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Squaraine Compounds: Tailored Design and Synthesis towards a Variety of Material Science Applications

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Dedicated to Professor Giorgio A. Pagani, a constant example of dedication and ingenuity in materials science

Keywords: Materials science / Photonics / Photovoltaics / Nonlinear optics / Squaraines

The interest in squaraine compounds, a relatively old class of dyes, has been recently renewed due to their potential usefulness in a large number of technologically relevant fields such as two-photon absorbing materials, field-effect transistors, solar cells, NIR-emitting fluorescent probes and sensitizers for photodynamic therapy. Aim of the present review is to summarize the most convenient strategies for squaraines and polysquaraines syntheses and to discuss the design strategies enabling for the preparation of squaraines having properties relevant for a given material application. In particular, in the first section of the review we will describe the various synthetic approaches for the preparation of squaraine and polysquaraine derivatives. The second section will focus on squaraines applications. We will describe in detail the use of squaraines in bioimaging and photodynamic therapy. Within the topic of bio-related applications we will also discuss the applications of squaraines as histological probes. Within the NLO-related applications, we will focus on squaraine-based electro-optic and two-photon absorbing materials. Dealing with photoconduction related applications, we will discuss the most recent applications of squaraine compounds in various kinds of devices such as solar cells, hybrid solar cells and NIR-responsive photodetectors. In all of the cases we will mainly focus on structure–property relationships highlighting the role of the active molecule design in the final device performances.

1. Introduction

Squaraines[1] are the dicondensation product of electron-rich molecules with squaric acid.[2] The main characteristic of this class of compounds is the sharp and intense low-energy absorption frequently associated with a strong fluorescence in solution. Scheme 1 shows the squaraine deriving from the condensation of 2,4-dimethylpyrrole and squaric acid, one of the simplest derivatives described. The scheme shows all of the three allowed canonical representations for derivative **1**, the two pyrrole rings are clearly equivalents and the squaraine structure is symmetric.

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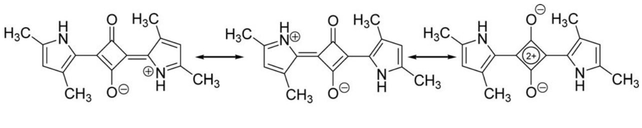

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Scheme 1.

Squaraines absorption bands generally become rather broad in the solid state as a consequence of strong charge transfer interactions and tendency to aggregation. From an electronic point of view, squaraines are reminiscent of cyanine compounds, with the noteworthy difference of being electrically neutral. Figure 1 shows the absorption and emission spectra of derivative **1** in $CHCl_3$ solution. These peculiar spectral features can be further complemented with other materials-relevant characteristics such as nonlinear optical behaviour and reversible redox capabilities. In fact, due to the vast flexibility of their synthetic precursors, almost any kind of activated arenes and electron-rich anhydrobases, it is immediately clear that one important endowment of squaraines composition is the extreme variety of their structures. Depending on the starting reagents it is possible to access a myriad of compounds with multivariate material functions, along with remarkable stability and wide substitution patterns imparting the required solubility.

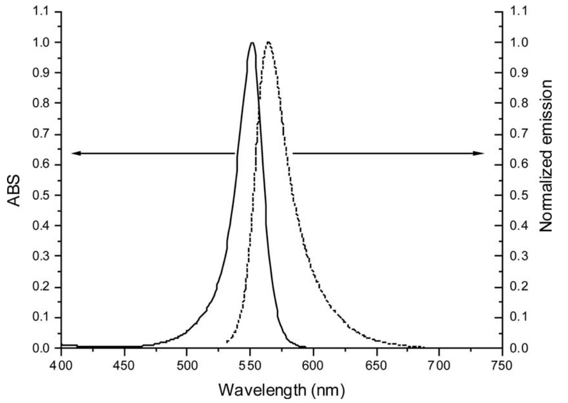


Figure 1. Normalized absorption (solid line) and emission (dashed line) spectra of derivative **1** in $CHCl_3$.

All of these favourable features promote their exploitation in a number of technologically relevant applications including photoconductivity[3] data storage,[4] light emitting field-effect transistors,[5] solar cells[6–8] and nonlinear optics.[9] Recently, it has been shown that squaraines can also behave as very efficient two-photon absorbers,[10] fluorescent histological probes,[11] highly stable fluorescent near-IR dyes,[12,13] active media for fluorescence patterning[14] and possibly as second-generation photosensitizers for photodynamic therapy (PDT).[15,16]

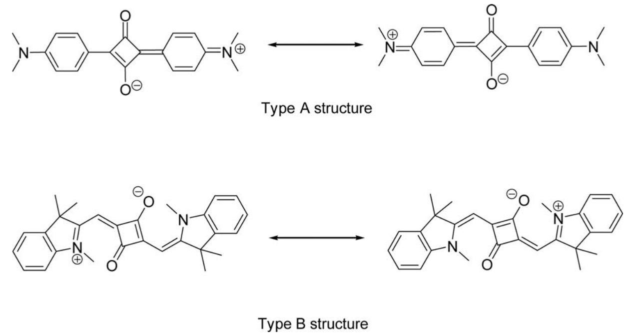
Aim of the present review is to summarize the most convenient strategies for squaraines and polysquaraines syntheses and to discuss the design strategies enabling for the preparation of squaraines having properties relevant for a given materials application. In doing so we will complement the nice review written by Ajayaghosh,[17] we will therefore focus on synthetic aspects of the squaraine chemistry and on the most recent results mainly concerning solid state and devices applications. In detail, in the first section of the review we will describe the various synthetic approaches for the preparation of symmetric derivatives, by far the most represented class of squaraines in the literature. We will then discuss nonsymmetric derivatives, core substituted derivatives, that is squaraines bearing a third functionalization group on the squarylium core, we will briefly discuss polysquaraines and we will conclude with squaraine-based rotaxanes. The second section of the review will focus on squaraines applications. As we already mentioned the interest in squaraines is mainly due to their linear and nonlinear optical properties and to their redox behaviour, we will thus describe the use of squaraines in bioimaging and photodynamic therapy. Within the topic of bio-related applications we will also discuss the use of squaraines as histological probes. We will not comment on the performances of squaraine derivatives in ion sensing as this topic was extensively and comprehensively covered in the previous review.[17] In this context we will just restraint to the citation of most recent papers in the field.[18] For the same reason we will not discuss squaraine-based light emitting transistors[5] and photopatterning.[14]

We will instead focus, within the NLO related applications, on squaraine-based electro-optic and two-photon absorbing materials. Dealing with photoconduction related applications, we will discuss the most recent applications of squaraine compounds in various kinds of devices such as solar cells, hybrid solar cells and NIR-responsive photodetectors. In all of the cases we will mainly focus on structure-property relationships highlighting the role of the active molecule design in the final device performances.

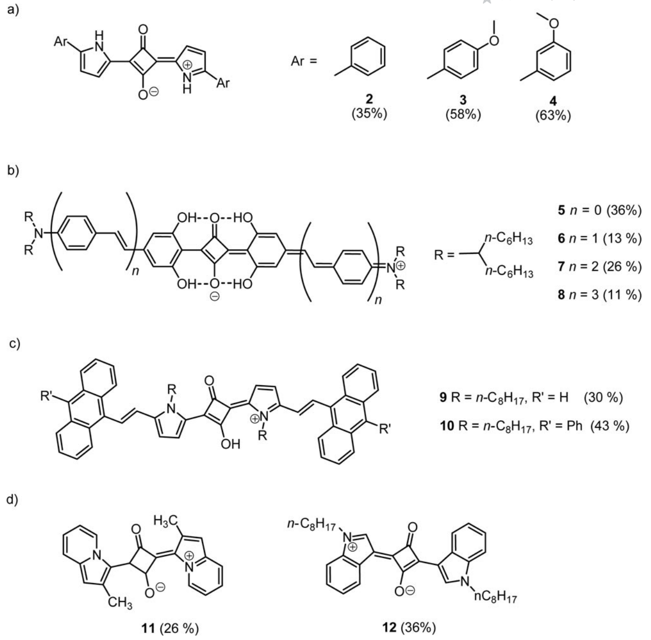
2. Syntheses of Squaraine Derivatives

2.1 Symmetric Derivatives

The vast majority of the so far reported squaraine derivatives possesses a symmetric structure and pertain to one of the two general structures represented in Scheme 2. Type A squaraines are the product of the condensation reaction of activated arenes or π-excessive heterocycles with squaric acid while type B squaraines are prepared starting from suitable anhydrobases. In both cases the squaraines are described by two equivalent canonical structures reflecting their symmetric electronic distribution. The standard synthetic pathway for their preparation requires the reaction of squaric acid with two equivalents of an electron-rich molecule. The reaction is usually performed in polar solvents such as acetic acid or high boiling point alcohols such as butanol, often in mixture with aromatic hydrocarbons such as toluene or benzene in order to azeotropically remove the water formed in the condensation reaction. In the case of particularly reactive reagents such as 2,4-dimethylpyrrole the reaction can be simply carried out in refluxing ethanol.[1]

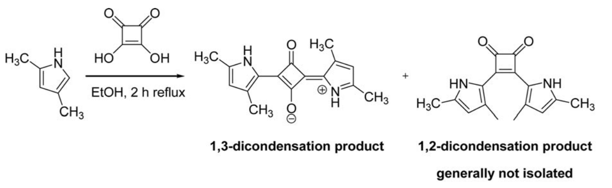


Scheme 2.



Scheme 4.

The commonly accepted reaction mechanism involves the condensation of the first electron-rich derivative with squaric acid leading to the formation of a semisquaraine intermediate. The condensation with the second equivalent of the electron-rich molecule affords the final compound. It should be noted that the reaction of the semisquaraine with the second equivalent of electron-rich counterpart is not completely regioselective and a certain amount of the 1,2-condensation product can be formed. The latter is however not characterized by a cyanine-like electronic structure, and thus it is not nearly as strongly coloured as the 1,3-derivative, and it is much more soluble in organic solvents. The 1,3-regioisomer is usually isolated simply by filtration from the cooled reaction mixture (Scheme 3).



Scheme 3.

Scheme 4 shows representative symmetric squaraine derivatives obtained by direct reaction of the corresponding precursor with squaric acid, reaction yields are reported under brackets. Bonnet synthesized a number of squaraines based on 2-arylpyrroles like derivatives **2**–**4**.[19] It is worthwhile to comment on the isolated yields, the more pronounced is the electron-rich character of the activated arene, the higher is the yield in the corresponding squaraine (Scheme 4, a).

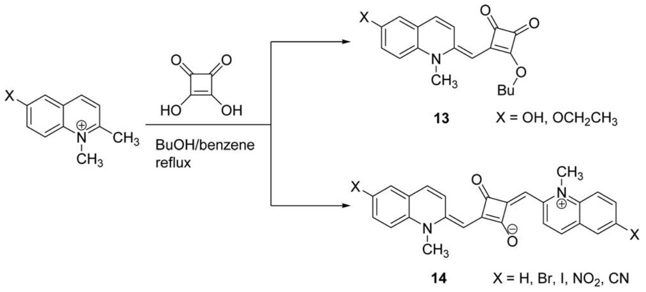
The same rule also applies to electron-rich heterocicles, for example 2,4-dimethylpyrrole readily react with squaric acid to give compound **1**, while thiophene does not react at all, unless substituted with a strong activating group such as amino groups, the same applies for thiazole.[20] Meier and co-workers prepared the series of stilbenoid squaraines **5**–**7** in order to establish structure-properties relationships between conjugation length and optical gap (Scheme 4, b).[21] In analogy with what is observed with other stilbenoid like donor acceptor compounds, they found a non monotonous relationship. The optical gap firstly decreases with the increase of conjugation, eventually increasing again in the more conjugated derivatives. The behaviour is due to the less efficient electron coupling of the end-capping donating unit and the electron deficient squarilyum core.[22]

Buschel and Ajayaghosh prepared derivatives **9** and **10** in order to study their spectroelectrochemical behaviour[23] (Scheme 4, c). Finally Beverina and Pagani prepared the first indolizine-derived squaraine **11** in the context of reactive oxygen species sensitization[24] and squaraine **12** in the context of optical limiting.[25] Note that the regiochemistry of indole reaction with squaric acid follows the standard rule for electrophilic substitution on this substrate. No 2-substituted squaraine was isolated and the regiochemistry of the reaction was confirmed by single-crystal X-ray (Scheme 4, d).[25]

2.2 Nonsymmetric Derivatives

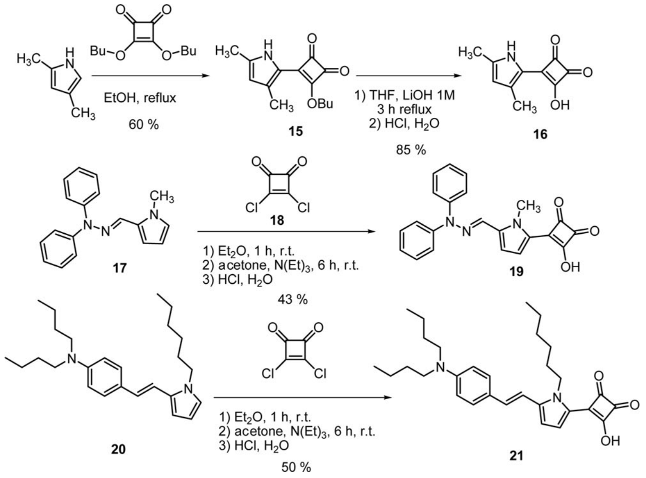
The preparation of nonsymmetric derivatives requires the isolation of the semisquaraine intermediate and its condensation with a different activated molecule in a subsequent step.

Semisquaraines can be prepared directly in one step only in the presence of a large excess of squaric acid. The chromatographic purification from the excess reagent is however tedious and inefficient. Recently Ramaiah and co-workers[26] observed that, in the case of particularly electron-rich anhydrobase derivatives of the quinoline series, the condensation reaction is selective towards the formation of the semisquarates **13**. If the quinoline ring is substituted with an electron withdrawing substituent, the reaction leads to the corresponding symmetric squaraines **14** (Scheme 5).



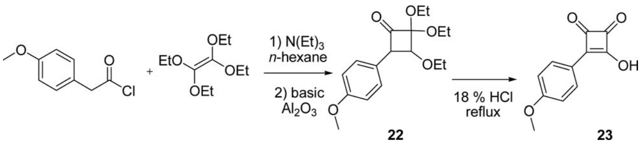
Scheme 5.

This behaviour is not general and semisquaraine derivatives are commonly prepared in a two step protocol starting from squaric acid derivatives (esters or squarylium chloride) according to the methods reviewed by Hartmann.[20] The squaric acid esters are commercially available, whilst squarylium chloride **18** can be prepared for example by reaction of squaric acid with oxalyl chloride. Strongly activated arenes such as 1,2-dimethylpyrrole and anhydrobases efficiently react with alkylsquarate, whilst less reactive derivatives such as pyrrole hydrazone or dialkylaniline react with squarilyum chloride. Both semichloride and semisquarate can be conveniently hydrolyzed to the corresponding semisquarine by basic or acidic hydrolyses. Scheme 6 shows a selection of semisquaraines syntheses.



Scheme 6.

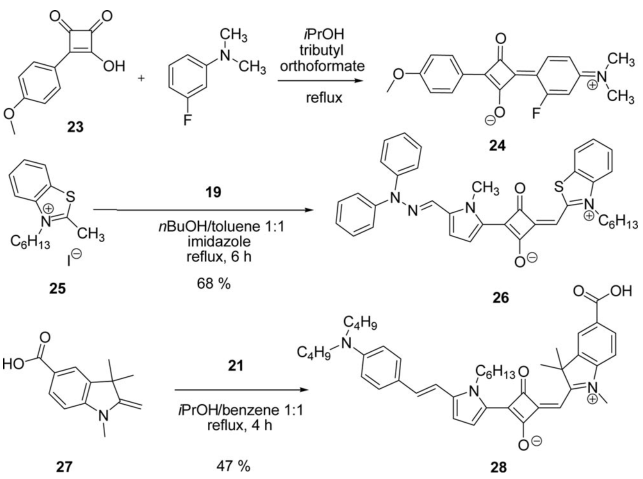
Early literature on squaraine compounds reports that the direct reaction of electron-rich derivatives with squaric acid affords products of low purity. This result was mainly due to the unavailability from commercial sources of squaric acid of suitable purity. The squaric acid had to be synthesized through a long and generally low yield process, at that time somewhat reducing the commercial appeal of squaraine dyes.[27] In 1992 Law[3c] optimized an original procedure introduced by Bellus[28] enabling for the indirect synthesis of semisquaraine derivatives not requiring the use of squaric acid. The method is exemplified in Scheme 7. Thus, (*p*-methoxyphenyl)acetyl chloride is treated with freshly prepared tetraethoxyethylene in the presence of triethylamine. The work-up of the reaction mixture in the presence of alumina, followed by acid hydrolysis affords the semisquaraine **23** in 57% yield. Although effective this method has been abandoned after the commercialization of high quality squaric acid and esters thereof.



Scheme 7.

The condensation of semisquaraines with a second equivalent of electron-rich reagent can be carried out according to two different route. In the case of reaction with an activated arene best results are obtained by refluxing the reagents in 2-propanol in the presence of tributyl orthoformate, according to the method of Law. As an example, semisquaraine **23** gave the nonsymmetric squaraine **24** in 60% yield.

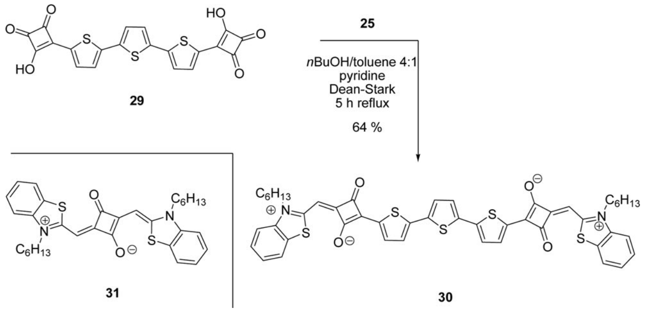
In the case of reaction with an anhydrobase, the procedure requires the refluxing of the reagents in either BuOH/toluene or *i*PrOH/benzene. The anhydrobase can be generated both in situ by the addition of a base such as quinoline or imidazole, or ex situ. By this way nonsymmetric squaraines **26** and **28** can be prepared in good yields (Scheme 8).[29]



Scheme 8.

The same two-step procedure, preparation of the semisquaraine derivative and condensation with a different electron-rich molecule, also applies to the synthesis of bis-squaraines.[30] Thus for example the bis-semisquaraine **29** can be easily converted into the bis-squaraine **30** according to the method shown in Scheme 9.

Derivative **29** can be prepared starting from *tert*-thiophene by lithiation with excess butyllithium and subsequent quenching with two equivalents of butyl squarate to give the bis-semisquarate; acidic hydrolysis yields **29**. Derivative **30** is used as a reactive oxygen species sensitizer in photodynamic therapy.[31]



Scheme 9.

The UV/Vis absorption spectra of squaraines and bis-squaraines are rather different. While in fact standard squaraines possess a sharp and intense absorption, bis-squaraines usually show a progression of vibronic replicas leading to a much broader spectrum. Figure 2 shows a comparison between the absorption spectra in CH_2Cl_2 of the bis-squaraine **30** and of the corresponding thiazole end-capped monosquaraine **31**.

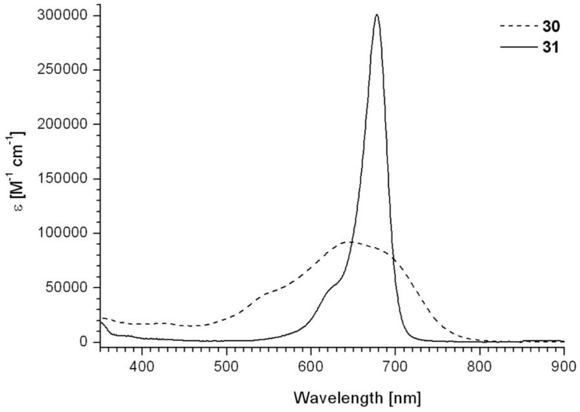


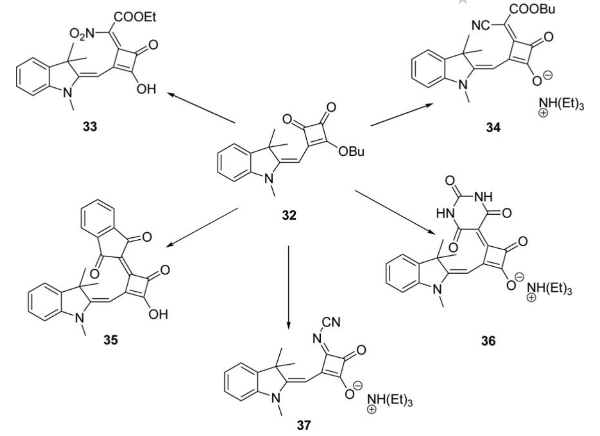
Figure 2. UV/Vis absorption spectra of bis-squaraine **30** (dashed line) and squaraine **31** (solid line) in CH_2Cl_2 solution.

2.3 Core-Substituted Derivatives

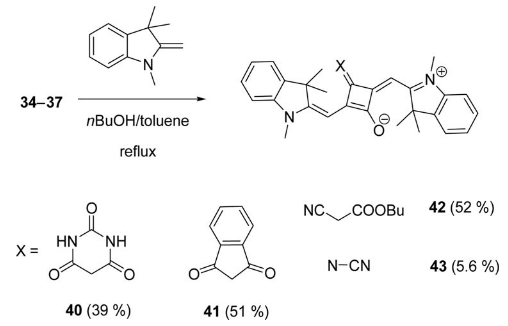
Tatarets and Terpetschnig have shown that semisquarate derivatives obtained by reaction of thiazole- and dimethylindolenine-derived anhydrobases with alkyl squarate, can react with methylene bases to give semisquaraine derivatives functionalized with an electron acceptor on the squaric core.[32] Scheme 10 shows representative derivatives obtained starting from semisquarate **32**.

The semisquaraines **33**–**37** can be reacted with a second equivalent of the trimethylindolenine anhydrobase or of a different activated derivative to give a number of core substituted squaraines. Scheme 11.

As an example of the effect of the core functionalization on the squaraine properties, Figure 3 shows the comparison between the absorption spectra of the standard symmetric squaraine **42** and that of the core substituted derivative **43** having the same molecular structure apart from the presence of a diethyl barbiturate residue on the squarylium core (Scheme 12).



Scheme 10.



Scheme 11.

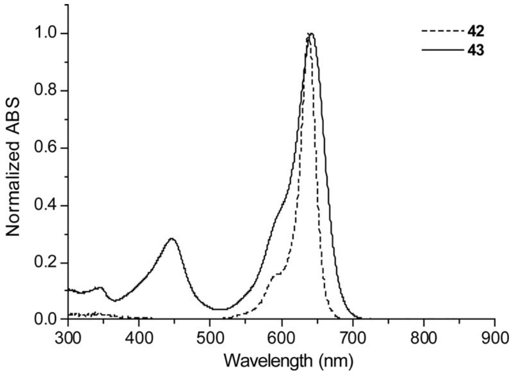
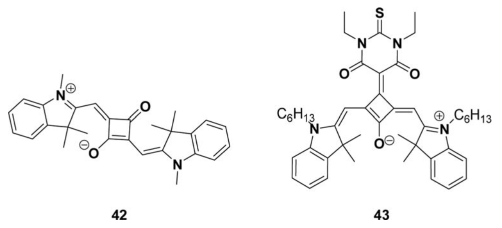


Figure 3. UV/Vis absorption spectra of derivative **42** (dashed line) and core-substituted squaraine **43** (solid line) in CH_3CN (adapted form ref.[33]).

Derivative **43** can be prepared following the same reaction procedure described in Schemes 10 and 11.[33] The spectrum of **42** shows the typical strong and sharp absorption band (λ_{max} = 638 nm, CH_3CN) arising from the cyanine-like transition associated with the delocalization of the nitrogen lone pairs all over the main conjugation axis of the



Scheme 12.

molecule. The low energy absorption band of **43** (λ_{max} = 642 nm, CH_3CN) is associated with the same cyanine like transition, whilst the additional high energy absorption band is pertinent to a different electronic transition due to the presence of the electron-withdrawing residue on the core.

The presence of the high energy absorption band in cross substituted derivatives can be exploited in the preparation of photovoltaic devices with improved light-harvesting capabilities, as we will show in section 3.4.

2.4 Squaraine-Based Rotaxanes

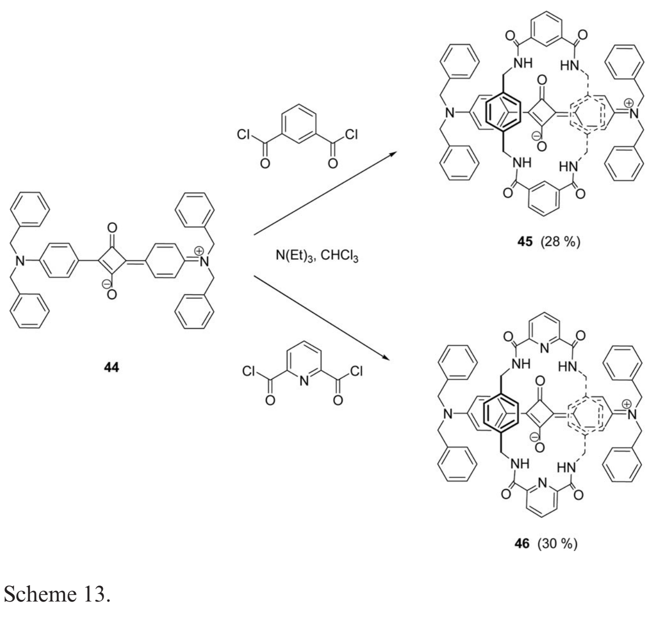
As we have shown so far, squaraine dyes can be designed in order to efficiently absorb and emit light in a large portion of the Vis/NIR spectrum. This, along with the possibility to introduce appropriate functionalities providing the required solubility, makes them good candidates for imaging applications. Their extensive exploitation in this context has so far suffered from two important limitations: chemical instability as the result of the attack by strong biological nucleophiles (thiols, for example) and a strong tendency to form nonfluorescent aggregates in biological media. Arunkumar and Smith introduced a smart supramolecular approach to solve both problems at the same time: the encapsulation of the squaraine as the thread component inside an interlocked rotaxane structure.[13]

Scheme 13 shows the synthetic strategy enabling for the preparation of such rotaxanes. The key reaction is a template Leigh-type macrocyclization that connects five building blocks in one step. The sterically hindered bis-*N*,*N*-benzylaniline-derived squaraine **44** is reacted with a mixture of 1,4-dibenzylamine and the appropriate diacyl chloride in the presence of triethylamine to give the corresponding rotaxanes **45** and **46**.

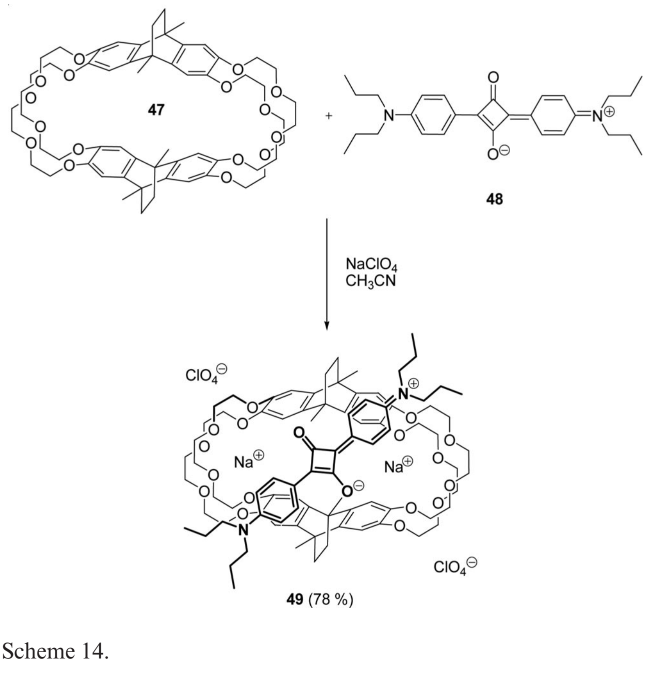
The steric shelter provided by the surrounding macrocycle is effective not only in the squaraine most reactive site protection, the squarylium core, but also in avoiding both the aggregation-induced broadening of absorption and the self-quenching of fluorescence observed for water-solubilized squaraines.[34] Even when the squaraine-rotaxanes are aggregated, the inner squaraine chromophores are unable to get close enough to interact. These favourable properties, along with a remarkably low intrinsic toxicity, make squaraine rotaxanes very versatile, high-performing molecular probes for in vitro and in vivo fluorescence imaging of cells and living animals.

More recently Grassensmith and Bradley have shown how it is possible to prepare squaraine pseudorotaxanes and to convert them into permanently interlocked rotaxane structures through a click-chemistry approach.[35]

Hsuen and Chiu introduced a different, higher yield, approach to the preparation of squaraine-derived rotaxane. The authors used a slippage strategy involving the complexation of the macrocycle **47** and squaraine **48** in the presence of sodium ions.[36] The process is efficient and simple, it should be noted however that this kind of complexes are stable in water only in the presence of a large excess of Na^+ ions. Other biological cations such as Li^+, K^+, Mg^{2+} and Ca^{2+} did not show the same effect (Scheme 14).



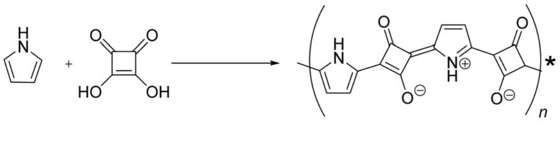
Scheme 13.



Scheme 14.

2.5 Polysquaraines

In principle any difunctional electron-rich molecule such as pyrrole, carbazole, difunctional ahydrobases and any complex molecule possessing two suitable electron-rich sites in its structure can react with squaric acid to form a polymer. The first reported reaction leading to a compound related to squaraine dyes is indeed a polycondensation. In 1965 in fact, Triebs and Jacob reported that the reaction of an equimolar amount of pyrrole and squaric acid leads to the formation of a strongly coloured and completely insoluble material later identified as the polysquaraine **50**[1] (Scheme 15).



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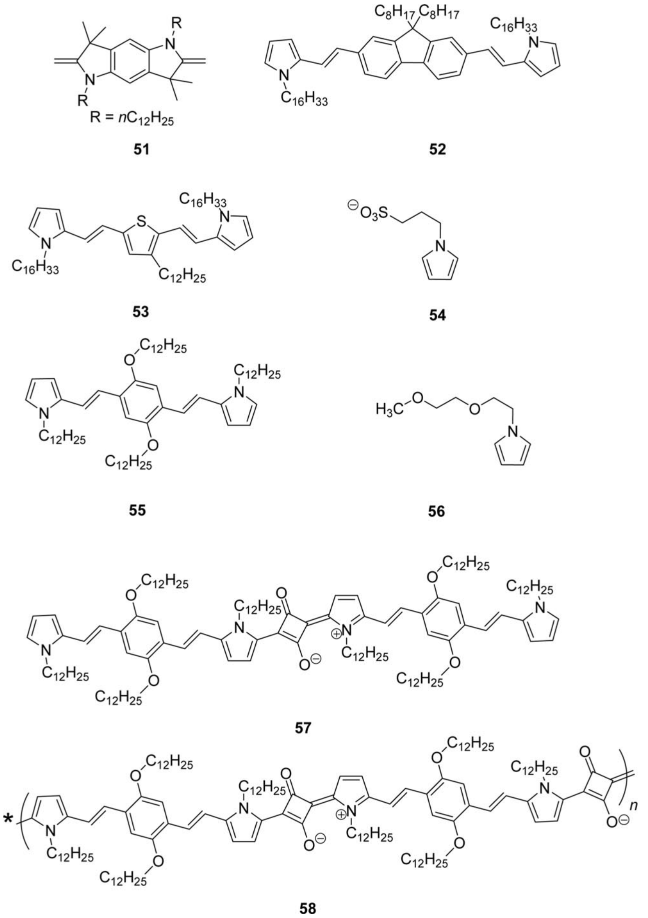
Scheme 15.

Polysquaraine compounds were, first theoretically,[37] then experimentally considered as suitable candidates for low band-gap semiconducting polymers. The latter application is becoming a relevant topic in the expanding field of plastic electronics.[38] The first attempts to produce solution processable materials were unsuccessful, mainly due to the extremely low solubility of these materials,[39] later works of Havinga group[40] and more recently of Ajayaghosh group demonstrated the possibility to synthesize soluble polymers having optical absorption in the technologically relevant 800–1200 nm window.[38] Scheme 16 shows a selection of the difunctional monomers so far polymerized with squaric acid, **51**,[40] **52**,[41] **53**,[42] **54**,[43] **55**,[44] **56**.[45]



Scheme 16.

In particular, Ajayaghosh performed a detailed study on the control of optical gap and electronic properties of the polysquaraines derived from monomer **55** and correlated structures.[44] He found in particular that there is little difference in the UV/Vis spectrum between the simple pyrrolic squaraine **1** and the corresponding polymer **50**. Conversely, the increase of conjugation length in the monomer through the introduction of an electron-rich spacer, is a convenient way to control the polysquaraines optical gap, enabling efficient absorption over a large portion of the Vis/NIR spectrum. Figure 4 shows the absorption spectra of the model monomeric squaraine **57** and of the corresponding polymer **58** in toluene solution, as an example of polymeric squaraines properties.

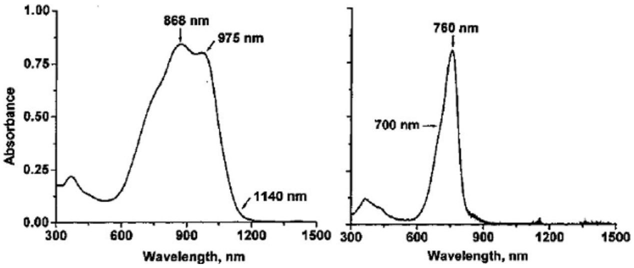
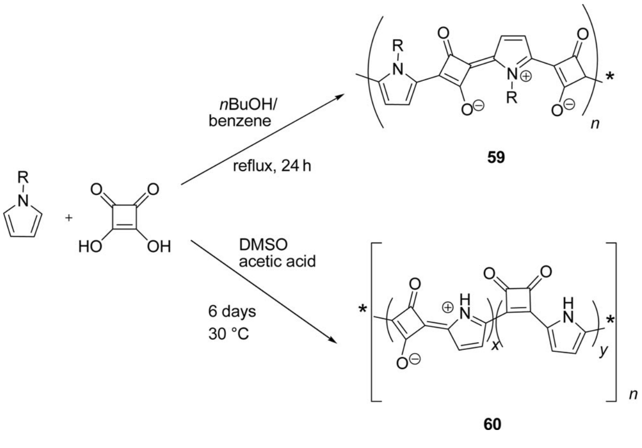


Figure 4. UV/Vis/NIR absorption spectra of a toluene solution of monomeric squaraine **57** (right) and of the corresponding polymer **58** (left) (adapted form ref.[44] with permission. © 2002 American Chemical Society).

It should be stressed that, as we mentioned in paragraph 2.1, the reaction of squaric acid with an activated compound is not completely regioselective. It is thus possible, depending on the reaction conditions, that the structure of a polysquaraine contains diketones defects derived from



Scheme 17.

1,2-dicondensation instead of the dominating 1,3 one. It has been shown that, under controlled conditions, it is possible to influence the condensation regiochemistry thus deliberately increasing the occurrence of 1,2-defects[46] (Scheme 17).

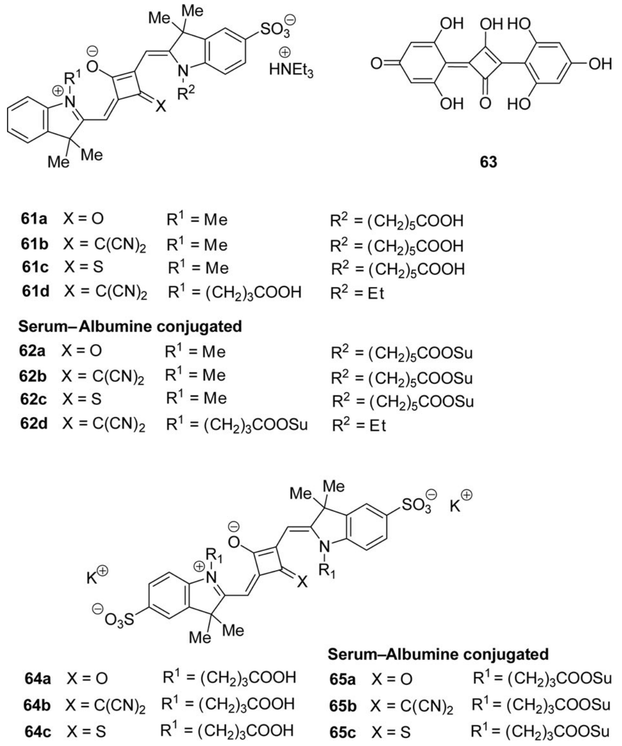
3. Applications of Squaraine Materials

3.1 Bio-Imaging Probes and Bioconjugation

Squaraines have been extensively used as the signalling units in chemosensors and chemodosimeters because of their absorbance and fluorescence spectra and fluorescence quantum yields which get perturbed with the polarity of the medium, temperature, pH, and other stimuli. Indeed, the intense absorption and the emission arising from charge transfer transitions during electronic excitation are highly environmentally sensitive.[47] Therefore, squaraine dyes can signal the binding event in the form of measurable changes in their optical properties. For example, the indolenine-based squaraines **61a** and **64a** are able to sense the alterations in the hydrophobicity of bilayer membranes. Their emission spectra in fact show a red shift together with a significant increase of the intensity on going from aqueous to lipidic environment[48] (Scheme 18). An even more striking example of this behaviour is shown by the squaraine **63**, fluorescence quantum yield of which is less than 0.002 in aqueous media and undergoes a 90-fold enhancement by encapsulation within the lipophilic core of β-cyclodextrin.[49] The fluorescence quantum yield is a function of the singlet excited state lifetime. The strong dependence of squaraine fluorescence quantum yield on their environment suggests their exploitation as molecular probes in applications based on fluorescence lifetime (FLT).[50] Terpetschnig described the spectroscopic properties of the water-soluble indolenine-based squaraines **61**–**62**, **64**–**65** before and after conjugation with bovine serum albumin (BSA).[51]

The results shows that all of the dyes possess a low quantum yield in water solution ($\Phi_f \approx 0.02$–0.10) and coherently a short fluorescence lifetime (from 0.15 to 0.29 ns for the nonsymmetrical squaraines **61a**–**c** and from 0.41 to 0.84 ns for the symmetrical ones **64a**–**c**), both classes of derivatives however show increased brightness ($\Phi_f \approx 0.13$–0.45) and fluorescence lifetimes upon covalent attachment to BSA (from 1.30 to 3.32 ns for **62** and from 1.84 to 3.26 ns for **65**).

We have already mentioned that the squarylium core of squaraine dyes is reactive towards strong nucleophiles. Ros-Lis et al. reported a method for the detection of cyanide[52] and thiols[53] based precisely on this reactivity. The reaction with the target analyte can in fact be easily monitored as either bleaching of the squaraine absorption and/or quenching of its fluorescence. A similar approach was also exploited by Ajayaghosh et al. in the detection of low molecular weight amino thiols in human blood plasma (HBP).[54] In this case they monitored the bleaching of squaraine **66** as a consequence of the reaction with the target thiol (Scheme 19).



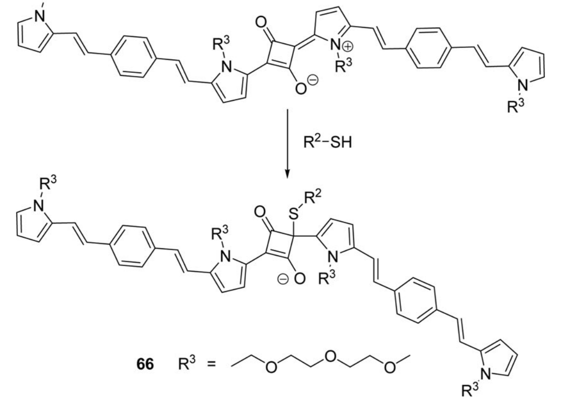
61a	X = O	R^1 = Me	$R^2 = (CH_2)_5COOH$
61b	$X = C(CN)_2$	R^1 = Me	$R^2 = (CH_2)_5COOH$
61c	X = S	R^1 = Me	$R^2 = (CH_2)_5COOH$
61d	$X = C(CN)_2$	$R^1 = (CH_2)_3COOH$	R^2 = Et

Serum–Albumine conjugated

62a	X = O	R^1 = Me	$R^2 = (CH_2)_5COOSu$
62b	$X = C(CN)_2$	R^1 = Me	$R^2 = (CH_2)_5COOSu$
62c	X = S	R^1 = Me	$R^2 = (CH_2)_5COOSu$
62d	$X = C(CN)_2$	$R^1 = (CH_2)_3COOSu$	R^2 = Et

			Serum–Albumine conjugated		
64a	X = O	$R^1 = (CH_2)_3COOH$	**65a**	X = O	$R^1 = (CH_2)_3COOSu$
64b	$X = C(CN)_2$	$R^1 = (CH_2)_3COOH$	**65b**	$X = C(CN)_2$	$R^1 = (CH_2)_3COOSu$
64c	X = S	$R^1 = (CH_2)_3COOH$	**65c**	X = S	$R^1 = (CH_2)_3COOSu$

Scheme 18.



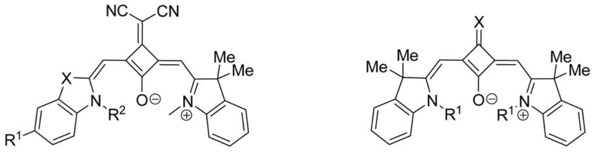
Scheme 19.

The ease of chemical modification of the squaraine backbone enables the ready incorporation of different reactive functionalities in order to study their interaction with biological targets and the tuning of optical properties.[55] Squaraine dyes have indeed been widely used as fluorescent protein labels.[56] Oswald et al. modified squaraine dyes with succinimidyl esters and linked covalently them to BSA and human serum albumin (HSA) proteins. The fluorescence quantum yields of the dyes increased from 0.15 to 0.6–0.7 when attached to protein allowing measurements in whole blood at detection limits twice as low as alternative assays employing Cy5.[57]

These excellent results led to the development of Seta dyes, a class of commercially available squaraine dyes successfully employed for example as conjugate with lysozyme

(Lz) to explore protein–lipid interactions.[58] and with biotin to monitor the biotin/antibiotin interaction by fluorescence lifetime analysis.[59]

Welder et al.[60] described the interaction of 3-oxosubstituted squaraines in the presence of various proteins. They concluded that both the symmetrical and unsymmetrical squarylium dyes show enhancement of fluorescence intensity upon noncovalent interactions with proteins such as HSA, β-lactoglobulin A and trypsinogen. More recently, Yarmoluk et al.[61] synthesized and evaluated structure–properties relationships in the series of 3-oxo- and 3-dicyanomethylene squaraines containing indolenine, benzothiazole and benzoxazole moieties **67**–**68** for detection of a variety of proteins such as bovine BSA, HSA, ovalbumin, avidin from hen egg white (AVI), and hydrolases such as trypsine and lysozyme (Scheme 20).



67a $X = O$ $R^1 = H$ $R^2 = Me$
67b $X = S$ $R^1 = H$ $R^2 = Me$
67c $X = C(CH_3)_2$ $R^1 = Me$ $R^2 = (CH_2)_5COOH$
67d $X = C(CH_3)_2$ $R^1 = SO_3^{\ominus}$ $R^2 = (CH_2)_5COOH$

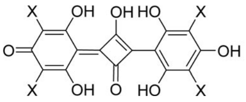
68a $X = NHBu$ $R^1 = Me$
68b $X = NHBu$ $R^1 = Et$
68c $X = NEt_2$ $R^1 = Me$
68d $X = C(CN)_2$ $R^1 = Me$

Scheme 20.

All of the investigated squaraines show considerable emission quantum yield enhancement in the presence of BSA only; fluorescence enhancing of the dyes in the presence of other albumins (HSA and ovalbumin) is significantly lower, while in the presence of hydrolases lysozyme or trypsin squaraines either insignificantly increased or even decreased their fluorescence intensity. Finally, Thomas et al. described the synthesis and glucose-biosensing performance of aniline- and benzothiazolium-based squaraines functionalized with a thiol-reactive iodoacetyl group when conjugated to mutants of the D-glucose/D-galactose-binding protein (GGBP).[62] In this case they found that the fluorescence intensity of the dye underwent significant changes in the presence of glucose, because of polarity changes in the squaraine binding site.

3.2 Photo Dynamic Therapy (PDT)

Squaraine dyes have also been successfully employed as second generation photosensitizers for photodynamic therapy (PDT). This well-established medical treatment involves the insurgence of cytotoxic species in the cellular environment following irradiation of a suitable dye with visible light in the presence of molecular oxygen. A number of different squaraines are currently considered as potential second generation photosensitizers for PDT, mainly as a consequence of their intense absorption and emission localized in the transparency window of biological tissue (600–900 nm). Amongst the different employed structural motifs are: heteoaryl anhydrobases,[16,63] aniline,[12] pyrrole,[19,34] indolizine,[24,34] quinoline,[26] and trihydroxybenzene derivatives.[15] Despite the huge synthetic effort so far reported, only a few of these dyes have been further investigated in vitro on tumour cells or in real PDT trials on small animals. Ramaiah et al.[15b] reported that the halogenation of squaraine **63** is essential in order to observe an efficient PDT treatment on AS52 Chinese hamster ovary cells. In particular, the tetraiodo derivative **69a** was used in small animal PDT treatments of mice having an implanted skin tumour. The treatment was able to considerably reduce the tumour volume[64] (Scheme 21).



69a $X = I$
69b $X = Br$

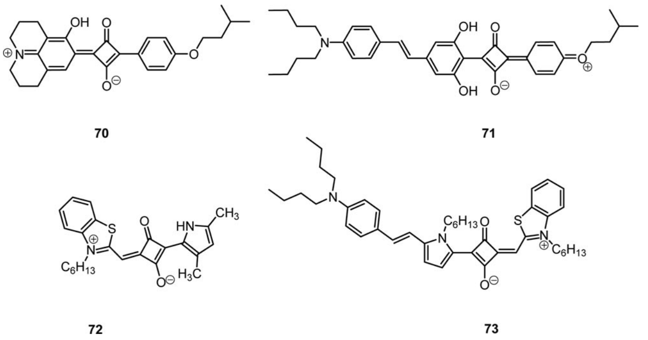
Scheme 21.

Moreover, Pagani and Xodo tested the photosensitizing properties of benzothiazole-based mono- and bis-squaraines (derivatives **31** and **30** of Scheme 9, respectively) in four different cancer cell lines. The authors found that in the dark these squaraines are largely nontoxic, but when they are irradiated with white light at a fluence of 15 J/cm^2, they promote a strong photodynamic effect on a number of tumour cells.[65] Since the transport of the sensitizer through cell membrane is critical to its effectiveness, different strategies have been studied in this regard. Good water solubility and prevention of the aggregation are indeed desirable properties for biological fluorescent labels and PDT sensitizers. Squaraine dyes are generally not soluble in water, their solubility has been thus increased upon suitable functionalization with polar functional groups. In particular, the sulfonate group,[51,61] carbohydrates,[66] quaternary ammonium groups,[50] the carboxy group,[50] polyethylene glycol residues,[24,34,43,44] hydroxy groups,[67] and the phosphonic group.[68] Other strategies take advantage of the strong affinity of some squaraines (i.e., trihydroxybenzene-based squaraines) with BSA[67] and of the synthesis of cholesterol conjugated dyes to enhance cell permeability and perform their photodynamic effect.[66]

3.3 Nonlinear Optical Applications

3.3.1 Second Harmonic Generating Squaraines

The interest in organic chromophores having strong Second Harmonic Generation (SHG) capabilities is related to their possible exploitation in low cost electro-optic devices such as high-speed photonic switching and electro-optic modulators.[69] Commonly, the extensive polarization of the chromophore π-electron structure required to generate highly efficient NLO chromophores is provided by the exploitation of a strong interaction between donor and acceptor groups connected by a conjugated bridge. This design strategy leads to the so called push-pull chromophores, by far the most studied class of second harmonic generating chromophores.[70]



Scheme 22.

The rationalization of push-pull chromophores behaviour is validated in the framework of the bond length alternation (BLA) model.[71] In particular, the plot of the molecular quadratic hyperpolarizability β, measured by electric-field-induced second harmonic generation (EFISH), vs. BLA shows that in push-pull polyenes it is possible to account for positive β values (BLA < 0) in the case of molecules showing an increase of their dipole moment on going from the ground to the excited state and for negative values (BLA > 0) when the excited state dipole moment is smaller than the ground state one.[71] Thus, while the majority of the push-pull derivatives show positive quadratic hyperpolarizability values, zwitterionic compounds are known to possess negative values.[72] At BLA = 0, the so called cyanine limit, the compound is expected to have no SHG behaviour, at least within the framework of the "two level model".[73] Symmetric squaraines are not expected to show SHG signal in solution,[74] as they fall exactly at the cyanine limit point in the BLA vs. β plot. It has been shown that, on going from symmetric to nonsymmetric squaraines, the two possible ground state canonical structures do not equally contribute to the description of the electronic distribution and a ground state static dipole moment can be measured.

One important consequence of such symmetry breaking is the emergence of a sizeable second order nonlinear optical (NLO) behaviour, as thoroughly discussed by Marder and co-workers[9] (Scheme 22) shows some of the most performing derivatives synthesized for second order NLO applications. In the case of derivative **71**, the authors measured $\beta(0)$ values as high as $170 \cdot 10^{-30}$ esu, thus ranking squaraines among the most performing dipolar chromophores for SHG.

In order to further characterize the electronic structure of nonsymmetric squaraines, Beverina and Pagani made a solvatochromic study on the series of benzothiazole containing squaraines **26** (Scheme 8), **72** and **73** (Scheme 22); Figure 5 shows their absorption in selected solvents.[29]

None of the derivatives display a particularly relevant solvatochromic behaviour. In standard push-pull dipolar chromophores, and according to the Two State Model, this feature would represent a likely hint of weak SHG behaviour. It is however important to stress that a discussion on squaraine solvatochromic behaviour restricted to the absorption maxima shifts upon variation of the surrounding polarity would be misleading. In fact, in cyanine-like compounds the absorption maximum position is not the only gauge of charge localization phenomena.[75] Symmetric squaraines most characteristic spectral feature is a particularly narrow band width, a direct consequence of their highly symmetric charge distribution. Conversely efficient push-pull chromophores are characterized by a strong charge-transfer transition connected with a major variation, and sometimes even a change in the sign, of their dipole moment. This effect generates particularly broad and featureless absorption bands.

The full width at half of the maximum (FWHM) of the absorption band can thus be considered as a good probe for charge delocalization, as it has already been shown by Tolbert in the context of charge localization in long chain cyanines.[76]

A common feature of the thiazole containing squaraines **26**, **72**–**73** is the increase of their FWHM upon increase of the solvent polarity. This behaviour can be rationalized in terms of increase of the charge transfer contribution to the HOMO–LUMO transition upon increase of the surrounding medium polarity.

The solvatochromic behaviour and the NLO characterization for **26**, **72**–**73** are consistent. Derivative **72** shows in fact a positive and rather large $\mu\beta_{1.907}$ value in $CHCl_3$, as determined by the EFISH technique working with a non-

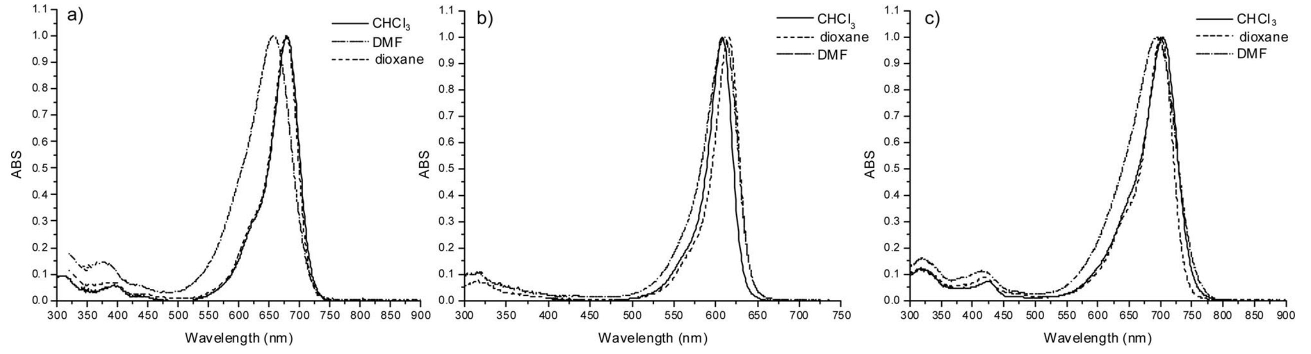


Figure 5. Absorption spectra of squaraines: a) **26**; b) **72**; c) **73** in $CHCl_3$, dioxane, and DMF.

resonant incident wavelength of 1.907 µm, of 800·10^{-48} esu along with a positive solvatochromic behaviour, whilst both **26** and **73** possess a negative solvatochromism and a negative $\mu\beta_{1.907}$ value (–650 and –335·10^{-48} esu, respectively).

Nonsymmetric squaraine can thus behave as efficient SHG derivatives, the entity of the NLO behaviour being dependent upon their deviation from a symmetric electronic distribution.[29]

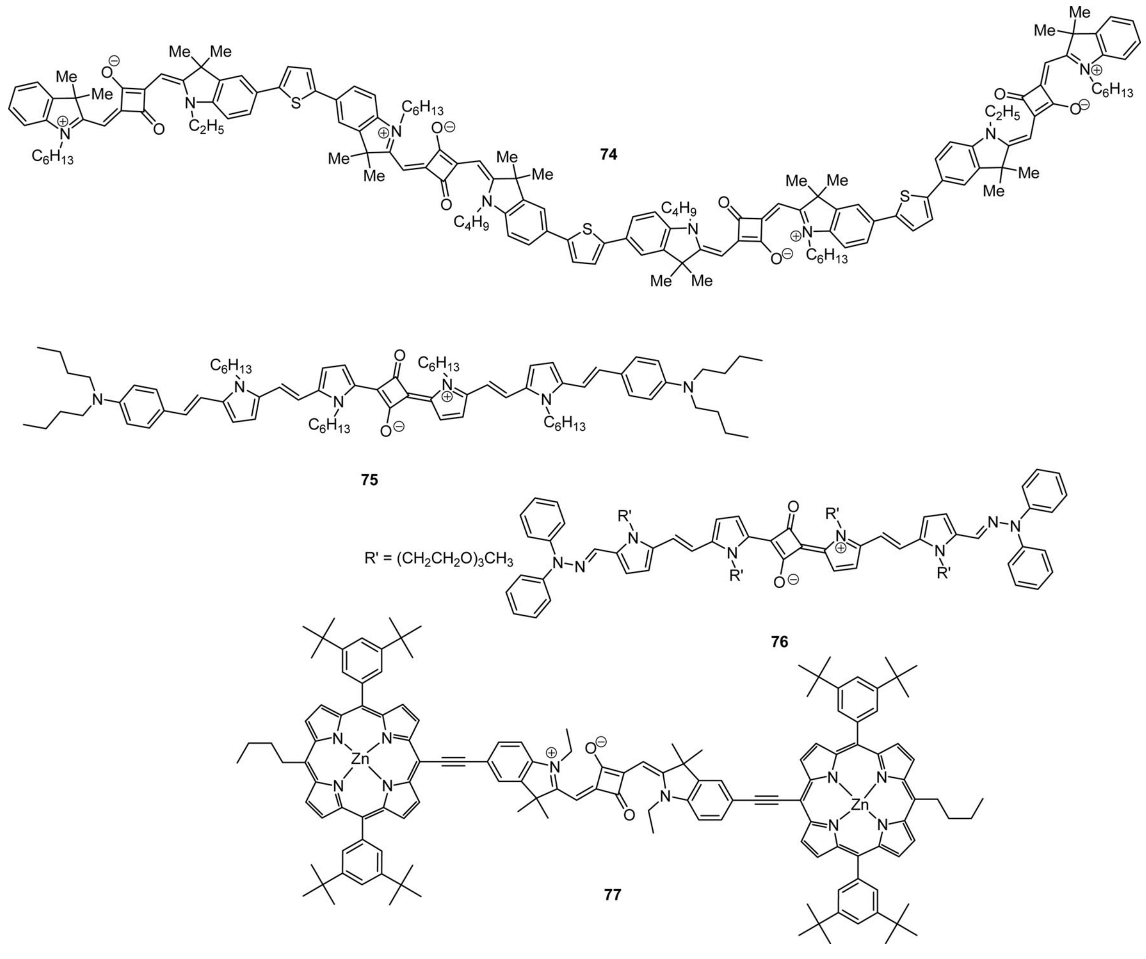
3.3.2 Two-Photon Absorbing Squaraines

Organic materials exhibiting large two-photon absorption (2PA) cross-sections (δ) are currently of considerable interest for applications in a number of new areas including photodynamic therapy, optical pulse suppression, two-photon fluorescence microscopy, 3D microfabrication, and 3D optical data storage.[70] TPA occurs when a molecule is able to simultaneously absorb two photons of the same or different energy, and be promoted to one of its excited states. The energy gap involved in a TPA process is the sum of the energies of the two involved photons. As a consequence, TPA takes place at much longer wavelengths than the cut-off wavelength of the linear absorption.

Various structural motifs have been found to exhibit high δ values. Amongst them, donor-acceptor-donor (D-A-D) conjugated species play a prominent role.[77] The study of squaraines as possible performing TPA dyes was pioneered by Scherer et al., who studied D-A-D squaraine chromophores with dimethylindoline anhydrobase donors bearing a variety of substituents.[10] Conjugated oligomers like derivative **74** of Scheme 23 were also considered. The authors reported δ values as high as 5000 GM observed for 2PA peaks in the 820–890 nm.

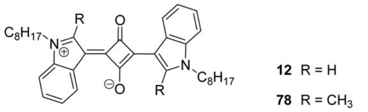
Marder et al. later observed that it is possible to further enhance the squaraine TPA performances by the extension of the conjugated π-system connecting the end capping donor groups to the electron deficient squarylium core. Derivatives **75** and **76** gave TPA values of 33000 and 14000 GM, respectively—by far the highest TPA values ever reported.[78]

In squaraine dyes the detuning energy, that is the difference in energy between the LUMO and the energy employed in the two photon excitation process, is rather small compared to those observed in other classes of chromophores. In many cases it is not possible to measure a TPA process at very small detuning energies values due to the onset of 1PA, whereas in squaraines this is possible due to their very sharp 1PA absorption bands. Other examples of chromophores with similarly small detuning energies and consequently large cross-sections include perylene derivatives[79] and porphyrin dimers.[80] Recently Odom and



Scheme 23.

Marder reported on the synthesys of a porphyrin–squaraine–porphyrin triad (**77** in Scheme 24) dysplaing a very high TPA cross section over a wide range of wavelenghts. The overall nonlinear performances also show a more than additive enhancement with respect to the porphyrins and squaraine subunits. The enhancement observed is believed to be due to substantial electronic coupling between the porphyrin and squaraine moieties, an interpretation also confirmed by the DFT frontier orbitals calculation. Derivative **77** could have applications in broadband NIR pulse suppression.[81]



Scheme 24.

Even if derivatives **74**–**77** show exceedingly strong TPA cross section, they are not applicable at least in the case of two relevant TPA technological applications, optical limiting and two photon induced photopolymerization.[25] Due to their very small linear optical gap, highly conjugated squaraines also possess very small TPA gap. The peak of their TPA performances is usually observed in the 900–1100 nm region. Now, while an ideal TPA photoinitiator should absorb at the shortest possible wavelengths to enable the best possible 3D resolution, optical limiting aimed at the eye protection usually requires peak performances only in the 700–1000 nm window.[82]

Pagani and Beverina proposed the indolic squaraines **12** and **78** as viable large optical gap TPA derivatives[25] (Scheme 24).

Note that while the structure of derivative **78** can be straightforwardly assigned by ^{1}H NMR spectroscopy and elemental analysis, structural characterization of **12** is challenging. In fact, even if indole electrophilic substitution usually occurs at the 3 position, the regioselectivity of the reaction leading to **12** is not obvious and in any case may not be easily probed by multinuclear NMR spectroscopy. Therefore, to further confirm the molecular structure and provide additional structural characterization, single crystals of both derivatives were grown from solution. Figure 6 shows the crystal structure of **12** and **78**. Clearly, the X-ray data confirm the reaction regioselectivity.

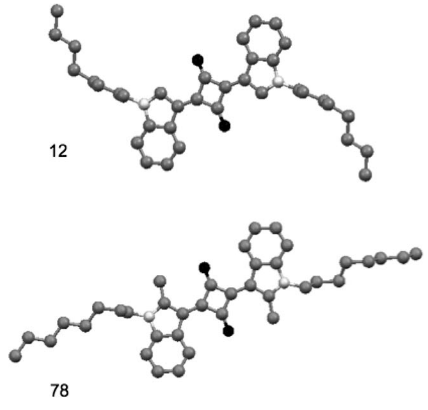


Figure 6. Crystal structures of compounds **12** (a) and **78** (b). Hydrogen atoms are omitted for clarity.

Compounds **12** and **78** exhibit large TPA performances in the 700–800 nm target region. Within this spectral region, derivative **12** in particular reaches a TPA cross section as high as 450 GM, which is remarkable considering the simple molecular structure, limited π-conjugation length and high thermal and photochemical stability. Figure 7 shows the one-photon and two-photon absorption spectra for the two derivatives.

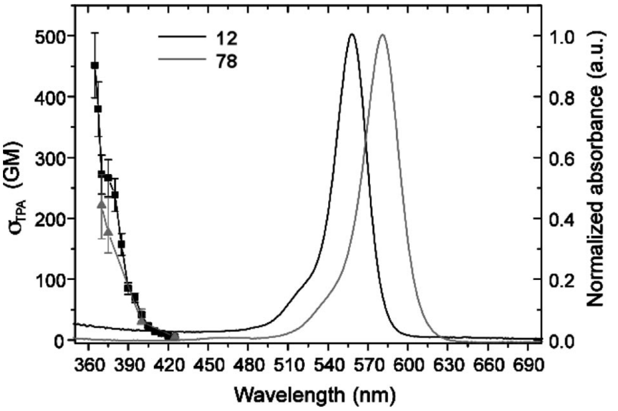
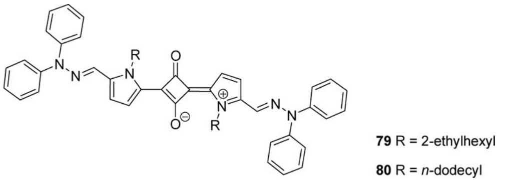


Figure 7. Linear (lines) and TPA (data points and lines) spectra in CH2Cl2 for compounds **12** (black), **78** (gray). TPA spectra plotted vs. the halved photon wavelength corresponding to the TPA transition energy (reproduced with permission from ref.[25], © 2008 American Chemical Society).

3.4 Photoconduction Related Squaraines Applications

Photovoltaic cells are potentially one of the most important emerging new technologies, since energy harvesting by solar cells promises to be of increasing necessity as an abundant and renewable alternative to fossil combustibles. Among the various kinds of organic-based devices proposed in recent years, two cells architectures appear to be the most promising embodiments for large-scale production: the bulk-heterojunction solar cells (BHJ-OPV)[83] and the dye-sensitised solar cells (Grätzel cells or hybrid electrochemical solar cells: DSCs).[84] Squaraine compounds are playing an important role in both technologies, as they possess a number of important features relevant for photovoltaic technology.

Dealing with the first class of cells, the BHJ-OPV devices, a suitable organic material, the donor, is usually mixed with a soluble n-channel fullerene derivative, (6,6)-phenyl C61 butyric acid methyl ester (PCBM). Performing donors need to fulfil a number of different requirements: a) efficient absorption in the largest possible portion of the Vis/NIR spectrum (panchromaticity), b) reversible redox behaviour, c) HOMO and LUMO levels in suitable positions in order to maximize both the rate of charge transfer to the acceptor and the difference in energy between the LUMO of the acceptor and the HOMO of the donor (this energy difference is related to the cell open circuit voltage), c) suitable solubility and stability enabling processability. One of the early applications of squaraines in materials includes photoreceptors in copiers and laser printers, thus already highlighting the attraction these dyes offer for applications involving photoinduced charge transfer processes.[3,85] Squaraines were studied as active components in single-layer OPVs during the ’70s and ’80s, affording maximum power conversion efficiencies (PCEs) of ca. 0.02 %.[6,86] More recently Pagani and Marks extensively employed the hydrazone end capped squaraines **79** and **80** in the preparation of performing OPV devices[87] Scheme 25.



Scheme 25.

The use of linear and branched alkyl chain substituents allows managing the solubility and at the same time offers a tool for the control of the solid state organization, a key feature in the BHJ-OPV technology.

Figure 8 shows normalized optical spectra of **79**,**80**-derived films (from $CHCl_3$) and solutions (in $CHCl_3$). As already discussed in the introduction, the absorption of the films is significantly broadened with respect to the solution, a favourable feature for OPV applications. The HOMO and LUMO energies of **79** an**d** **80**, as estimated by cyclic voltammetry, are –3.3 eV and –5.0 eV, respectively, for both molecules. These energies are suitable for the preparation of an OPV device exploiting PCBM as the acceptor. As it is shown in Figure 8 in fact the squaraine LUMO level is above the PCBM LUMO, thus making a photoinduced charge-separation energetically favourable, while the squaraine HOMO is nearly 1 eV below the PCBM LUMO. This value is a prerequisite for high open-circuit voltage.

Squaraine-based BHJ OPV can be fabricated by spin-coating under ambient atmosphere, a very important advantage over polymer-based devices.

Spin-casting of a 1:3 squaraine **79**:**PCBM** blend from $CHCl_3$ solutions yields a maximum efficiency of 1.26 %, with a short circuit current of 5.70 mA/cm^2, at that time one of the highest efficiencies reported for small-molecule OPVs.[88] Studies are currently underway to better define and optimize processing/microstructure/photovoltaic response relationships.[89]

As we already mentioned, one possible way to further increase the reported efficiencies is the sensitizer absorption spectrum broadening. Torres and Pagani proposed a supramolecular approach enabling for the preparation of a squaraine–phthalocyanine ensemble able to absorb over a larger portion of the solar spectrum with respect to the isolated compounds.[90]

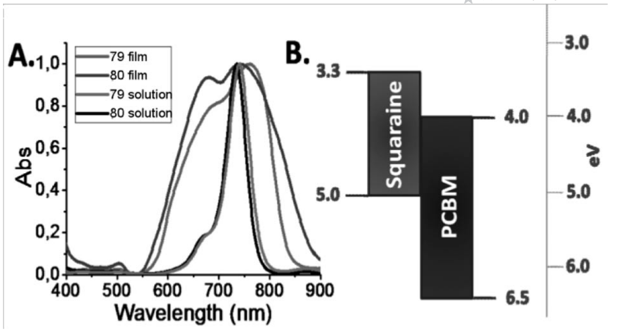


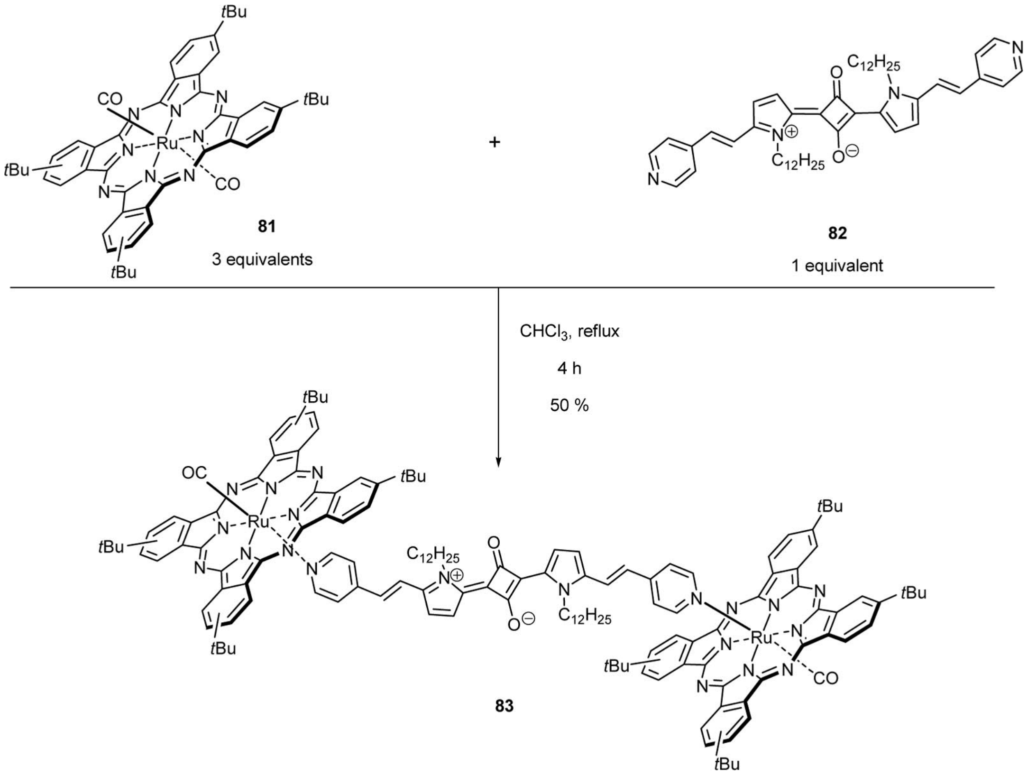
Figure 8. A. Normalized optical absorption spectra: **79** (grey line) and **80** (black line) as solutions in $CHCl_3$; **79** (grey line) and **80** (black line) as films from $CHCl_3$. B. HOMO/LUMO levels for **79** and **80** vs. PCBM (reprinted with permission form ref.[87], © 2009 American Chemical Society).

The ensemble **83** was prepared in 50 % yield by reacting 3 equiv. of the Ru-phthalocyanine **81**[91] with 1 equiv. of the bidentate squaraine ligand **82** in refluxing chloroform (Scheme 26).

Figure 9 shows the normalized optical spectra of **83** in $CHCl_3$ solution and film (from $CHCl_3$). The hybrid molecule efficiently covers the 550–850 nm region. Additional high energy absorption bands are also present in the 270–400 nm region. While the most intense absorption at 646 nm is due to the phthalocyanine portion, the band centered at 706 nm is attributed exclusively to the squaraine fragment. The squaraine band is 25 nm red-shifted with respect to the free base **82**, while the phthalocyanine absorption is almost unchanged. This behaviour is ascribed to the interaction between the squaraine pyridic nitrogen and the ruthenium ion, resulting in an enhancement of the pyridine ring electron-withdrawing capabilities.

The occurrence of an intramolecular charge transfer process within the ensemble **83** fragments upon photoexcitation was confirmed by steady-state/time-resolved fluorescence and time-resolved transient absorption measurements. In a few explorative trials the Authors measured an efficiency of ca. 0.3 %, mainly related to the low short circuit current, commonly ascribed to low mobility (i.e., typical of the starting materials).[5,92] Rational tailoring of the redox properties of the bridging squaraine is believed to allow a further improvement of the device performances.

Although squaraine-based OPV devices are usually produced by solution processes, recently Wang, Forrest and Thompson obtained a very efficient device by vacuum evaporation of squaraine **84** in an heterojunction structure of composition ITO/squaraine 78/C60/bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline). The thickness of the various layers was optimized to give a remarkable 3.1 % efficiency for a device possessing a 65 Å layer of derivative **84**.[93] This impressive result opens the way for sublimable squaraines as performing sensitizers in high vacuum grown OPV devices, a class of cells where polymeric materials are inapplicable (Scheme 27).



Scheme 26.

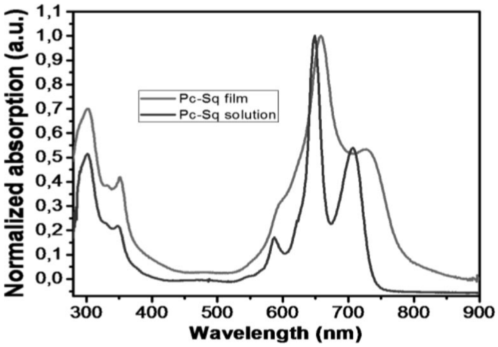
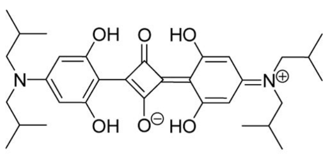


Figure 9. Normalized optical absorption spectra of ensemble **83** in $CHCl_3$ solution (black line) and films from $CHCl_3$ (gray line) (adapted with permission form ref.[90], © 2009 Royal Society of Chemistry).



Scheme 27.

The device architecture for a Grätzel cell is quite different. In such cells the light is absorbed by an organic dye (sensitizer) forming an excited state (exciton). Electron transfer takes places from the dye excited state to an inorganic semiconductor, usually titania, in close proximity to the sensitizer, and the charge is then collected at a metal electrode. At the same time, the hole is transferred from the dye, through a liquid or solid electrolyte, to the counter electrode (Figure 10).

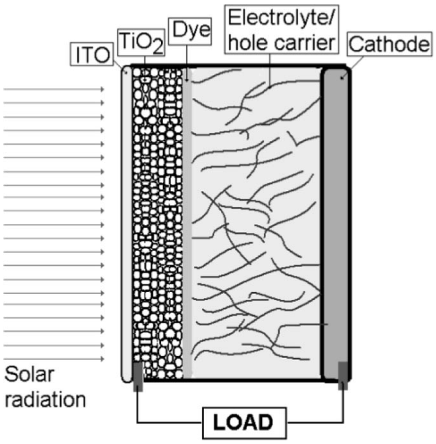
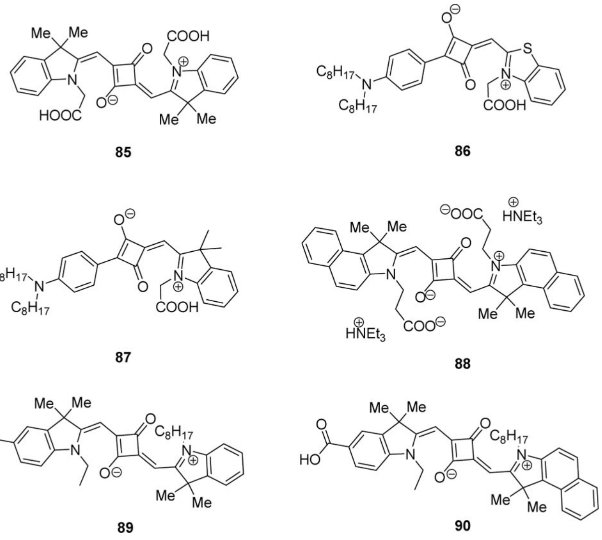


Figure 10. Schematic representation of a Grätzel electrochemical solar cell.

The main advantage of this scheme is the spatial separation between the hole-conducting electrolyte and the electron-conducting inorganic semiconductor, reducing the probability for charge recombination, one of the most severe limitation of other organic-based devices.

Much attention has been recently devoted to the design and synthesis of chromophores absorbing in the Vis/NIR region, where common organometallic sensitizers are less efficient. Amongst the different classes of chromophores so far proposed for this application,[94] squaraine dyes have been considered due to their intrinsic strong absorption in the 600–800 nm region and to their high thermal and chemical stability. One of the first studies in this respect was made by Das and co-workers who characterized a series of both symmetric and nonsymmetric squaraine dyes possessing a nonconjugated -COOH grafting group enabling the stable anchoring of the dye on the titania surface[95] (Scheme 28).



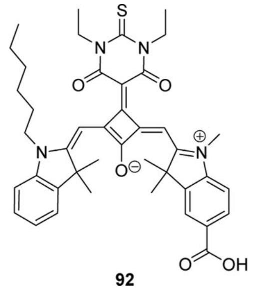
Scheme 28.

The Authors observed that nonsymmetric squaraines generally lead to higher conversion efficiencies. Indeed, while the efficiency measured for derivative **85** is barely 0.07%, it grows to 1.25% for derivative **86**, eventually reaching 2.08% for derivative **87**. As we have already discussed in section 3.3.1 properly designed nonsymmetric squaraines show a somewhat directional HOMO–LUMO excitation. It has been shown that the absorption of self assembled dyes on TiO_2 can be efficiently converted into a photocurrent only in the presence of a directional HOMO–LUMO excitation providing a charge displacement from a region distant from the surface (in the ground state) to the surface close proximity (in the excited state). In derivative **86** both benzothiazole and aniline are efficient donor groups and the directionality of the excitation is very limited. Conversely, being dimethylindolenine a weaker donor than both benzothiazole and aniline, **87** possess a definite excitation directionality, thus a higher conversion efficiency.

Later works by Burke and Grätzel demonstrated that even symmetric squaraines can efficiently perform, as long as the dye is absorbed as the corresponding ammonium salt and in the presence of chenodeoxycholic acid in order to prevent dye aggregation at the surface.[96] Cells based on derivative **88** gave efficiencies as high as 3.7%. With derivatives **89** and **90**, Nazeeruddin, Nüesch and Geiger significantly enhanced the dye performances by introducing the carboxy docking group directly on the squaraine main conjugation axis.[8,97] By this way the authors achieved at the same time a better coupling between surface and sensitizers electronic states and a stronger directionality for the squaraine HOMO–LUMO transition. The best reported efficiencies for cells based on **89** and **90** are 4.5 and 5.4%, respectively.[98]

However, both symmetric and nonsymmetric squaraines possess an important drawback. Their absorption, although very efficient, is limited to one relatively narrow band located in the aforementioned 600–800 nm region.

In order to overcome this limitation, Beverina et al. exploited the core functionalization strategy discussed in paragraph 2.3 in order to prepare the panchromatic, carboxy-functionalized squaraine **91**. Derivative **92** absorption spectrum, in analogy with the already discussed derivative **43** shows two distinct absorption bands[33] (Scheme 29).



Scheme 29.

To gain insight in the nature of the excited states of the dye, particularly regarding to the high energy band, the authors performed DFT/TDDFT calculations. Interestingly, upon optimization of the dye ground state geometry, authors found that its *cis* form, that is the isomer having both the indolenine residue in *cis* configuration with respect to the squarilium core, is more stable by 10.2 (7.1) kcal/mol than the corresponding *trans* form (Figure 11).

The two different bands observed in **92** absorption spectrum where thus unambiguously assigned to two distinct processes, one related to the efficient conjugation along the main equatorial squaraine axis, and the other associated with the nature of the substituent on the squarylium core.

DSCs based on derivative **92** gave an overall efficiency of 4.70%, but more importantly, the whole absorption spectrum of **92** was found to be photoactive, as shown in the photoaction spectrum shown in the upper part of Figure 12.

To conclude the section devoted to photoconduction-related applications, we will now briefly discuss organic-based photodetectors, a class of devices closely related to photovoltaic cells.

A photodetector is a device able to convert an optical signal into an electrical one.[99] The device differs from a photovoltaic cells in one important respect: a photovoltaic cell is optimized in current and open-circuit voltage while a photodetector is optimized with respect to operational window and response time. The operational window is a critical issue, the main applications of organic photodetectors in fact is related to the technology of plastic optical fibers (POF).[100] POF fibers are characterized by a low-loss window located in the Vis/NIR region. On this respect redox-

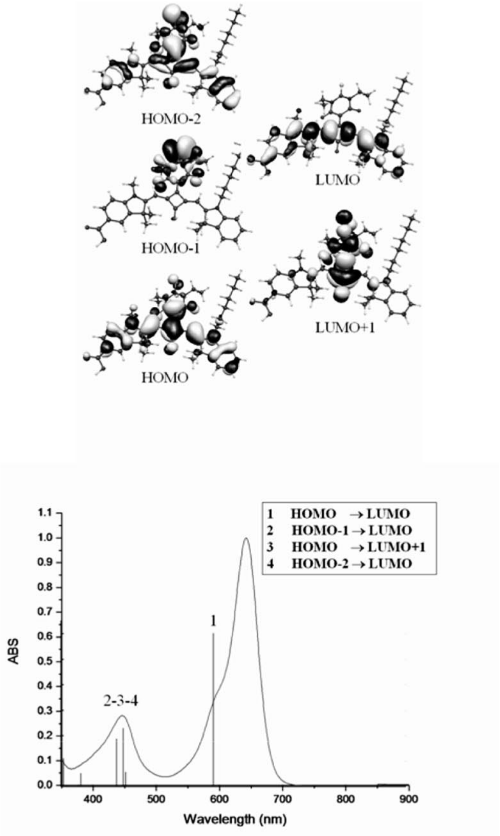


Figure 11. Bottom: experimental UV/Vis absorption and calculated vertical transitions of derivative **92** in CH_3CN solution. Top: isodensity plot of selected molecular orbitals of squaraine **92**. (Adapted form ref.[33]).

reversible squaraines are attractive candidates as active compounds. In its simplest possible configuration a planar photodetector is constituted by two prelithographed metal contacts on an insulating substract. The active, photoresponsive layer is deposited on top of the interdigitated contacts by cast or spin coating. A constant bias is applied between the contacts and the device is illuminated. Analogously to the mechanism described for solar cells, the absorption leads to the formation of an exciton. At the donor-acceptor interface the exciton is split in free charges, eventually collected at the electrodes.

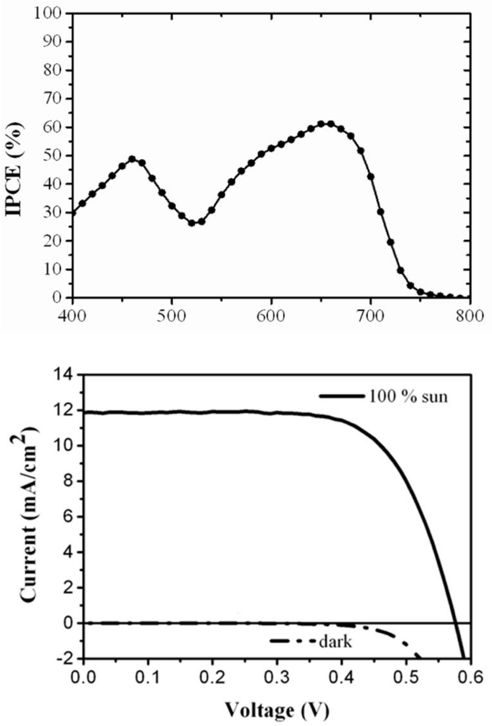


Figure 12. Bottom: current-voltage characteristics of squaraine **92** devices obtained with a nanocrystalline TiO_2 film deposited onto a conducting glass sheet. Top: photocurrent action spectrum (adapted form ref.[33]).

Figure 13 shows the schematic representation of a planar organic photodetector. Employing the squaraine **93** both in pristine form and in bulk heterojunction configuration with PCBM, Binda et al. developed NIR photodetectors with efficiencies in the range of few percents and response speed in the microsecond range.[101] Even more interestingly, the

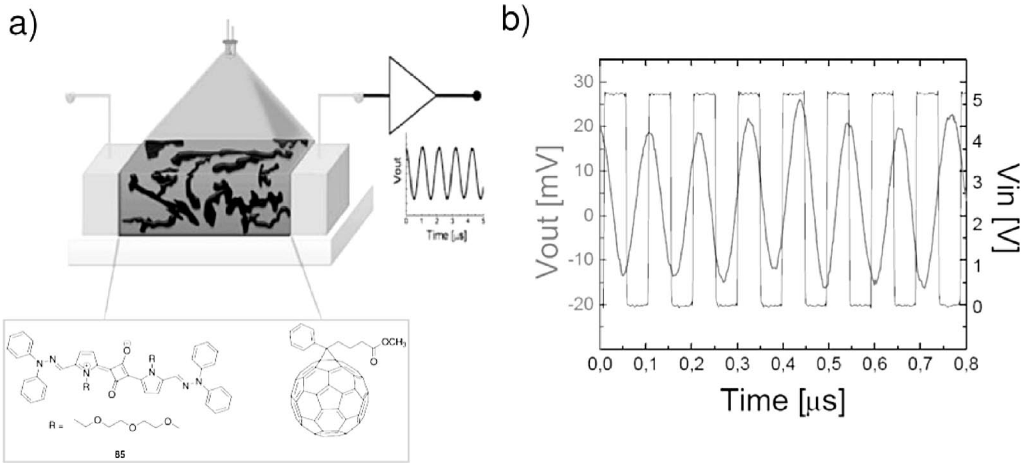


Figure 13. a) Schematic representation of a squaraine-based planar photodetector. b) Time response of the photodetector based on a **93**/PCBM (1:3) blend to a train of light pulses at a wavelength of 670 nm and with a 9 MHz frequency.

devices could be operated in air and a shelf lifetime in excess of one year was demonstrated.

Part b of Figure 13 shows the time response of the photodetector based on a **93**/PCBM (1:3) blend to a train of light pulses at a wavelength of 670 nm and with a 9 MHz frequency.

Conclusions

Since their first isolation in 1959, squaraine compounds have gained an increasingly important role in modern materials science. Although they primarily played a role as sensitizers in xerography during the ’80s, in most recent years all of their most characteristic features (stability, strong and localized low energy absorption, efficient emission, reversible redox behaviour, nonlinear optical performances, ion sensing, wide molecular diversity) have been successfully exploited in many different technologically relevant research fields including, but not limited to organic photovoltaics, bioimaging and therapy, electro-optics and multiphoton absorption promoted phenomena. The very large number of different structural motifs so far proposed for this class of dyes only represent a minor fraction of the possible structures accessible through the synthetic strategies we have discussed. This, along with the sizeable number of structure–properties relationships studies recently proposed, open the way for an even larger exploitation of squaraine dyes in years to come.

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