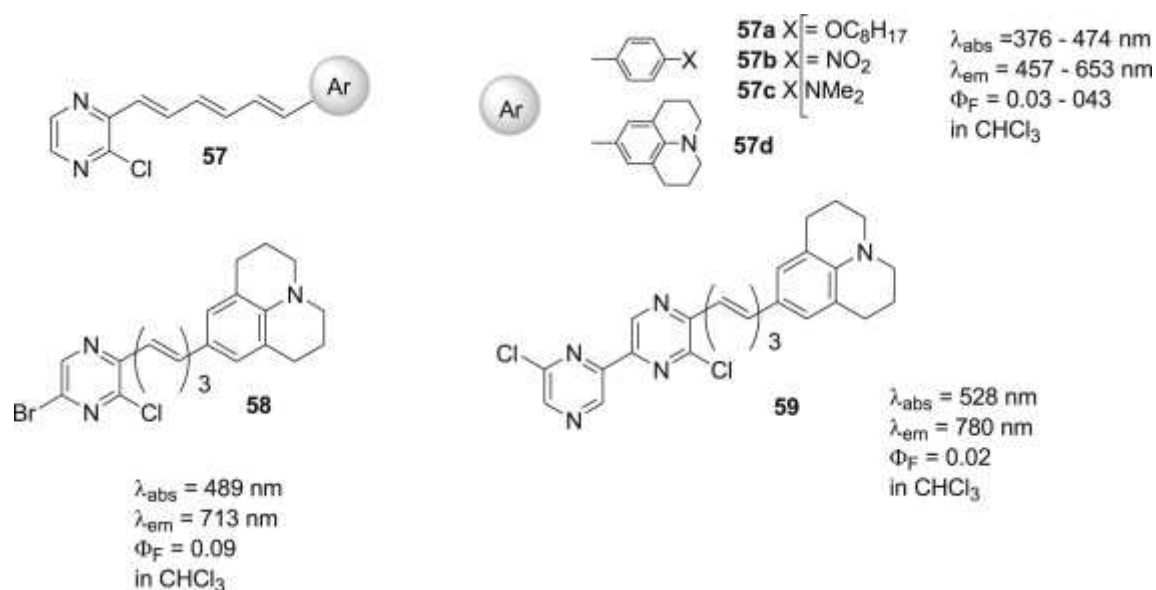
Wu and coworkers have explored the nature of binding interaction of a fluorescent pyrazine-Zn probe **56** with calf thymus deoxyribonucleic acid (*ct*-DNA) (Scheme 31) [54]. Absorption titration of DNA with **56** was performed by fluorescence polarization measurements. All

results showed that the interaction mode between the complex Zn-**56** and the (*ct*-DNA) was electrostatic interaction.



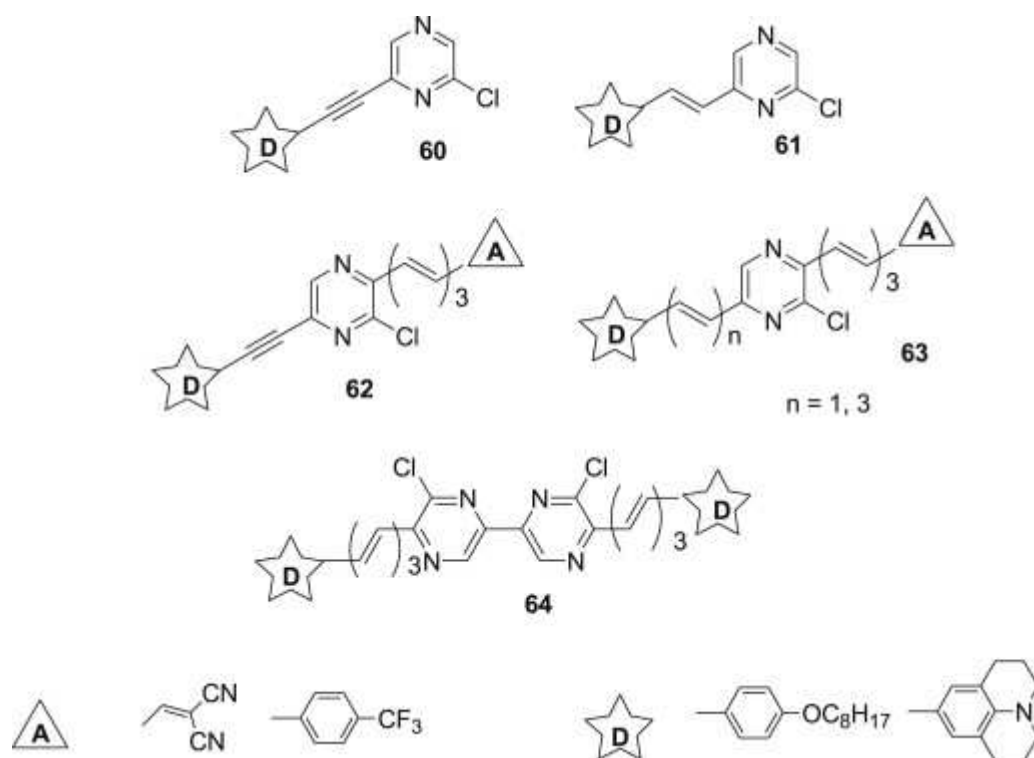
Scheme 31. Structure and photophysical data of compound **56**.

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 (λ_{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 ($\mu\beta = 1048 \text{ } 10^{-48} \text{ esu}$) for compound **57b**.



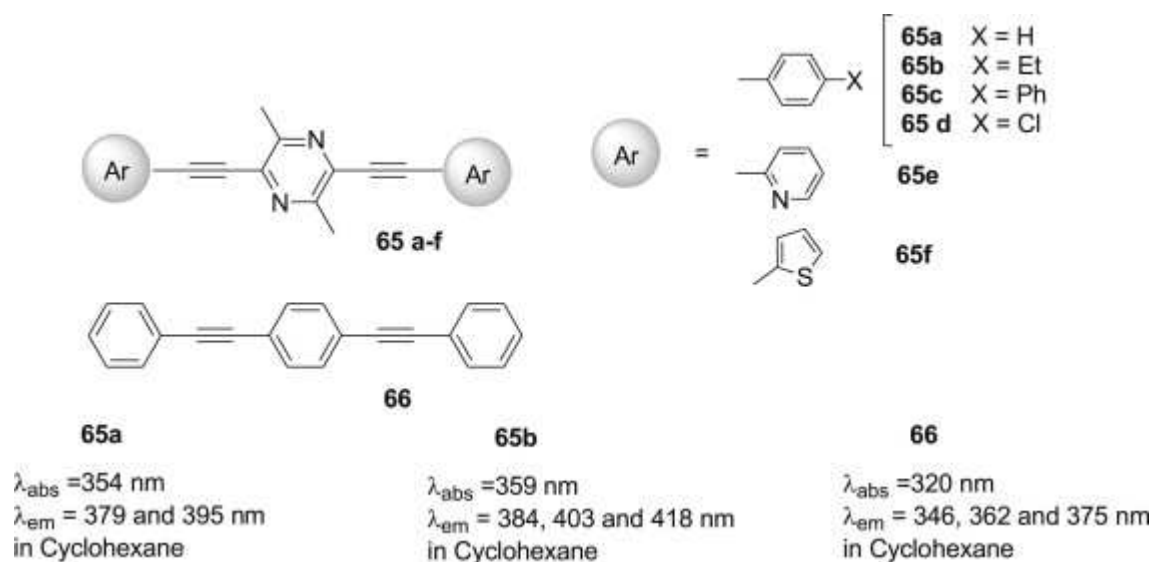
Scheme 32. Structure and photophysical data of compounds **57–59**.

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.



Scheme 33. Structure and photophysical data of compounds **60**–**64**.

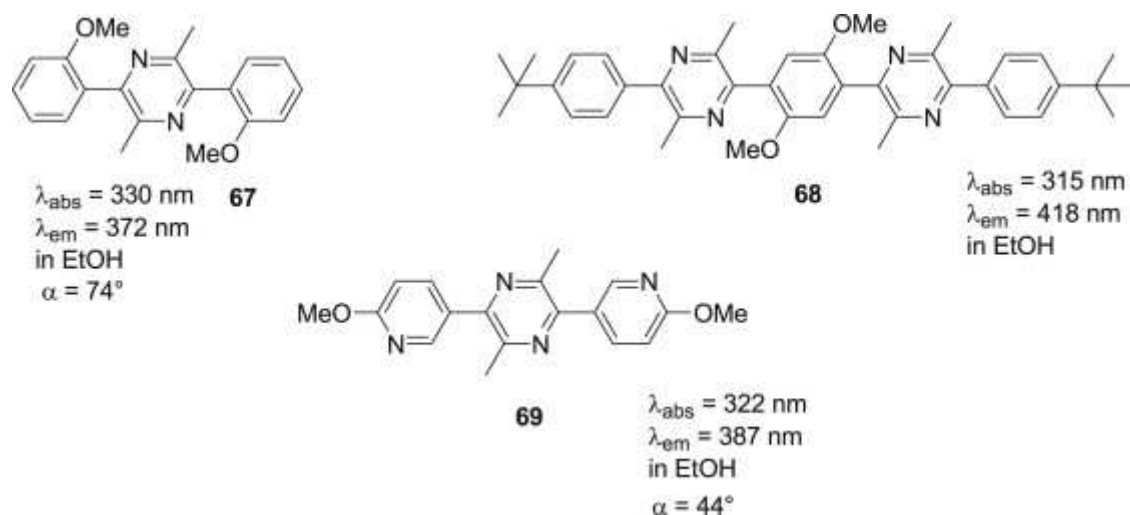
A series of 2,5-di(aryleneethynyl)pyrazine derivatives **65** was synthesized by Zhao *et al* (Scheme 34) [57]. The structure, electrochemical and photophysical properties of derivative **65a** have been compared with those of di(phenylethynyl)benzene **66**. The presence of the pyrazine ring leads to 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.



Scheme 34. Structure and photophysical data of compounds **65** and **66**.

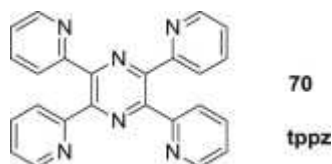
2.5. Other pyrazine structures

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 α determined by X-Ray crystallography. Blue electroluminescence, λ_{max} 444 nm, is observed for the device structure ITO/PEDOT/**68**/Ca with no long-wavelength emission from π -aggregates or exciton states.



Scheme 35. Structure and photophysical data of compounds **67–69**.

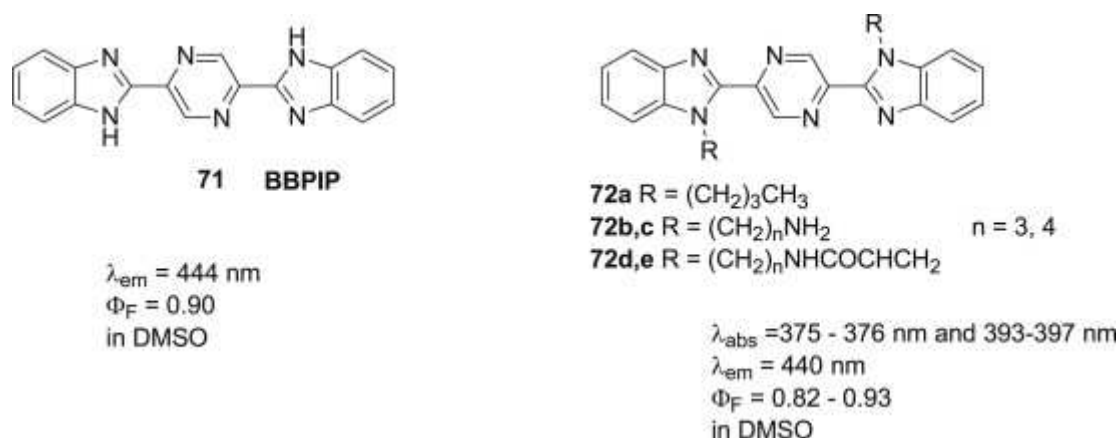
Fugisawa *et al* have reported the complexation of 2,3,5,6-tetra(2'-pyridyl)pyrazine (tppz) **70** and 1-octadecanol with Eu^{3+} ions through formation of luminescent Langmuir films at the air/liquid interface (Scheme 36) [59].



Scheme 36. Structure and photophysical data of compound **70**.

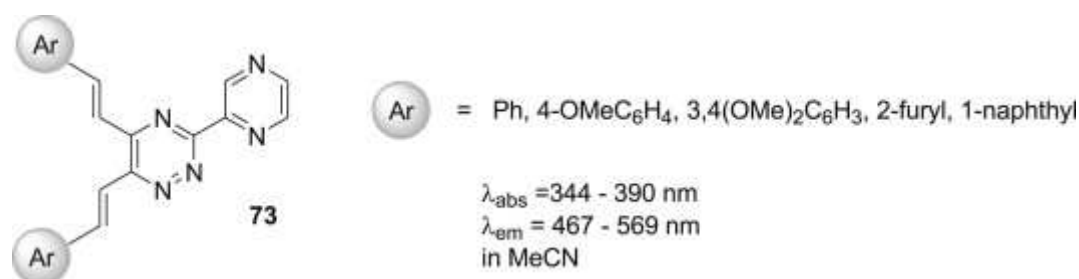
Saito and coworkers have reported that 2,5-bis(benzimidazol-2-yl)pyrazine (BBPIP) **71** exhibited extremely intensive blue-fluorescence with maximum emission at 444 nm and a fluorescence quantum yield of 0.90 in DMSO [60]. In order to improve the solubility, derivatives **72** with two alkyl chains 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.



Scheme 37. Structure and photophysical data of compounds **71** and **72**.

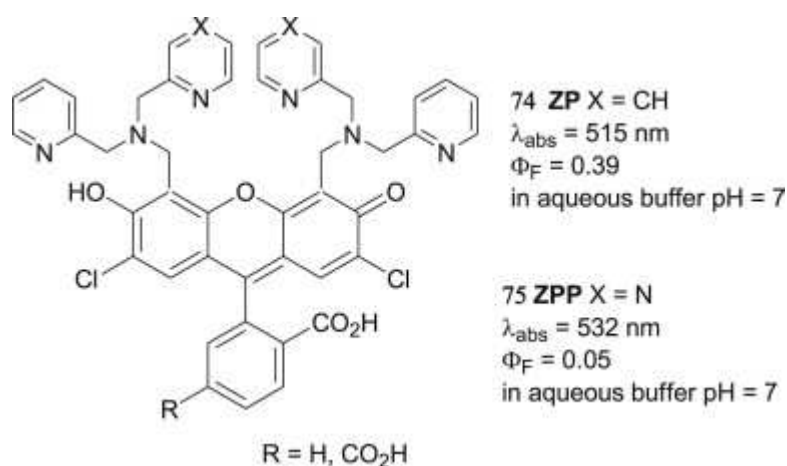
Various 5,6-bisarylvinyl-3-pyrazine-1,2,4-triazine derivatives **73** were synthesized by Thirumurugan *et al* and have highlighted good sensor property with Fe(III) ions even in micro level concentrations (Scheme 38) [62].



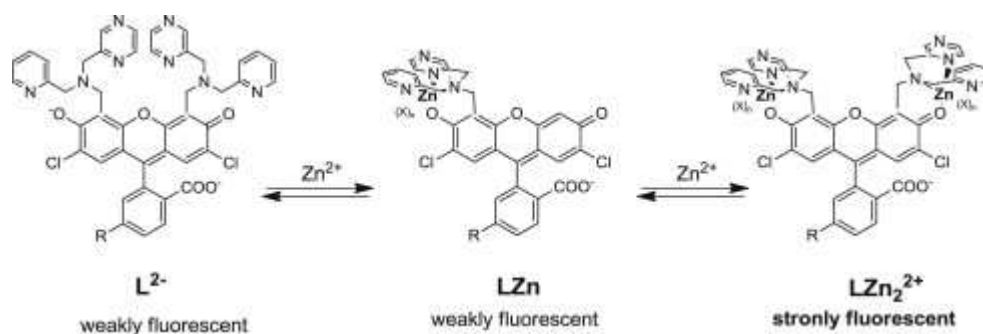
Scheme 38. Structure and photophysical data of compound **73**.

New fluorescent sensors for Zn²⁺ 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**.

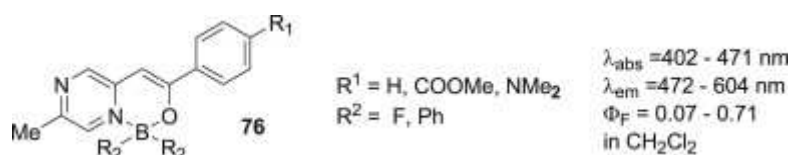


Scheme 40. Structure of compound **75** and its Zinc complexes.

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.

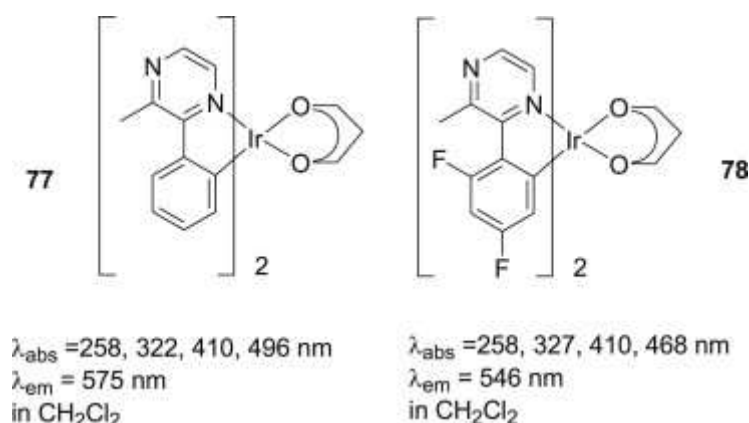
A novel series of fluorescence dyes based on pyrazine-boron complexes **76** bearing a β -iminoketone ligand were prepared from methylpyrazine and benzoate derivatives (Scheme

41) [65]. All synthesized complexes exhibited fluorescence in dichloromethane (λ_{max} : 472–604 nm) and in the solid state (λ_{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.



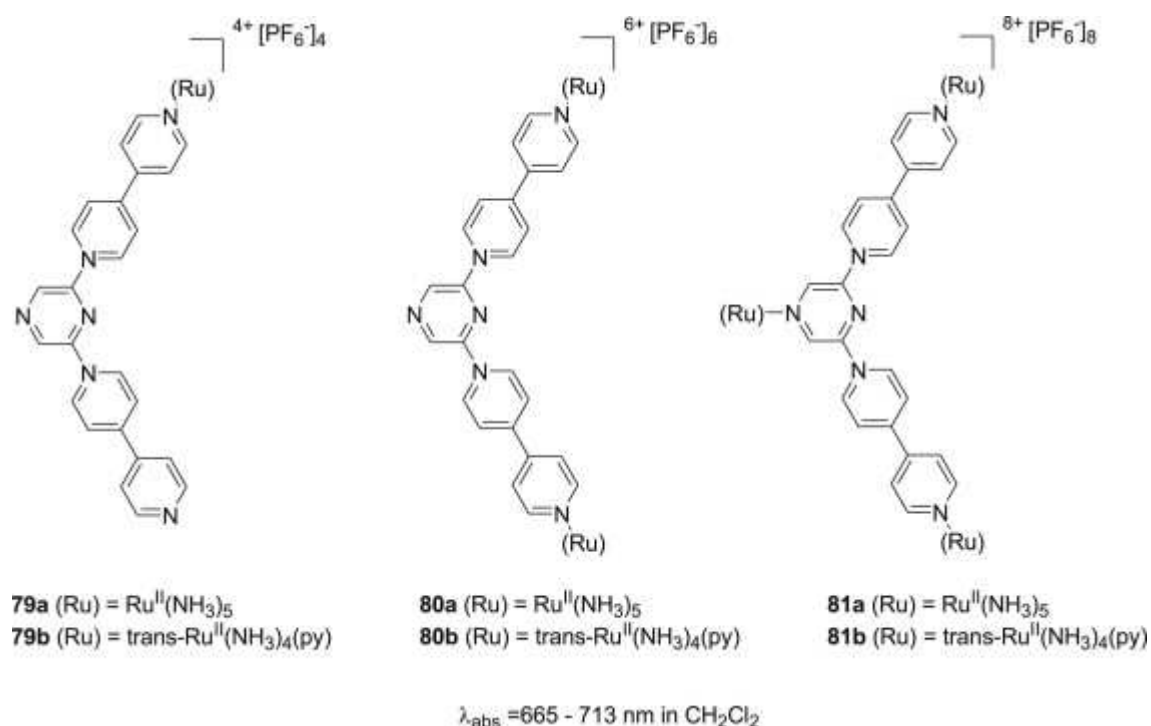
Scheme 41. Structure and photophysical data of compounds **76**.

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 ($\lambda_{\text{max}} = 575 \text{ nm}$). Efficient OLEDs using the complex **77** as phosphorescent dopant were demonstrated.



Scheme 42. Structure and photophysical data of compounds **77–78**.

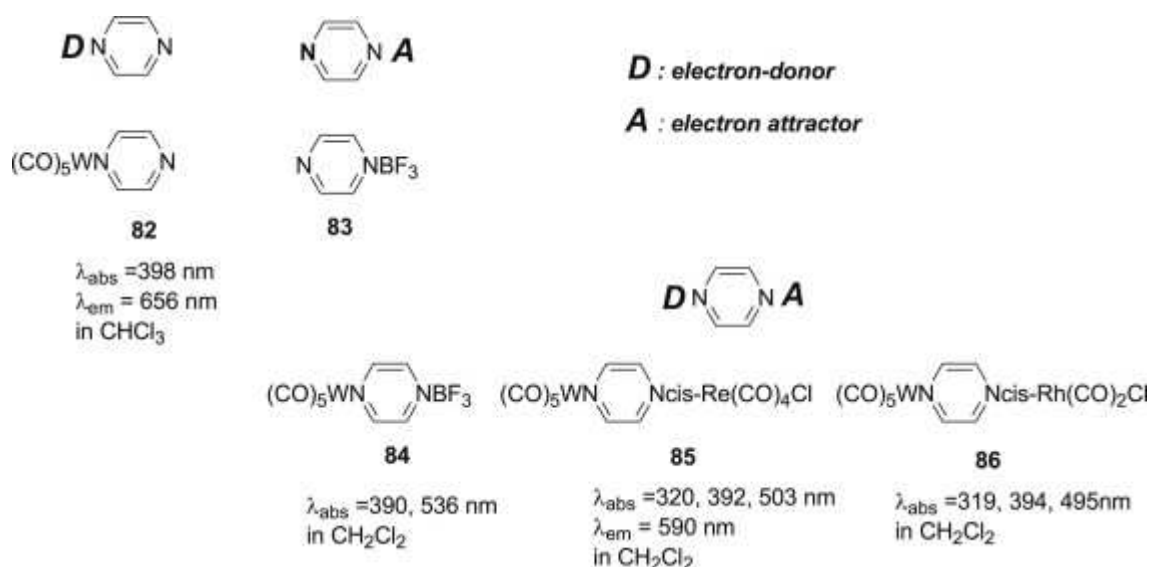
Coe and coworkers have synthesized nonlinear optical (NLO) chromophores **79-81** with pyrazinyl-pyridinium electron acceptors complexing a known pro-ligand with electron-donating $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ or $\text{trans-}\{\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{py})\}^{2+}$ (py = pyridine) centers (Scheme 43) [67]. These cationic complexes were characterized as their PF_6^- salts. Molecular first hyperpolarizability β were determined by using hyper-Rayleigh scattering (HRS) with a 1064 nm laser exhibiting relatively large β values. Depolarization measurements confirm the strongly 2D nature of the NLO responses for the symmetric complexes. The β_0 value increases on moving from **79** to bimetallic species **80**.



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 “ $\text{W}(\text{CO})_5$ ” 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.



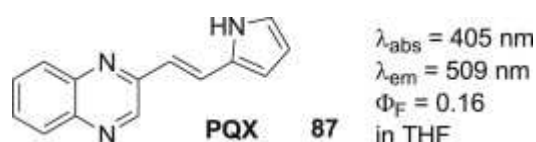
Scheme 44. Structure and photophysical data of compounds **82–86**.

3. Quinoxalines derivatives

3.1. Arylvinylquinoxalines

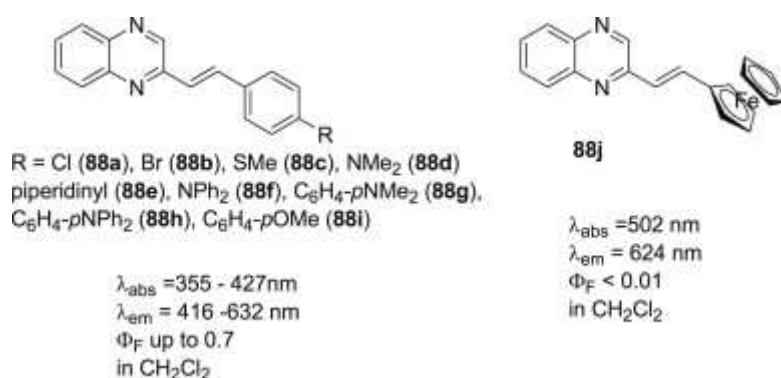
The push-pull molecule **PQX 87** with a quinoxaline as π -deficient moiety, linked to a pyrrole ring through an ethenyl linker was designed by Kudo and coworkers (Scheme 45) [69]. This compound, soluble in many common solvents, exhibits a full-color solvatochromic

fluorescence ($\lambda_{em} = 430\text{-}607\text{ nm}$) and was described as a promising fluorescent sensor for binding sites in proteins or other host molecules, especially in aqueous solution.



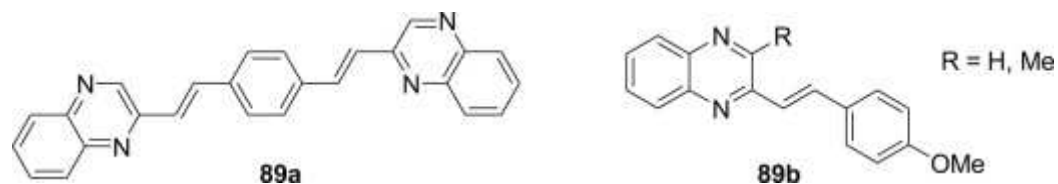
Scheme 45. Structure and photophysical data of compounds **87**.

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 $\mu\beta = 300\ 10^{-48}$ esu, the quinoxaline derivative **88d** exhibits a better value than the pyrimidine, pyrazine and pyridazine derivative.



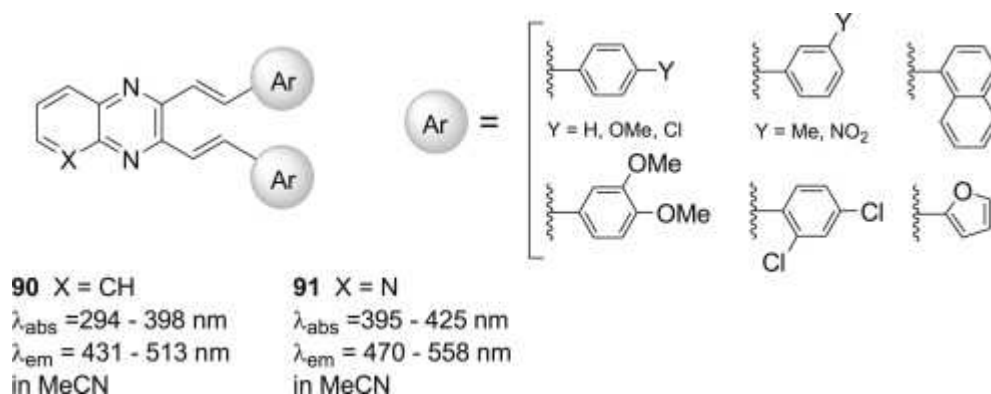
Scheme 46. Structure and photophysical data of compounds **88**.

Other fluorescent arylvinylquinoxalines **89** were reported by Bachowska *et al.* and are described as pale blue luminescent structures (Scheme 47) [70].



Scheme 47. Structure of compounds **89**.

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 ($\lambda_{\text{em}} = 431 - 558 \text{ nm}$) as well as very good fluorescence lifetimes. Moreover, the pyridopyrazine derivatives exhibit halochromism.



Scheme 48. Structure and photophysical data of compounds **90** and **91**.

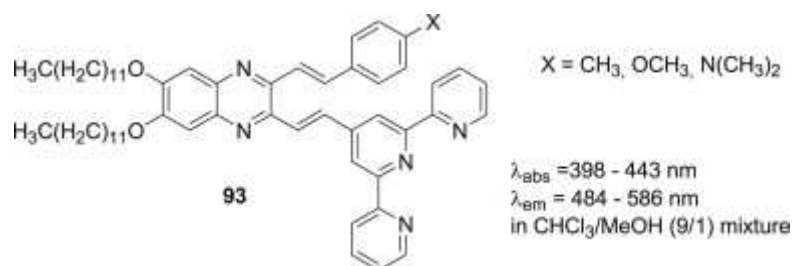
Various 6,7-bis-(3-methylbutoxyl)quinoxaline derivatives **92** (Scheme 49), with different electron-donating arylvinyl moieties were described and studied by Jaung [72] These

compounds are fluorescent ($\lambda_{em} = 470\text{--}567$ nm in $\text{CHCl}_3/\text{MeOH}$ 10/1 mixture) with a red-shifted emission in acidic media.



Scheme 49. Structure and photophysical data of compounds **92**.

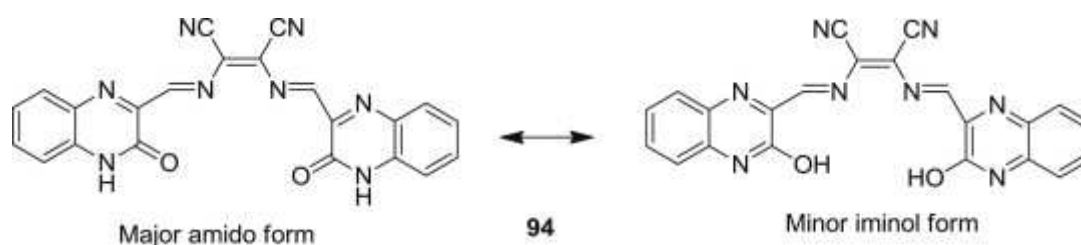
A series of quinoxalines derivatives **93** with a 2,2',6',2''-terpyridine moiety in one arm have also been synthesized and studied (Scheme 50) [73]. The absorption and fluorescence maximum of these compounds were observed at 398–443 nm and 484–586 nm, respectively. These compounds were used as fluorescence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



Scheme 50. Structure and photophysical data of compounds **93**.

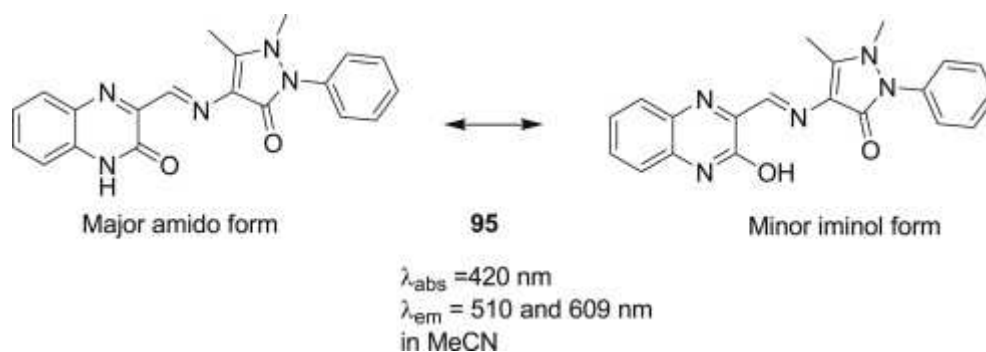
3.2. Azomethine Quinoxalines

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.



Scheme 51. Tautomer equilibrium of compound **94**.

Another Schiff base, the 3-hydroxyquinoxaline-2-carboxalidine-4-aminoantipyrene **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: β ($1.48 \times 10^{-6} \text{ cmW}^{-1}$), imaginary part of the third-order non-linear optical susceptibility: $\text{Im } \chi^{(3)}$ ($3.36 \times 10^{-10} \text{ esu}$) and its optical limiting threshold (340 MW cm^{-2}), make that **95** could be used for applications in photonic age.

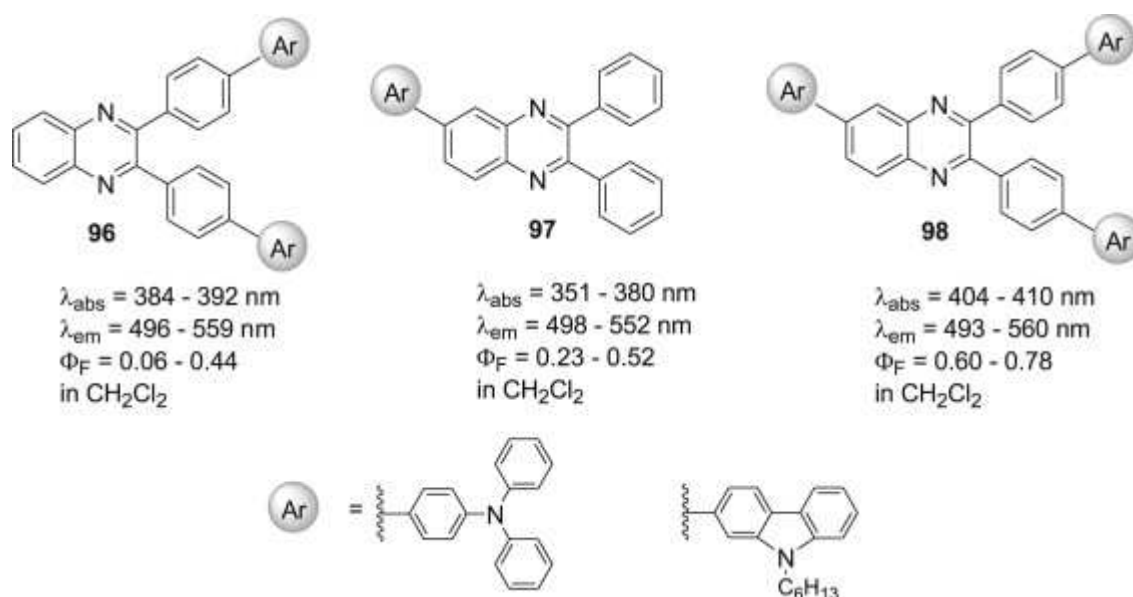


Scheme 52. Tautomer equilibrium of compound **95**.

If substitution of the quinoxaline core with arylvinyl or arylimine moieties gave generally good fluorescent compounds, other quinoxaline structures bearing aryl moieties with different electronic characters have also intensively reported.

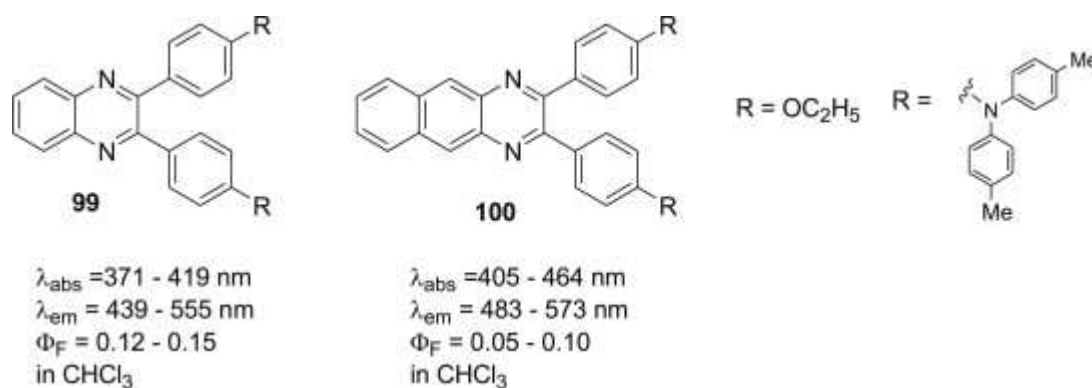
3.3. Arylquinoxalines

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 ($\lambda_{\text{em}} = 493\text{--}560 \text{ nm}$) and are presented as potential emissive and electron-transport materials for organic light-emitting diodes.



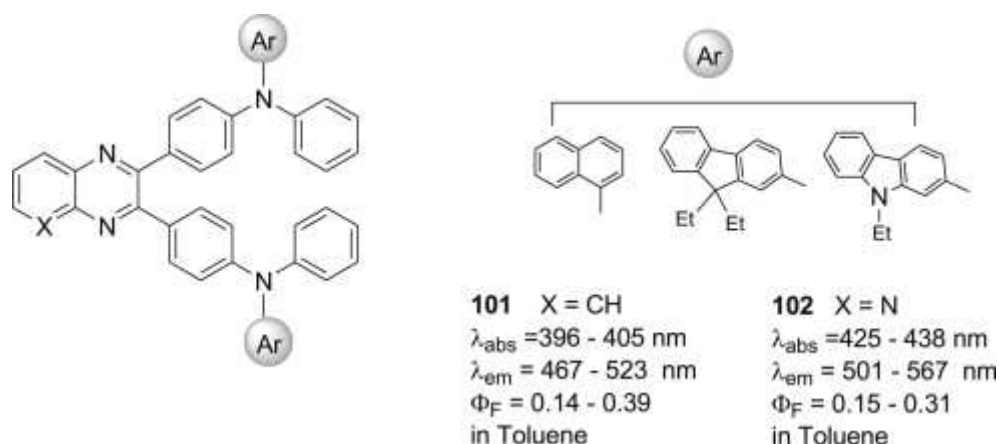
Scheme 53. Structure and photophysical data of compounds **96–98**.

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 ($\delta_{2\text{PA}}$) around 160 GM in the laser light wavelength range of 780–820 nm.



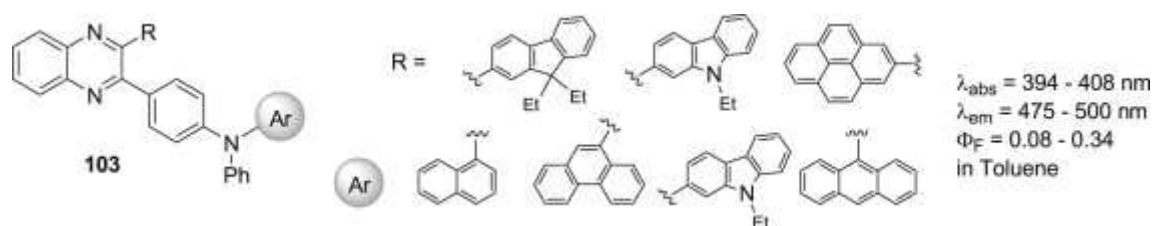
Scheme 54. Structure and photophysical data of compounds **99** and **100**.

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.



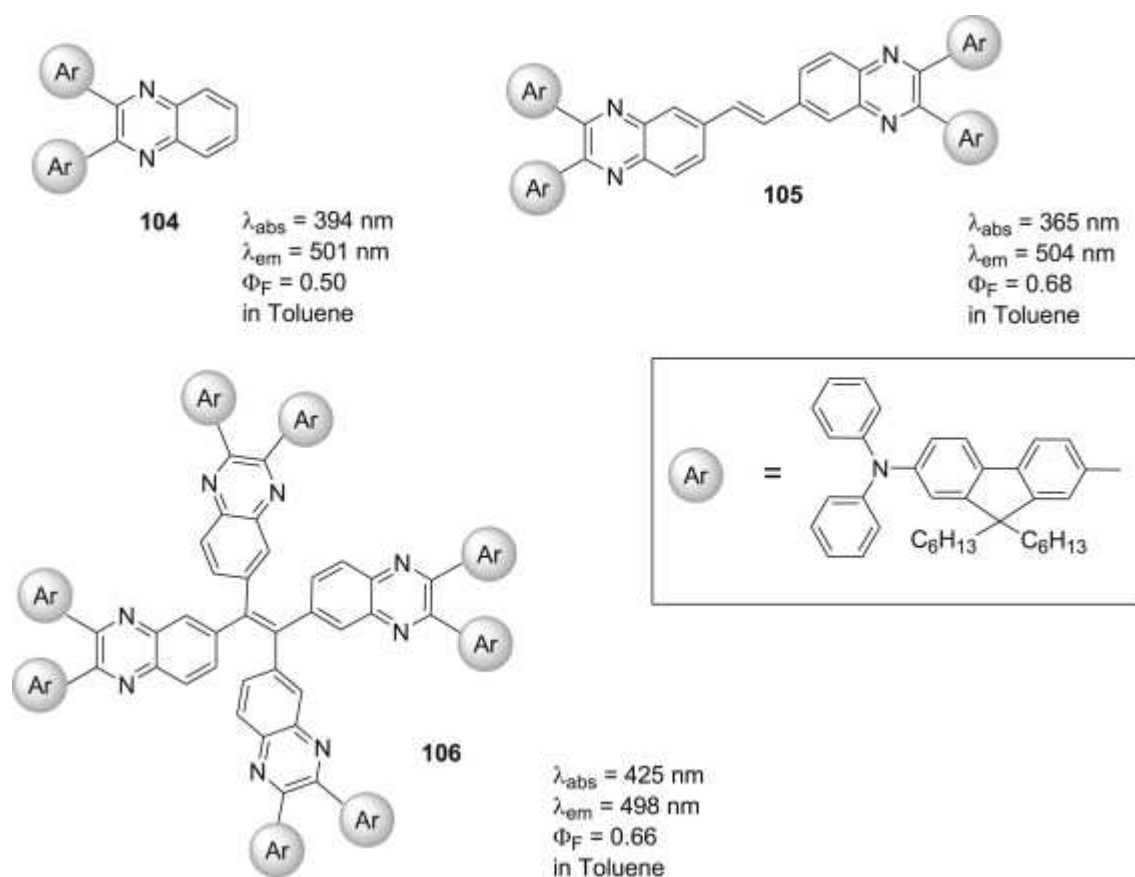
Scheme 55. Structure and photophysical data of compounds **101–102**.

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.



Scheme 56. Structure and photophysical data of compounds **103**.

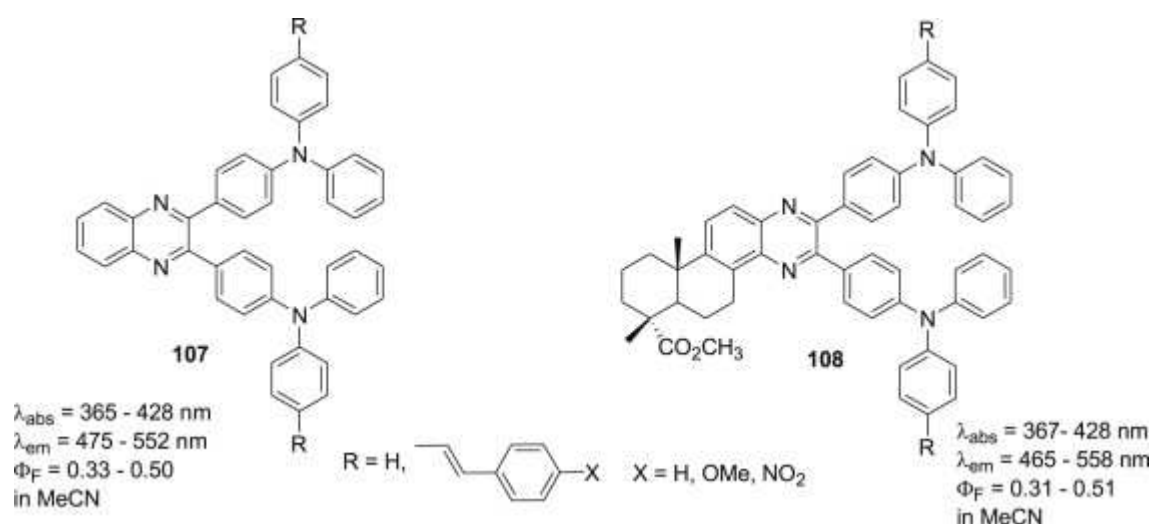
A series of multi-branched fluorophores with a quinoxaline or with a di- or a tetraquinoxalinylene as the core and diphenylaminofluorene units incorporated at the peripheral positions was synthesized by Lin and coworkers (Scheme 57) [80]. These derivatives (**104–106**) possess good fluorescence quantum 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

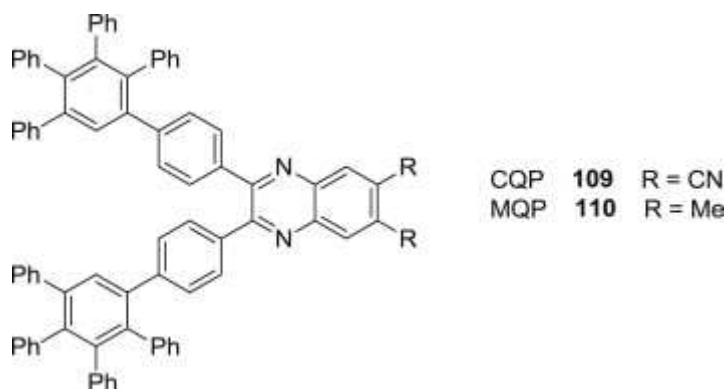
and coworkers (Scheme 58) [81]. Incorporation of the bulky dehydroabietic methyl ester group in the scaffold of compounds **108** was achieved to improve solubility and to prevent crystallization, without affecting their photophysical behaviors. These compounds exhibited relatively strong fluorescence, 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**.

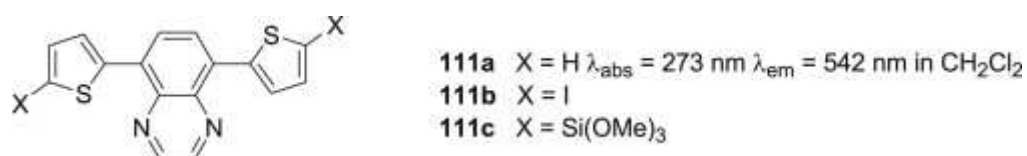
The photophysical properties of two polyphenylphenyl compounds CPQ **109** and MPQ **110** with a quinoxaline core were investigated in aqueous solutions (Scheme 59) [83]. For these compounds, the abnormal photoluminescent phenomena observed in THF-water mixtures could be explained by combinational effects 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 \geq cytosine.



Scheme 59. Structure of compounds **109** and **110**.

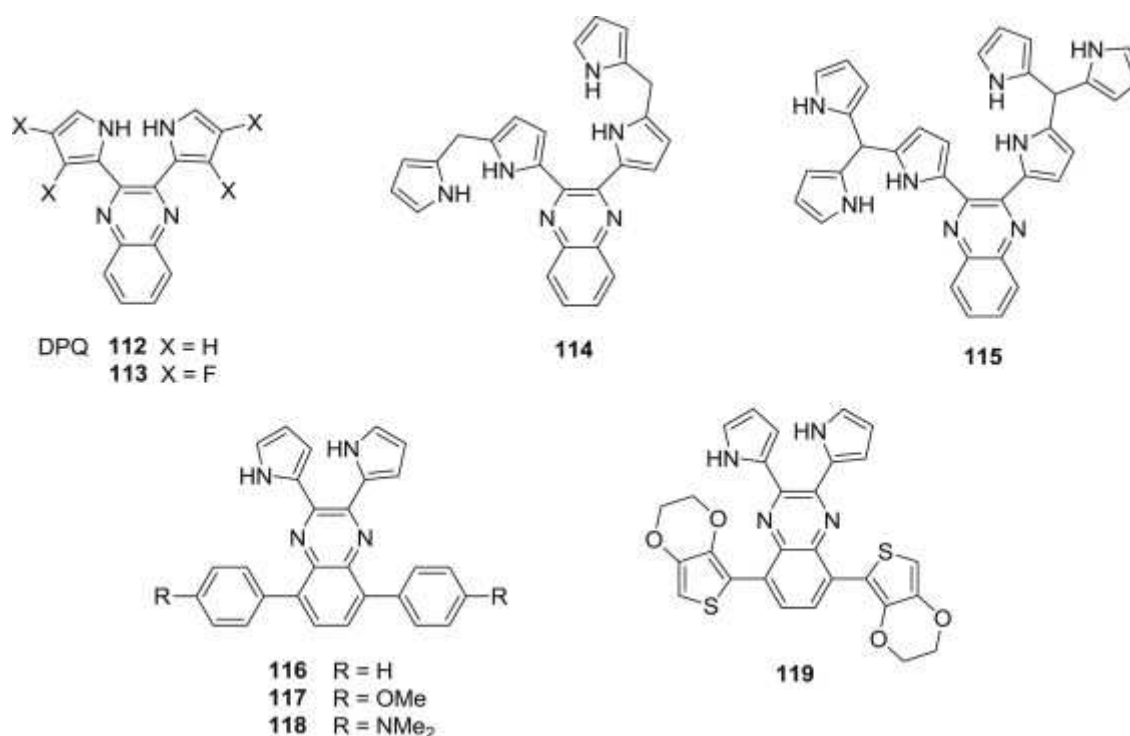
Various 5,8-dithienyl quinoxaline derivatives **111** substituted on the thienyl ring were described by Hemgesberg and coworkers (Scheme 60) [84]. Compound **111a** is fluorescent with high Stokes shift ($\lambda_{\text{abs}} = 273$ nm and $\lambda_{\text{em}} = 542$ nm) and could be used to access fluorescent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



Scheme 60. Structure and photophysical data of compounds **111**.

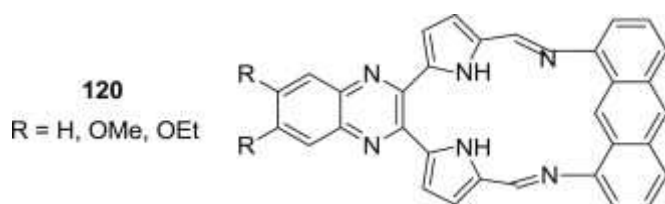
The 2,3-dipyrrole-2'-ylquinoxaline (DPQ) **112** [85] and its derivatives with substituents either on the pyrrole ring **113-115** or on the phenyl ring of the quinoxaline moiety, leading to extended chromophores **116-119** (Scheme 61), are described as sensors for inorganic anions

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.



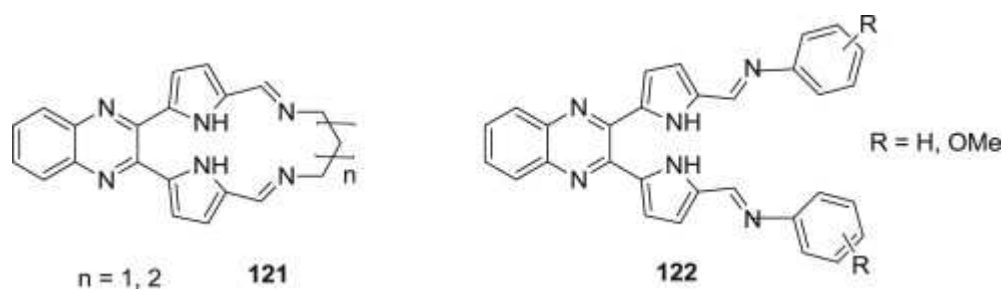
Scheme 61. Structure of compounds **112–119**.

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].



Scheme 62. Structure of compounds **120**.

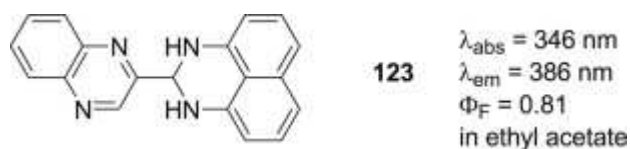
Wang and coworkers have described a series of dipyrroloquinoxaline-bridged Schiff bases **121** as fluorescent sensors for Hg^{2+} ion [88]. More recently, other Schiff bases **122**, synthesized and studied by Hu *et al.* were reported as fluorescent ON/OFF switching system (Scheme 63) [89]. These compounds displayed good sensitivity toward transition metal ions with Cd(II), Zn(II) turn-on and Cu(II), Hg(II) turn-off in fluorescence.



Scheme 63. Structure of compounds **121–122**.

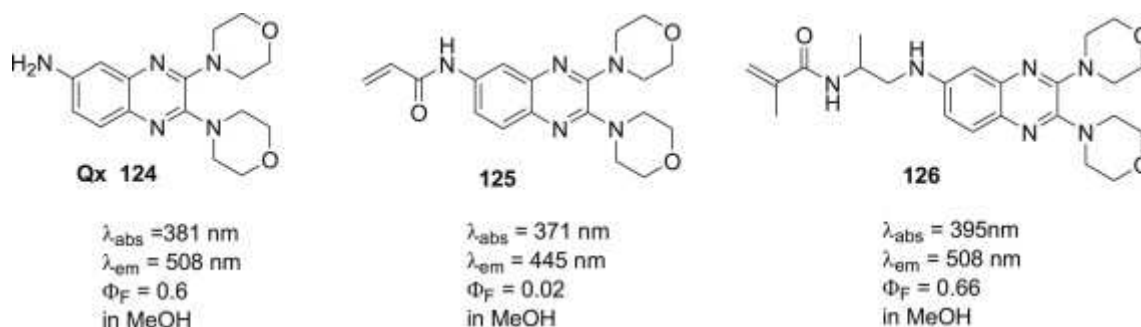
3.4. Micellaneous substituted Quinoxalines

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** ($\lambda_{\text{em}} = 386 \text{ nm}$, $\Phi_{\text{F}} = 0.81$ in ethyl acetate), exhibits a negative fluorosolvatochromism in polar solvents, and presents interesting antibacterial activities.



Scheme 64. Structure and photophysical data of compound **123**.

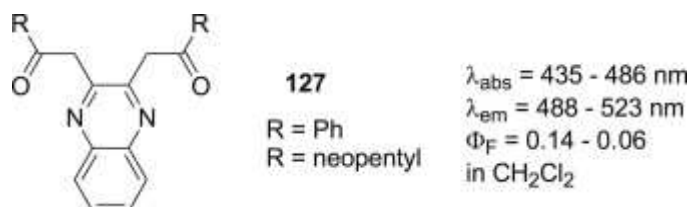
Katoh and coworkers have described the strong fluorescence of the 2,3-dimorpholino-6-aminoquinoxaline (Qx) **124** [91]. Two other fluorescent monomers **125** and **126** incorporating the quinoxaline skeleton Qx in their scaffold were described by the same group (Scheme 65) [92]. Compounds **125** 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.



Scheme 65. Structure and photophysical data of compounds **124–126**.

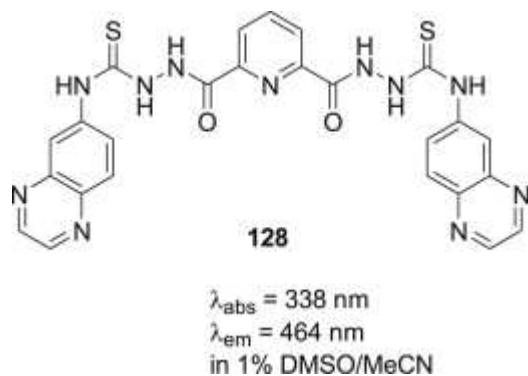
Touzani and coworkers have described two 2,3-functionalized quinoxalines **127** (Scheme 66) [93]. These compounds exist as the keto-enamine form in both solution and solid state. These

structures are slightly fluorescent ($\lambda_{\text{em}} = 488\text{-}523\text{ nm}$, $\Phi_{\text{F}} = 0.06\text{-}0.14$ in dichloromethane solution) and are presented as interesting ligand for metallo-organic NLO-phores.



Scheme 66. Structure and photophysical data of compounds **127**.

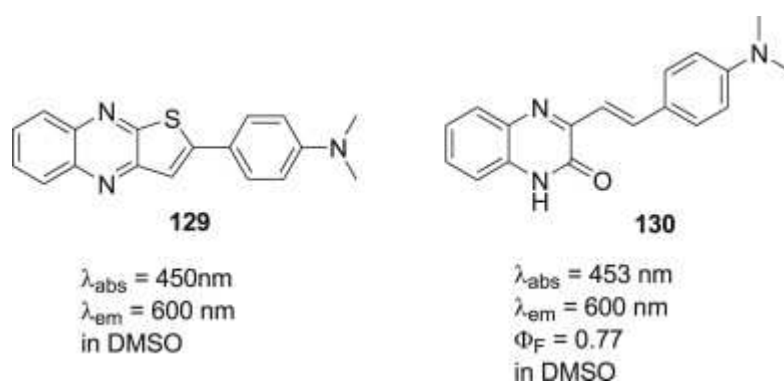
With the aim of forming a pre-organized molecular cleft, the quinoxaline derivative **128**, possessing a 2,6-pyridyl-based amidothiurea moiety, was developed by Duke *et al.* and was studied as a fluorescent anion sensor (Scheme 67) [94]. The anion-sensing occurs most likely via deprotonation of the amidothiurea 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**.

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 A β (1-40)-peptide by a fluorescence “turn on” mechanism [95]. Thienoquinoxaline **129** allowed the detection of lysozyme and A β (1-40) fibers at $\lambda = 555$ and 532 nm, respectively, with excitation at $\lambda = 450$ nm. Styryl-quinoxaline **130** stained lysozyme and A β (1-40) fibers with fluorescence at $\lambda = 579$ and 567 nm, respectively, upon excitation at $\lambda = 453$ nm. The apparent K_d values for A β (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.

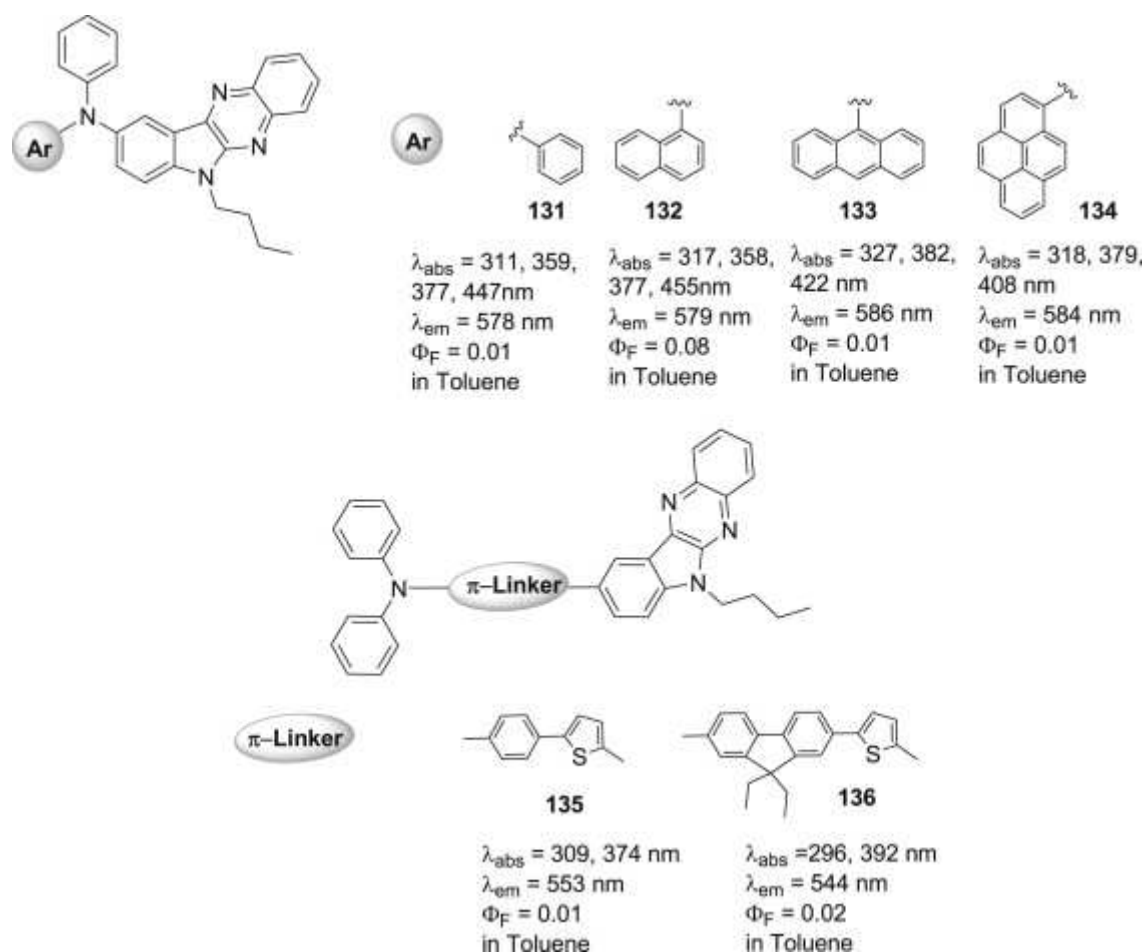


Scheme 68. Structure and photophysical data of compounds **129** and **130**.

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

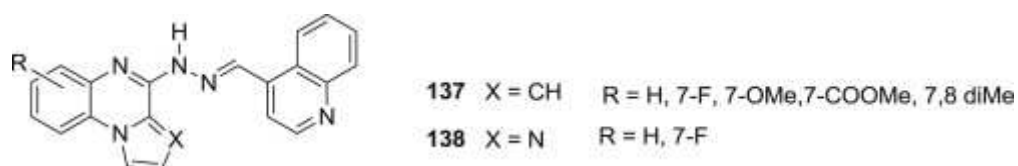
nature of the diarylamine segment and they displayed green or yellow emission ($\lambda_{\text{em}} = 544 - 586 \text{ nm}$, $\Phi_{\text{F}} = 0.01\text{-}0.08$). For the derivatives **135** and **136**, with an insertion of a conjugating aromatic linker between the amine and the indoloquininoxaline unit, a hyperchromism and a bathochromic shift of the absorption values are observed, due to an extended conjugation.



Scheme 69. Structure and photophysical data of compounds **131–136**.

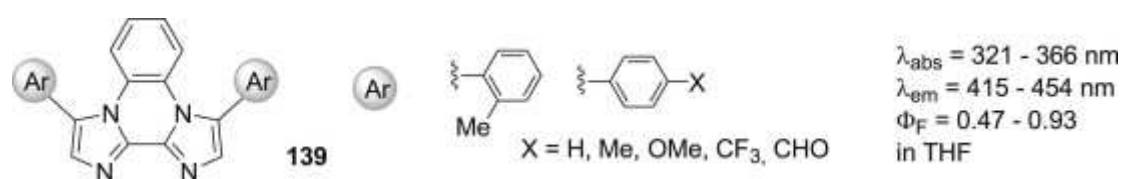
Gemma and coworkers have studied a class of pyrroloquininoxaline and imidazoloquininoxaline hydrazones **137** and **138** as fluorescent probes for $\text{A}\beta_{1-42}$ fibrils (Scheme 70) [97]. All these compounds were able to bind amyloid fibrils formed *in vitro* and some of them displayed an increase 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. Structure of compounds **137** and **138**.

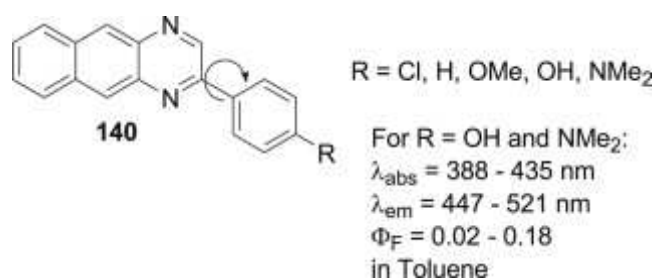
Diimidazo[1,2-a:2',1'-c]quinoxalines **139** were described by Matsumoto *et al.* (Scheme 71) [98]. These derivatives exhibit blue fluorescence with high quantum yield ($\lambda_{em} = 415\text{--}454$ nm, $\Phi_F = 0.47\text{--}0.93$). They were also applied to organic light-emitting devices (OLED)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



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

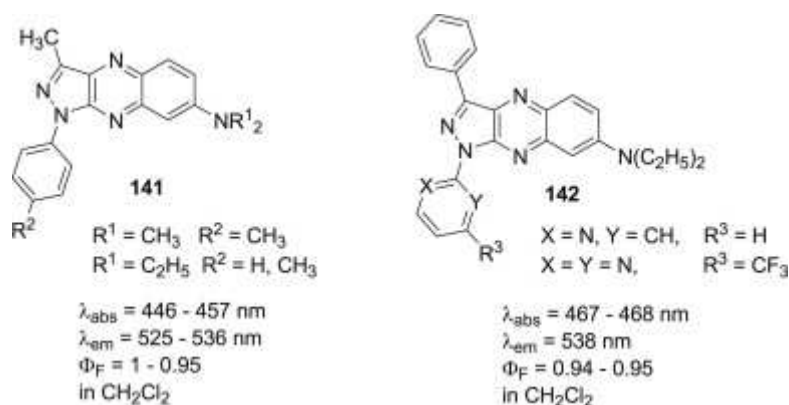
A series of substituted 2-phenylbenzo[g]quinoxalines **140** with a rotatable *para*-substituted phenyl moiety were synthesized and used as fluorophore for viscosity-sensitive probes (Scheme 72) [99]. The fluorescence properties of these compounds were investigated in the media of the ethylene glycol–glycerol 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.



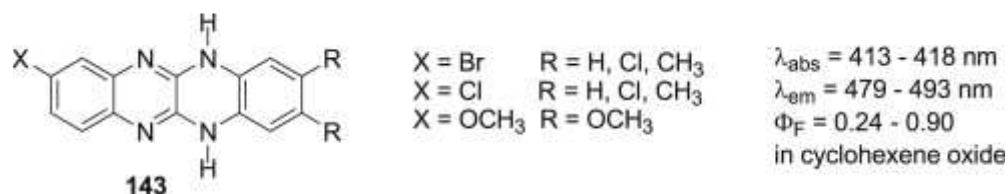
Scheme 72. Structure and photophysical data of compounds **140**.

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.



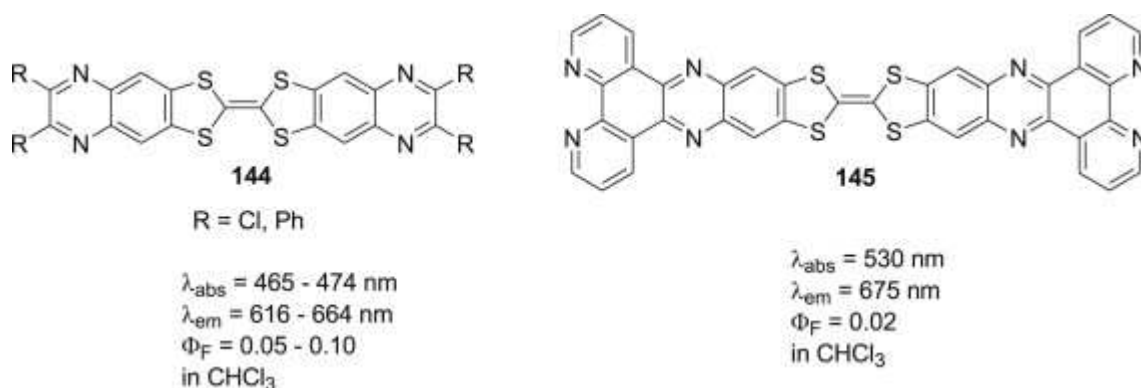
Scheme 73. Structure and photophysical data of compounds **141** and **142**.

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 [$\Phi(^1\text{O}_2)$] have been measured, in accordance with the “heavy atom effects” the much greater [$\Phi(^1\text{O}_2)$] values was determined for the 6-bromo-2,3-dichloroquinoxaline.



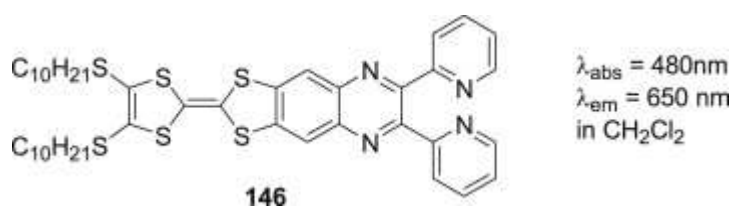
Scheme 74. Structure and photophysical data of compounds **143**.

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) moieties (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.



Scheme 75. Structure and photophysical data of compound **144** and **145**.

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.



Scheme 76. Structure and photophysical data of compound **146**.

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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