2,2′:6′,2″-Terpyridines Functionalized with Thienyl Substituents: Synthesis and Applications

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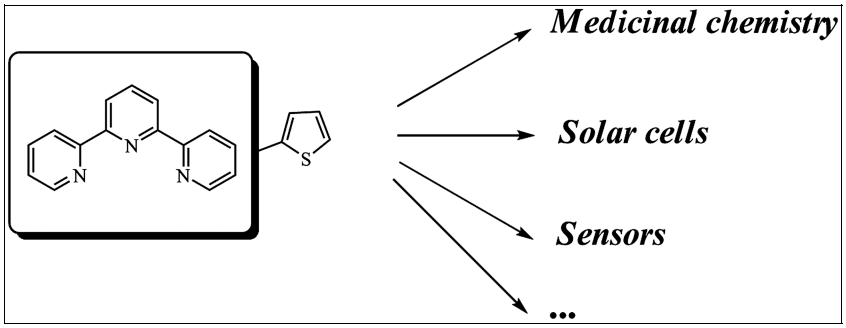

This review deals with the synthesis and applications of 2,2′:6′,2″-terpyridines which are functionalized with thiophene ring, directly linked to the terpyridine core or via a spacer. Two main methodologies were used, ring closure of diketo-derivatives and cross coupling reactions. The obtained compounds find applications in various fields especially in material sciences such as solar cells or macromolecular sciences.

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Contents

1. INTRODUCTION

2,2′:6′,2″-Terpyridine (Fig. 1), generally abbreviated terpy or tpy, has been the subject of a growing interest since its first description by Morgan and Burstall [1,2] in the early 1930.

Since this pioneering work, a plethora of derivatives have been prepared by introducing different substituents

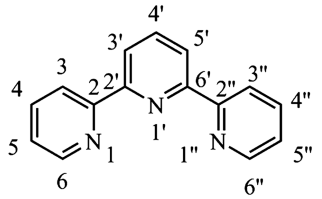
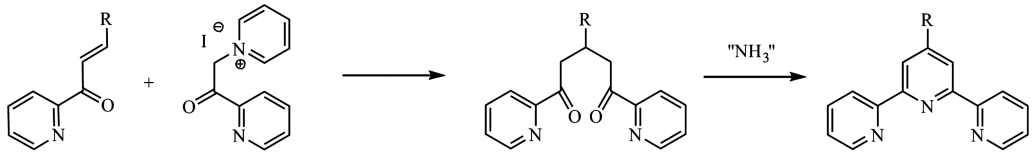
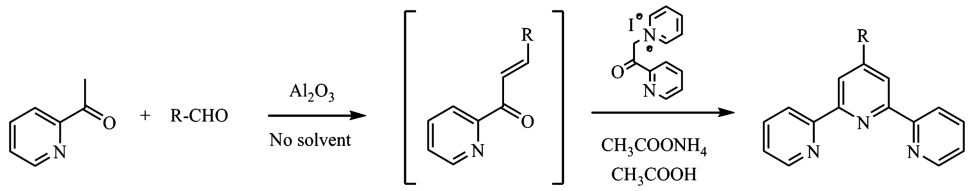


Figure 1. Structure and atom numbering of 2,2′6′,2″-terpyridine.

Scheme 1. Kröhnke's pathway to terpyridine derivatives.



Scheme 2



Scheme 3

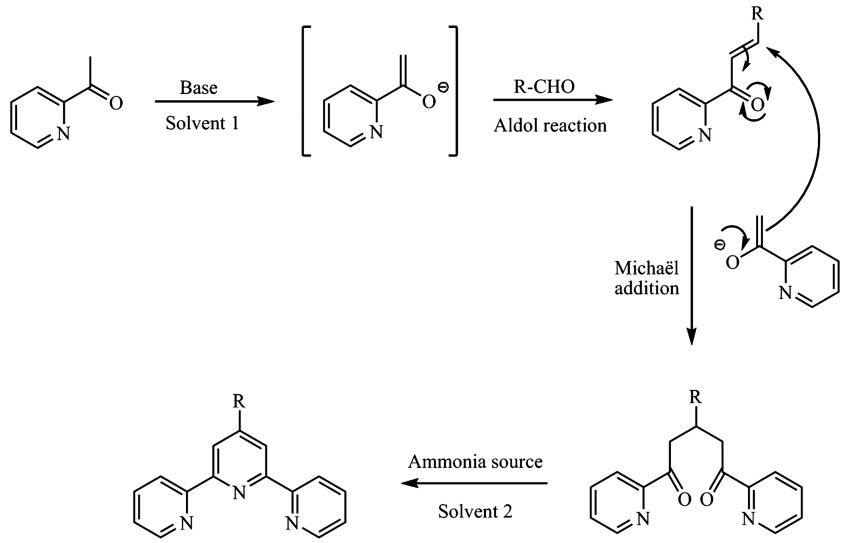


Table 1

Various conditions for the preparation of terpyridines via Kröhnke's like methods.

Method	Base	Solvent 1	Ammonia source	Solvent 2	References
3	NaOH	Acetamide	CH_3COONH_4	H_2O	25
4	tBuOK	THF	CH_3COONH_4	THF/EtOH/CH_3COOH	26
5	NaOH	No solvent	CH_3COONH_4	CH_3COOH	27–29
6	$Ba(OH)_2$	No solvent	CH_3COONH_4	CH_3COOH	24
7	NaOH	EtOH/H_2O	CH_3COONH_4	EtOH	30
8	KOH	EtOH	NH_3	EtOH	31

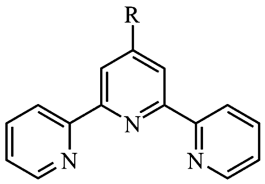


Figure 2. 4′-Functionalized terpyridines.

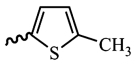
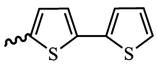
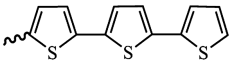
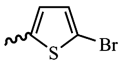
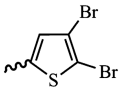
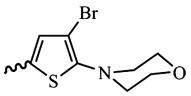
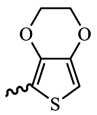
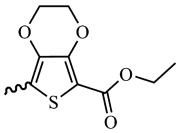
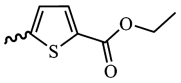
onto the terpy core using various synthetic procedures [3–6]. Terpyridine molecules contain three nitrogen atoms, thus, making these aromatic compounds capable of chelating a wide range of main group, transition metal, and even lanthanides ions. The great stability of coordination compounds with transition metals centres is in part due to the thermodynamic chelate effect, furthermore the σ-donor/π-acceptor character of the dative $M—N_{pyridine}$ bond contributes to the stability of the resulting coordination compounds. Numerous complexes were prepared by varying the nature of the metal, the substitution pattern of the tpy moiety, and finally the character of the other ligands involved in the coordination sphere. These complexes exhibit interesting redox and photophysical properties, which can be fine-tuned by the nature of the substitution pattern onto the tpy ligand. As a consequence of all these interesting features, these compounds found applications in various fields including materials for photovoltaic applications [7,8], nanomaterials [9,10], biomarkers [11,12], in medicinal chemistry [13–15], or as catalysts [16]. Supramolecular chemistry is another field, where terpyridines and their derived complexes are widespread. Introduction of a terpyridine complex into supramolecular assemblies may confer them with the above-mentioned properties [5,17].

On the other hand, thiophenes and oligothiophenes are widely used to prepare conjugated polymers by chemical or electrochemical oxidative coupling reactions [18,19]. In addition oligothiophenes and polythiophenes generally possess photophysical and redox properties, making them interesting materials in optoelectrical devices [20,21]. Finally, the rich chemistry associated with thiophene derivatives allows various chemical modifications easily. With respect to these applications, substitution of a terpyridine with a thiophene ring appears very promising, because combining the intrinsic properties of the two aromatic heterocycles should allow both the conception of original molecular compounds and new polymeric materials with novel properties [22].

Therefore, this review emphasizes with the preparation and utilization of terpyridine derivatives, which are connected to a thiophene ring. The latter may be directly attached to the terpyridine or linked via a spacer unit.

Table 2

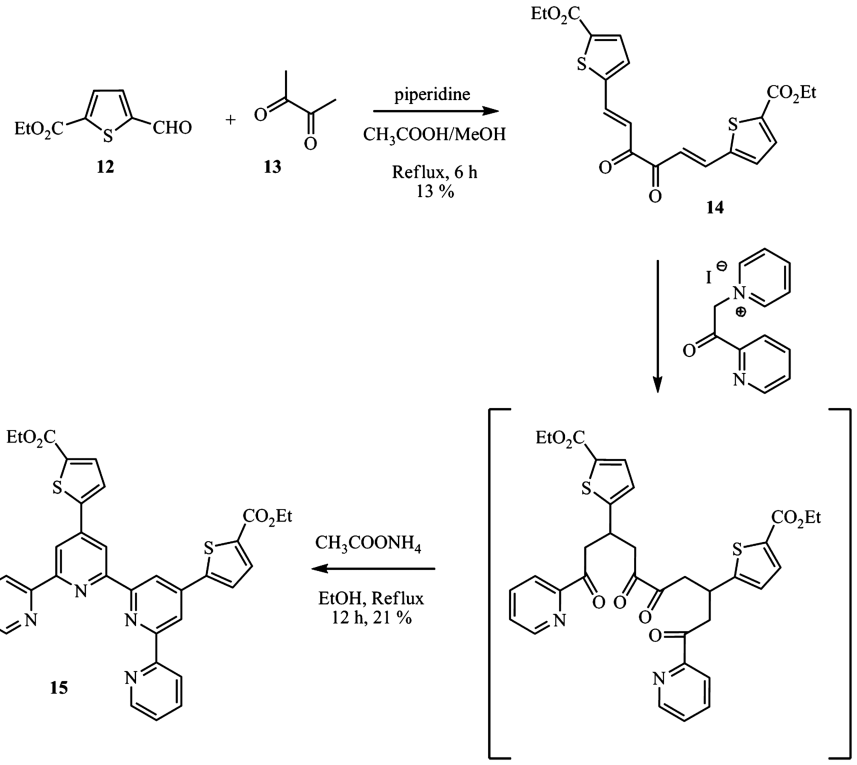
Thienyl substituted tpys obtained via Kröhnke's like methods.

Compound	R =	Preparation method	References
1		1 4 7 8	13,32,33 26,34,35 30,34 37,38
2		1 3 5 7	13 39 40 26
3		1	41
4		4	34
5		4	34
6		2 4 5 6 7	24 42 24 24 43
7		2	24
8		2	24
9		8	38
10		8	38
11		1	38

2. SYNTHESIS OF THIOPHENE-CONTAINING 2,2′:6′,2″-TERPYRIDINES

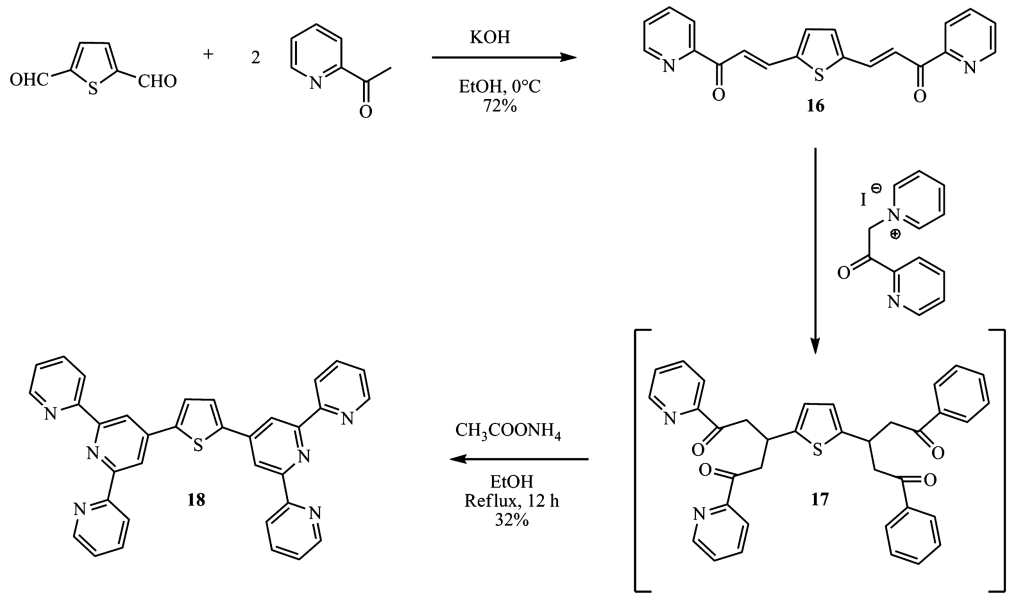
2.1 Via ring-closure of 1,5-diketones. In 1976, Kröhnke introduced a synthetic method for the preparation of pyridine rings based on ring closure of 1,5-diketones in the presence of an ammonia source [23] (method 1). This methodology was applied to the preparation of various 4″-substituted tpy derivatives, the suitable 1,5-diketone intermediate being obtained by a Michael addition between a pyridinium salt and an α,β-unsaturated ketone (Scheme 1).

Scheme 4. Synthesis of thienyl-containing quaterpyridine.

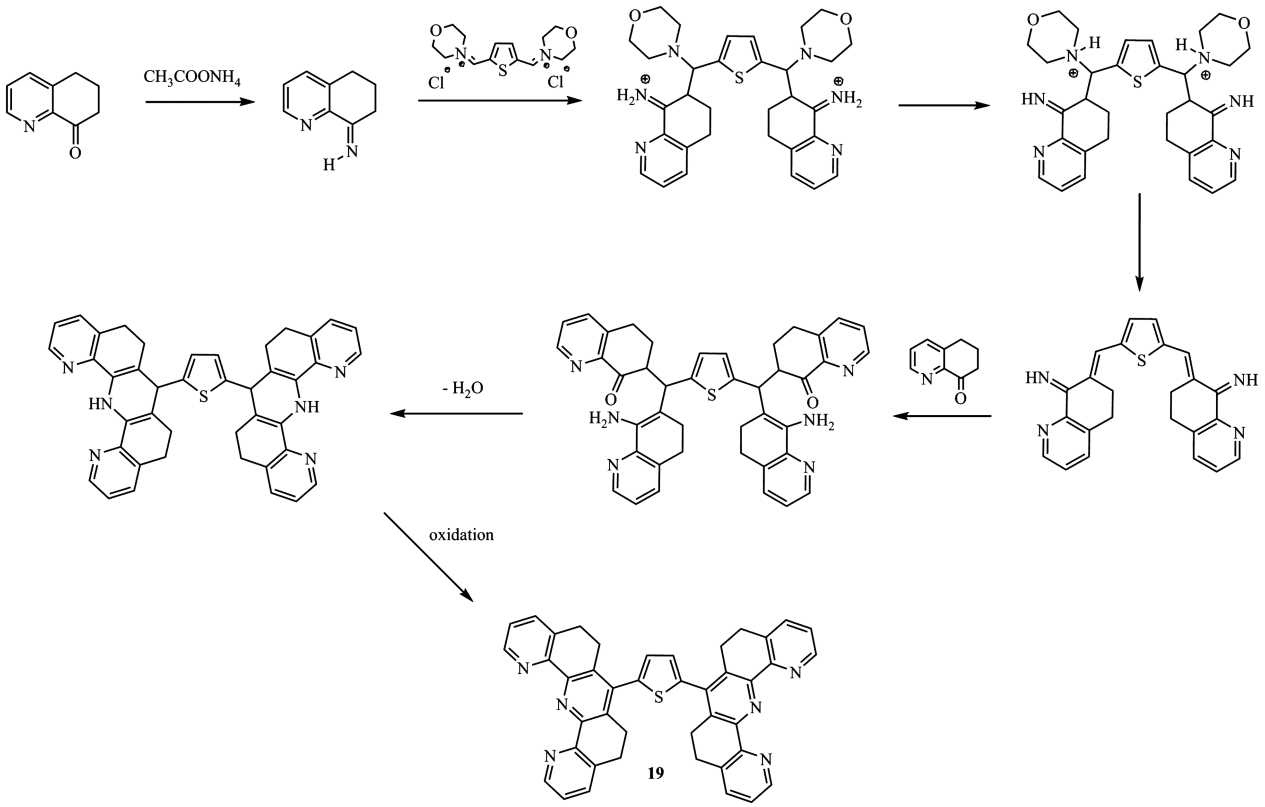


The desired α,β-unsaturated ketone was generally prepared by an aldol condensation between 2-acetylpyridine derivatives and a thiophene-containing aldehyde in an alkaline media, with subsequent isolation of the product. Unfortunately, in some cases, the yield of ketone was very low, probably due to sensitivity of some aldehydes under basic conditions. To circumvent this problem, an improved protocol was recently described, in which the ketone was prepared under mild solvent-free conditions, using alumina (method 2). The α, β-unsaturated ketone was not isolated, but directly reacted with the pyridinium salt in refluxing acetic acid, using ammonium acetate as ammonia source [24] (Scheme 2).

Scheme 5



Scheme 6. Utilization of iminium salts.



Although the two above-mentioned synthetic routes use a pyridinium salt as the nucleophilic moiety in the Michael addition to afford 1,5-diketone, different variations appeared in literature, in which an enolate was used instead. These methods generally proceed according to the same pathway. The first step is the generation of an enolate by deprotonation of 2-acetylpyridine derivatives by a base. An aldol reaction then occurs between the enolate and an aldehyde affording an α,β-unsaturated ketone. The latter undergoes Michael addition with a second equivalent of enolate to afford the diketo-derivative. Ring closure of the latter on reaction with an ammonia source yields the desired terpyridine (Scheme 3).

A collection of several protocols leading to 4″-substituted tpys, using different solvents, different bases, and different ammonia sources is summarized in Table 1.

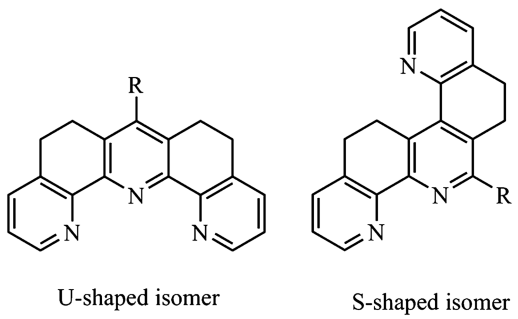
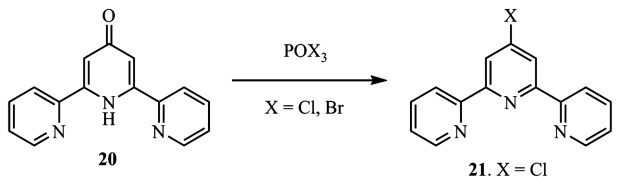


Figure 3. Structure of U- and S-shaped isomers.

Scheme 7. Preparation of 4′-halogenated terpyridines.



Scheme 8. Stille cross-coupling producing 40-thiophene-functionalized terpyridines.

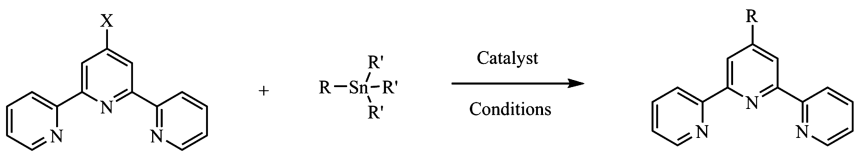
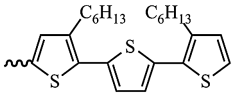
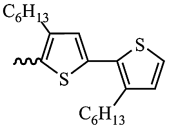


Table 3

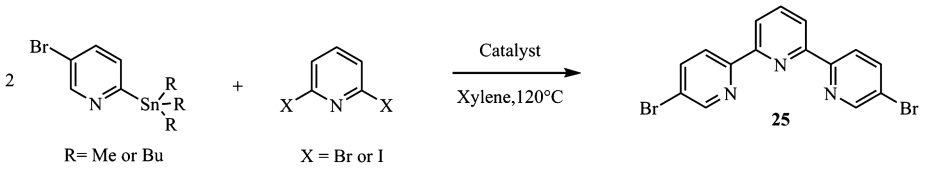
Stille cross-coupling of 4″-halogenated tpys.

Terpyridine	X =	R =	R′ =	Catalyst	Conditions	Reference
23	Cl		Bu	$Pd(PPh_3)_4$	DMF, 100°C, 5 h	52
24	Br		Me	$PdCl_2(PPh_3)_2$	THF, Reflux 12 h	53

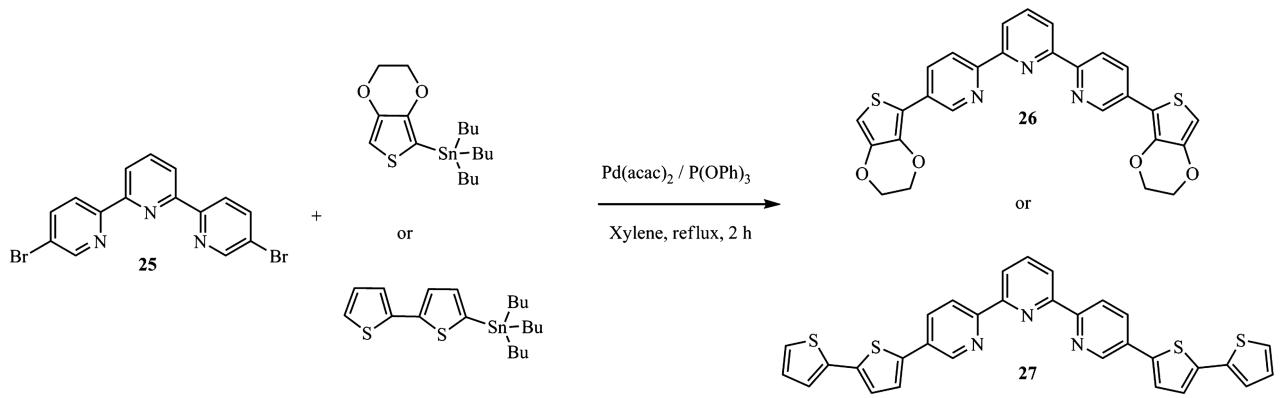
All these strategies are also suitable for the synthesis of terpyridines bearing a thiophene ring, directly linked to the oligopyridine core at the 4′ position (Fig. 2), starting from 2-acetylpyridine derivatives and thiophene aldehydes (Table 2).

These synthetic routes also allow the design of more complicated terpyridines. Kröhnke's method was used to prepare a quaterpyridine, which can be regarded as a terpyridine containing an additional pyridine ring [44]. Treatment of ethyl-5-formyl-2-thiophenecarboxylate **12** with 2,3-butanedione **13** in the presence of piperidine yielded enone **14**. Reaction of the latter with a pyridinium salt and ammonium acetate afforded quaterpyridine **15** (Scheme 4).

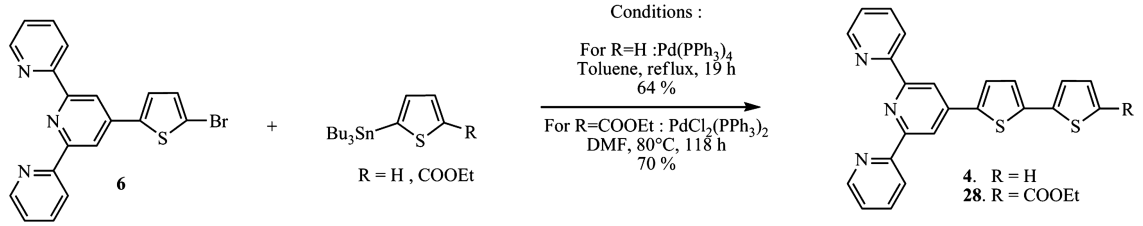
Scheme 9. Preparation of 5,5″-dibromo-2,2′:6′,2″-terpyridine by Stille reaction.



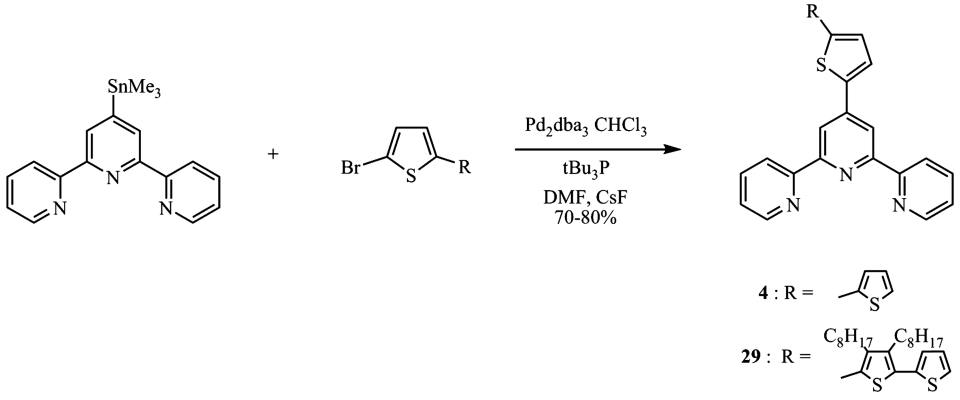
Scheme 10



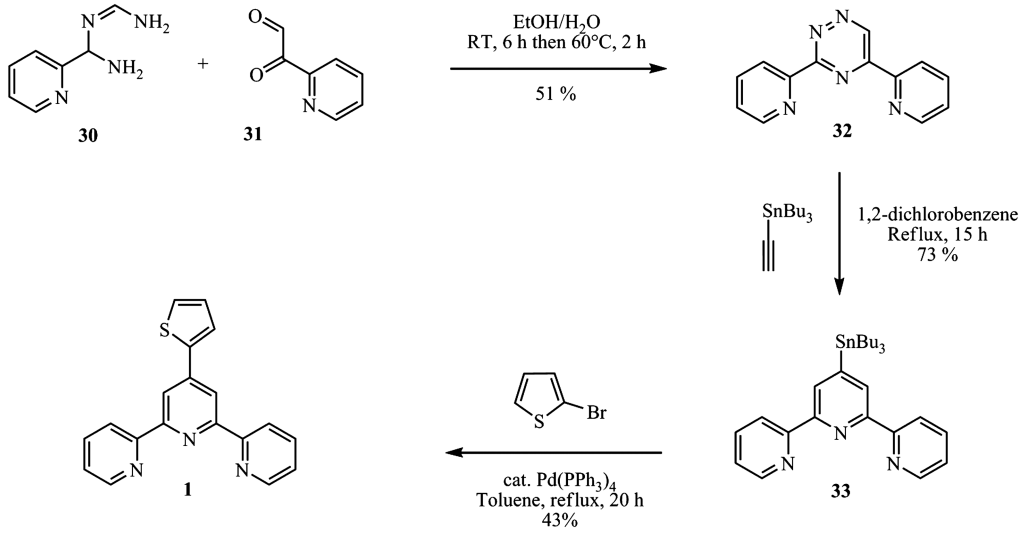
Scheme 11



Scheme 12



Scheme 13

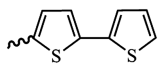
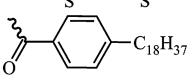


Linking two terpyridine units through a thiophene spacer [26] was also achieved by using method 1. Treatment of 2,5-diformylthiophene and 2-acetylpyridine with potassium hydroxide as base afforded diketo compound **16**. Reaction with pyridinium salt lead to the formation of tetraketo intermediate **17**, which undergoes ring closure in the presence of ammonium acetate to give bis-terpyridine derivative **18** (Scheme 5).

In all methods previously described, the intermediate diketo derivatives were obtained via Michael addition across α,β-unsaturated ketones. An interesting alternative is the use of iminium salts. In fact the latter are versatile intermediates for the preparation of terpyridine derivatives in a twofold domino-sequence [45]. This allowed the preparation of bis-terpyridine **19**, according to the mechanism [46,47] depicted in Scheme 6.

Table 4

Thienyl-containing tpys obtained via cycloaddition and Stille reaction.

Compound	R =	R′ =
34		H
35	C_8H_{17}	
36	H	

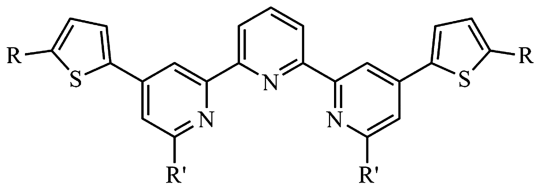
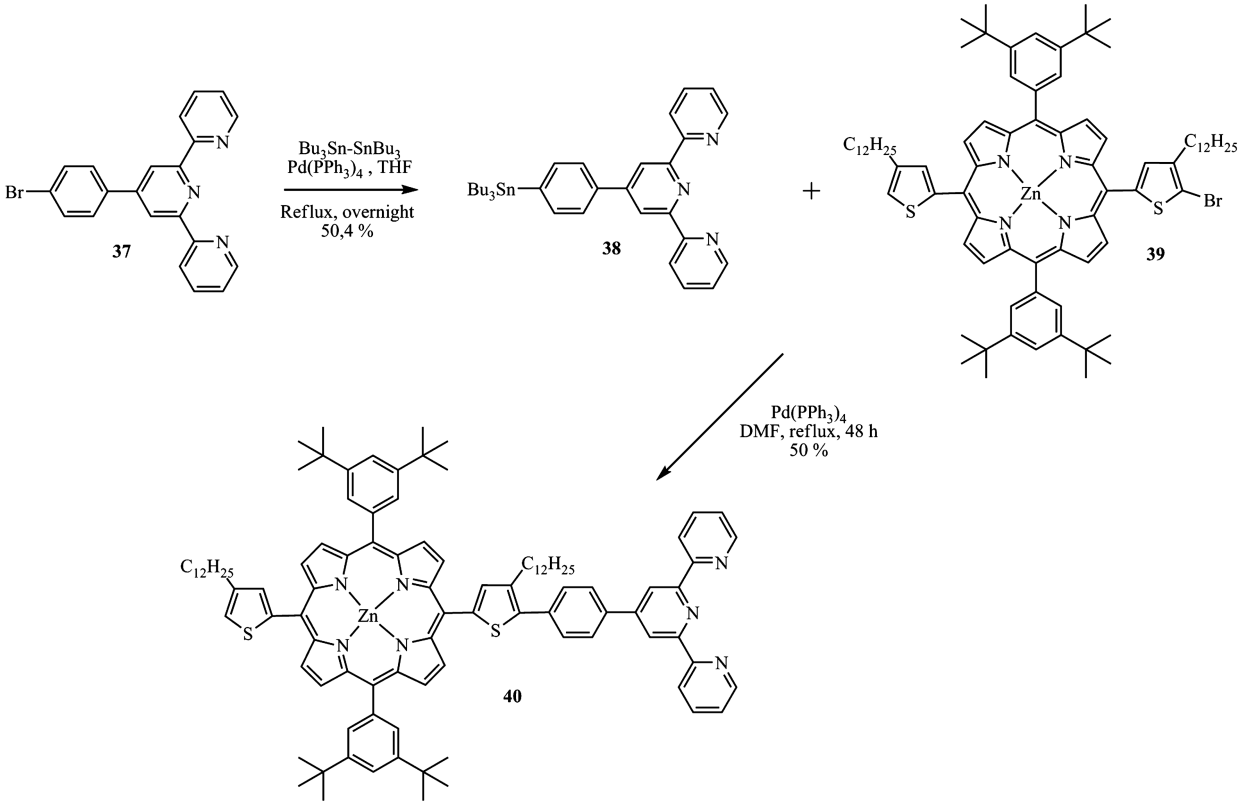


Figure 4. Thienyl-substituted terpyridines obtained via a cycloaddition/Stille cross-coupling sequence.

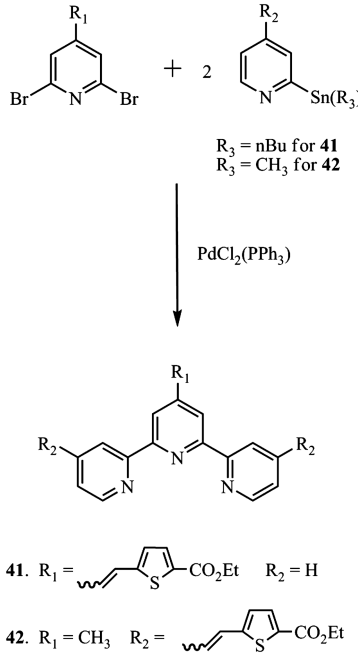
Scheme 14. Synthesis of a porphyrin-terpyridine adduct with a thiophene spacer.



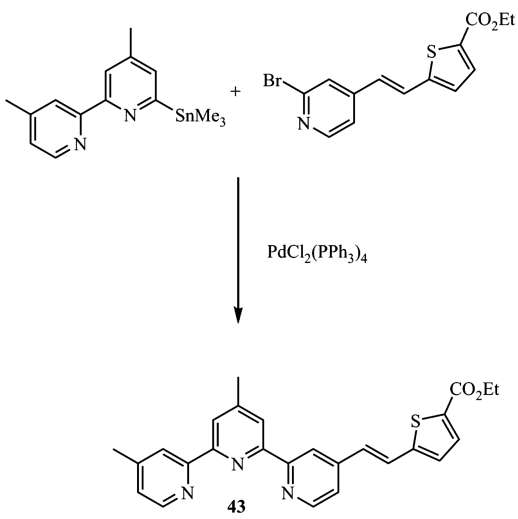
This method may *a priori* lead to the formation of two isomers, namely the U-shaped and S-shaped one (Fig. 3). However, in the case of the synthesis of terpyridine **19**, no trace of the undesired S-shaped isomer was noticed.

2.2 By cross-coupling reactions. Many thiophene-containing terpyridines have been prepared using a cross-coupling reaction, generally to link a terpyridine moiety to a thiophene containing unit. Some examples are gathered below:

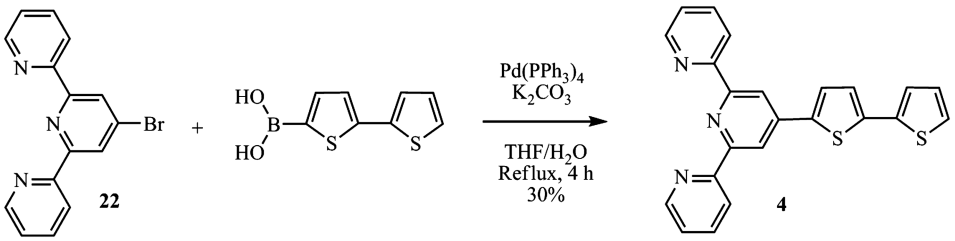
Scheme 15. Stille coupling of outer pyridine rings.



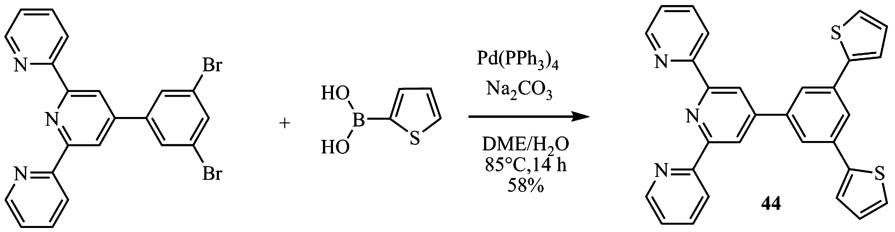
Scheme 16



Scheme 17



Scheme 18



Scheme 19. Linking two terpyridines via a thiophene spacer with Suzuki cross-coupling.

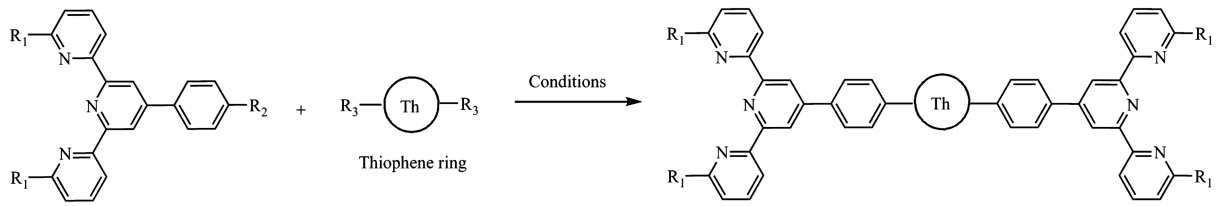
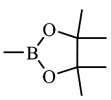
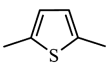
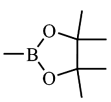
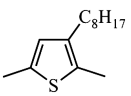
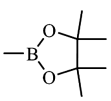
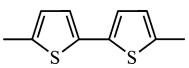
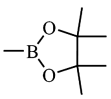
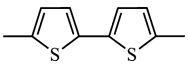
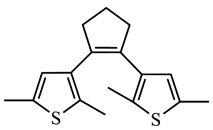
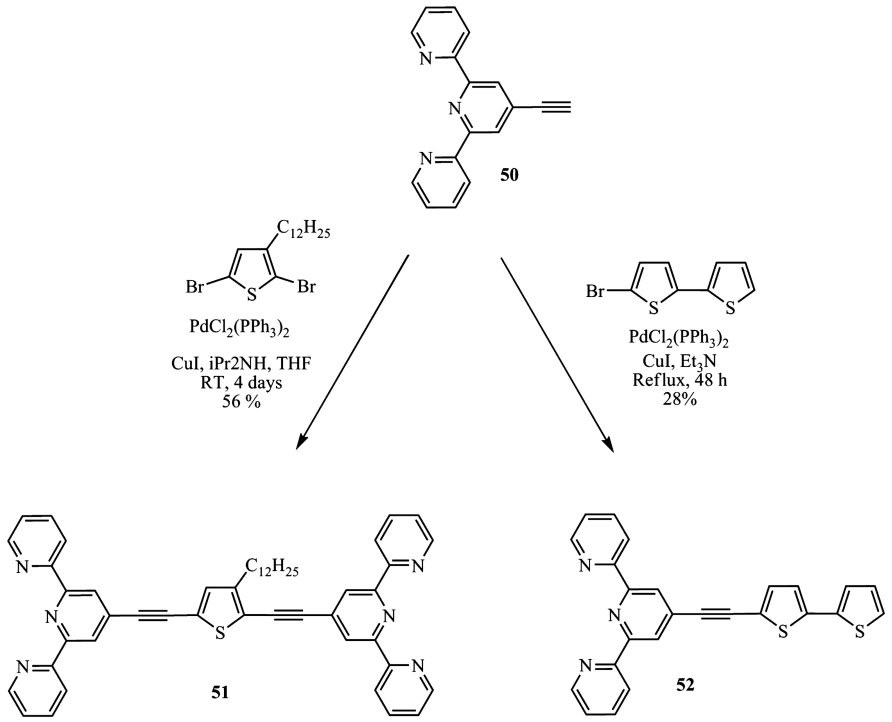


Table 5

Thienyl-tpys via Suzuki cross-coupling.

Compound	R_1	R_2	R_3	Th	Conditions
45	H		Br		$PdCl_2(PPh_3)_2$ K_2CO_3 DMSO, 80°C 59%
46	H		Br		$PdCl_2(PPh_3)_2$ K_2CO_3 DMSO, 80°C 48%
47	H		Br		$PdCl_2(PPh_3)_2$ K_2CO_3 DMSO, 80°C 38%
48	—OCH_3		Br		$PdCl_2(PPh_3)_2$ K_2CO_3 DMSO, 80°C 26%
49	H	Br	—$B(OBu)_2$		$Pd(PPh_3)_4$ Na_2CO_3 DMSO/H_2O 80°C, 12 h 56%

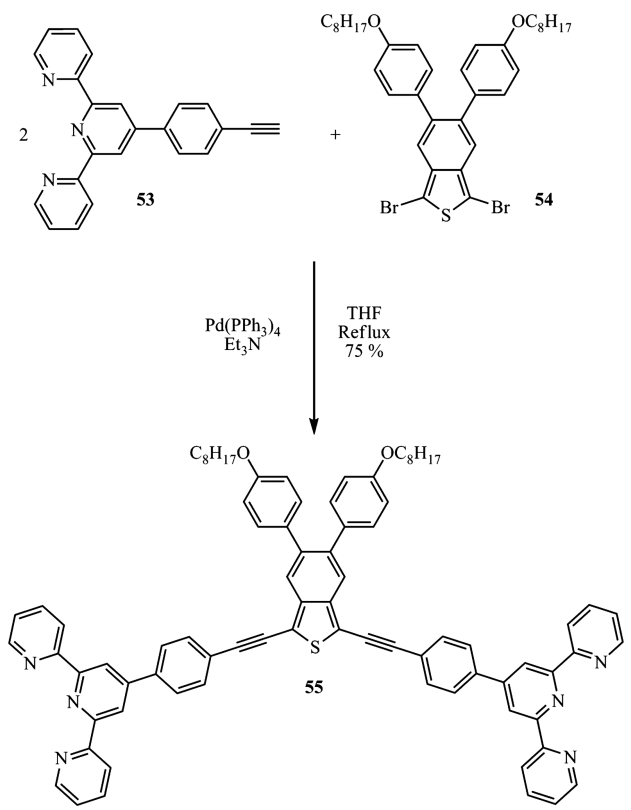
Scheme 20



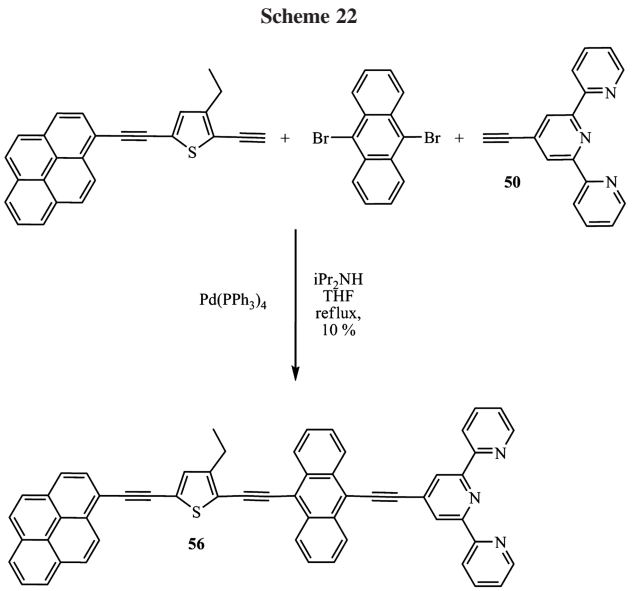
2.2.1 Stille cross-coupling. The Stille coupling allows C—C bond formation by reaction between an halogenated compound and an organotin-containing molecule in the presence of a catalyst [48]. As halogenated terpyridines are easily accessible, the latter have been used as substrates in Stille cross-coupling reactions. Thus, treatment of 2,6-di-2-pyridyl-4(1H)-pyridone [49] **20** with $POCl_3$ or $POBr_3$ afforded 4″-chloro [50] and 4″-bromo-2,2′:6′,2″-terpyridine [51] **21** and **22** (Scheme 7).

Coupling of **21** and **22** with various stannylated thiophenes, under various conditions, afforded 4″-thiophene-substituted tpy **23** and **24** (Scheme 8 and Table 3).

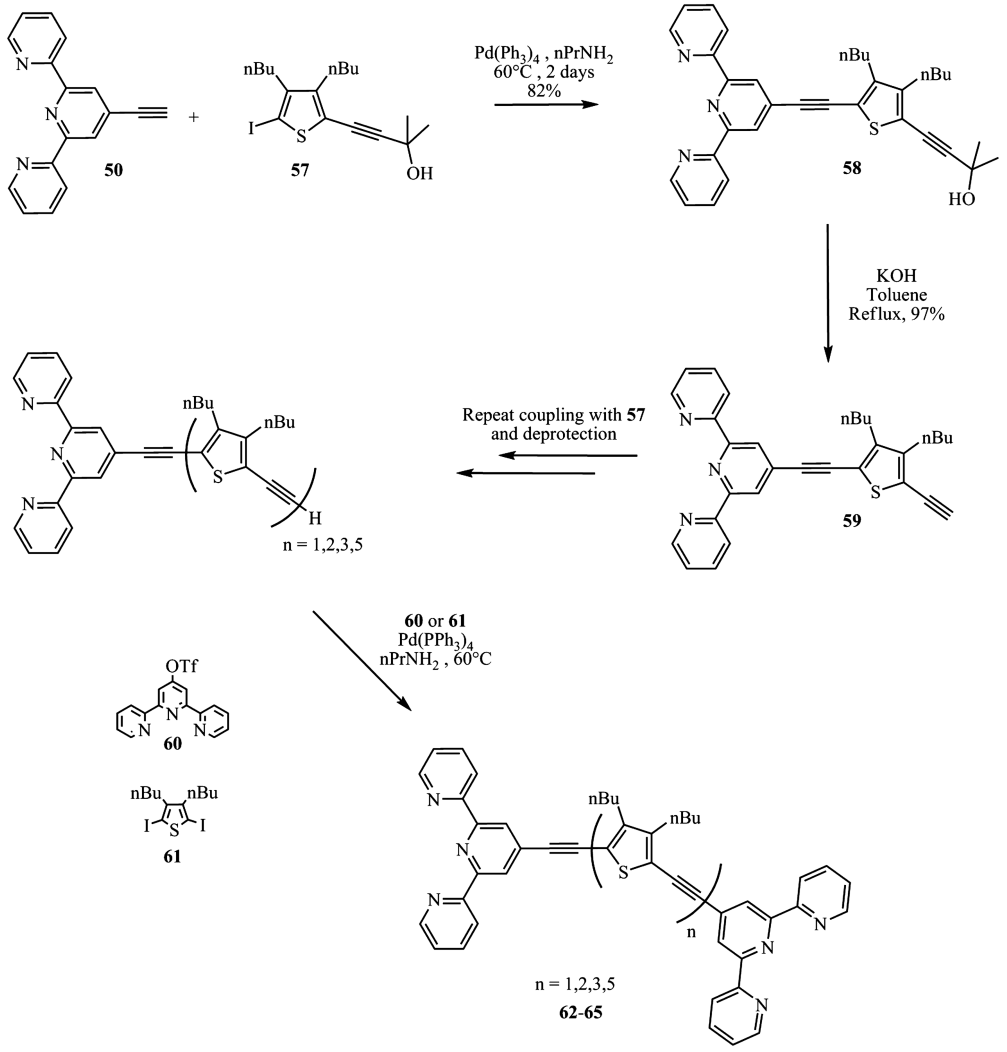
Scheme 21



Scheme 22



Scheme 23



Recently, an extensive study on the Stille cross-coupling reaction in pyridine and terpyridine series has been conducted [54]. In the first step, the reaction was used to prepare 5,5"-dibromo-2,2′:6′,2″-terpyridine **25** (Scheme 9).

Many catalysts were tested, and best results were achieved with four catalyst/additional ligand combinations. The 5,5"-dibromo-substituted compound **25** was then reused in a second Stille reaction with two different trialkylstannyl-thiophene reagents to afford tpys **26** and **27** (Scheme 10).

Other halogen-containing tpys can be prepared via Kröhnke's like methods. A typical example is compound **6**. The latter was also used as a starting material in cross-coupling reaction to obtain bithienyl derivatives [35,36] **4** and **28** (Scheme 11).

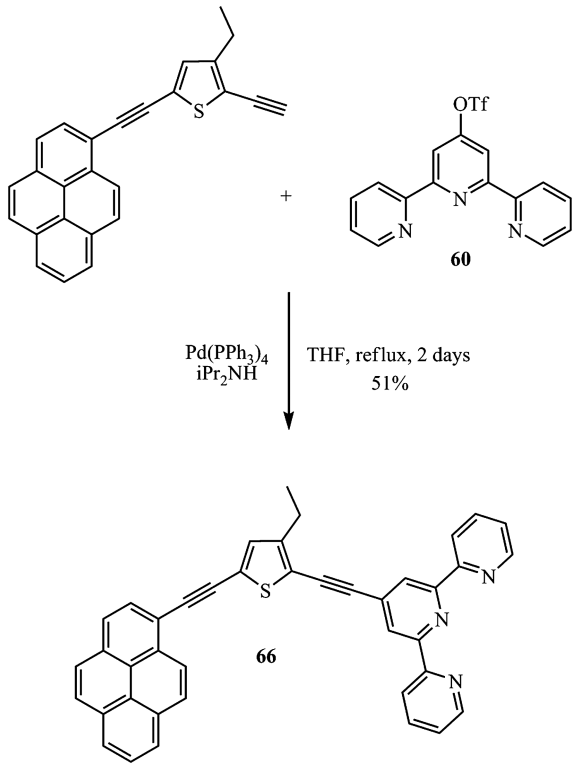
Another possibility to prepare thiophene-containing tpys via Stille reaction is the use of stannylated terpyridines and halogen-containing thiophene derivatives. This methodology was used to prepare compounds **4** and **29** (Scheme 12) from 4″-trimethylstannyl-2,2′:6′,2″-terpyridine [55].

An elegant way to obtain stannylated terpyridines is the use of a cycloaddition reaction between 1,2,4-triazines and tributyl(ethynyl)tin [56]. Treatment of 2-pyridylcarbamidrazone [57] **30** with 2-pyridylglyoxal **31** afforded 3,5-bis-(2-pyridyl)-1,2,4-triazine **32**. Treatment of the latter with tributyl(ethynyl)tin yielded 4″-tributylstannyl-2,2′:6′,2″-terpyridine **33,** which undergoes Stille cross-coupling reaction with 2-bromothiophene to give terpyridine **1** (Scheme 13).

This methodology was extended to the synthesis of more sophisticated thiophene-containing terpyridines (Fig. 4 and Table 4) by varying the nature of the pyridylcarbamidrazone, glyoxal derivative, and bromothiophene derivative [58].

Recently, a stannylated tpy was used to prepare a porphyrin-tpy adduct, the two units being linked via a

Scheme 24



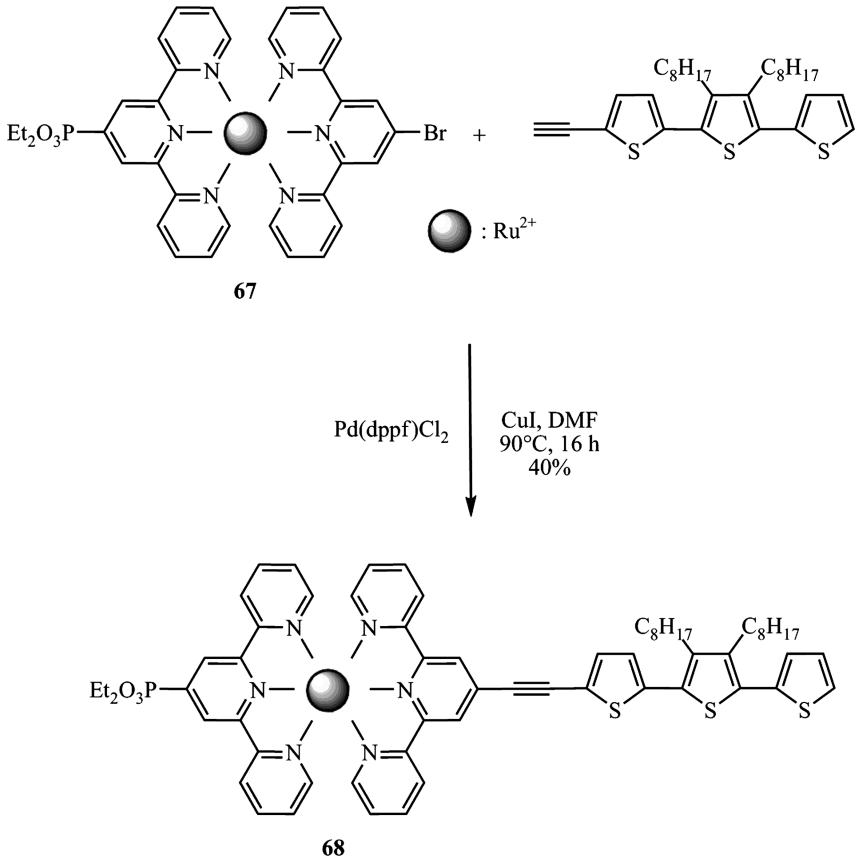
thiophene spacer [59]. Treatment of 4″-(4-bromophenyl)-2,2′:6′,2″-terpyridine [60] **37** with Bu_3Sn-$SnBu_3$ in the presence of a palladium catalyst afforded stannylated tpy **38**. The latter was reacted with the porphyrin-appended bromo-thiophene **39** thus yielding compound **40** (Scheme 14).

In all the above-mentioned examples, the Stille reaction was used to link an already preformed terpyridine unit with a thiophene moiety. Another pathway that was envisioned is the use of the Stille cross-coupling to construct the terpyridine core. Terpyridines **41**–**42** were assembled by coupling the two outer pyridine rings to the central one [61], with one or another pyridine nuclei linked to a thiophene ring through a vinyl spacer (Scheme 15).

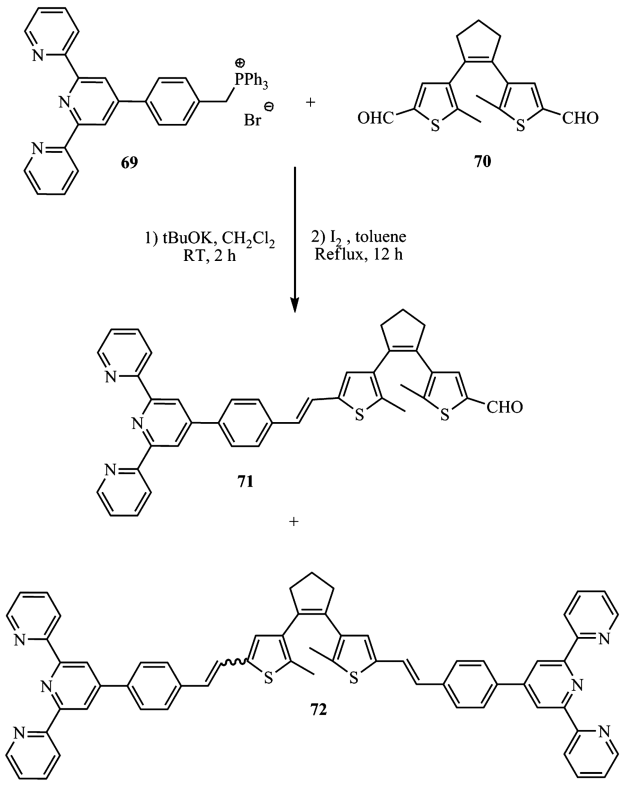
Asymetric terpyridine **43** was obtained in an analogous manner by coupling a stannylated bipyridine with a thiophene-containing pyridine (Scheme 16).

2.2.2 Suzuki cross-coupling reaction. The Suzuki cross-coupling reaction involves reaction between an halogenated compound and a organo-boronate derivative in the presence of a catalyst [62] to form a C—C bond. This reaction was also used to prepare different terpyridines with pendant thiophene rings.

Scheme 25. Sonogashira coupling onto a complex.

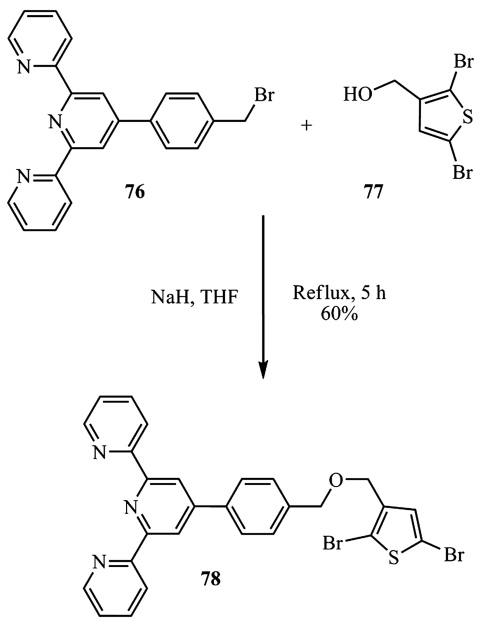


Scheme 26



Treatment of terpyridine **22** with 5-(2,2″-bithiophene)-boronic acid in the presence of $Pd(PPh_3)_4$ as catalyst in a THF/water mixture afforded compound **4** in 30 % yield [36] (Scheme 17).

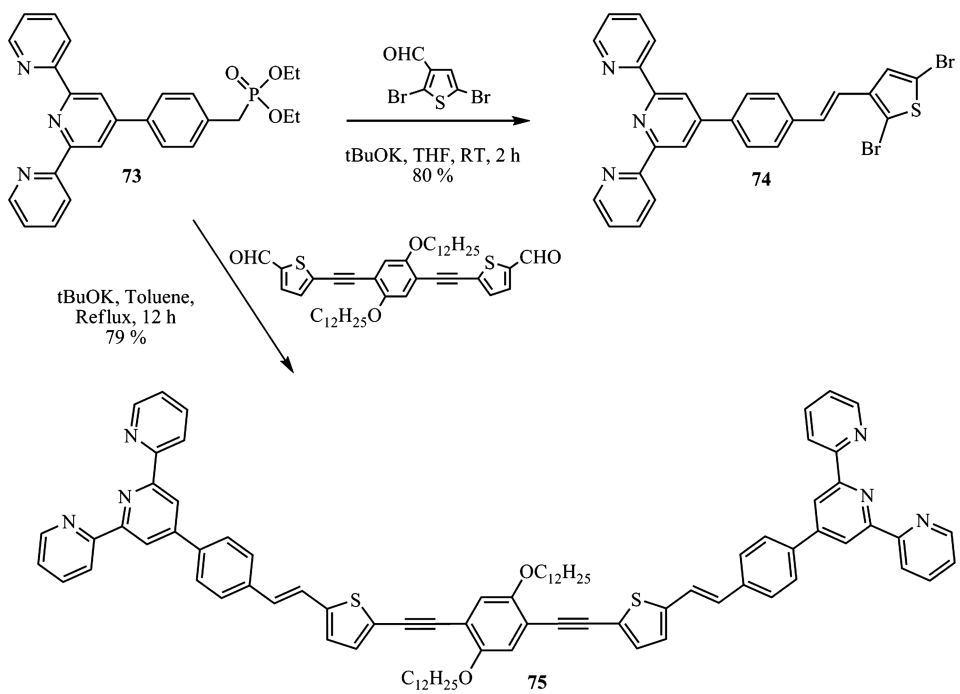
Scheme 28



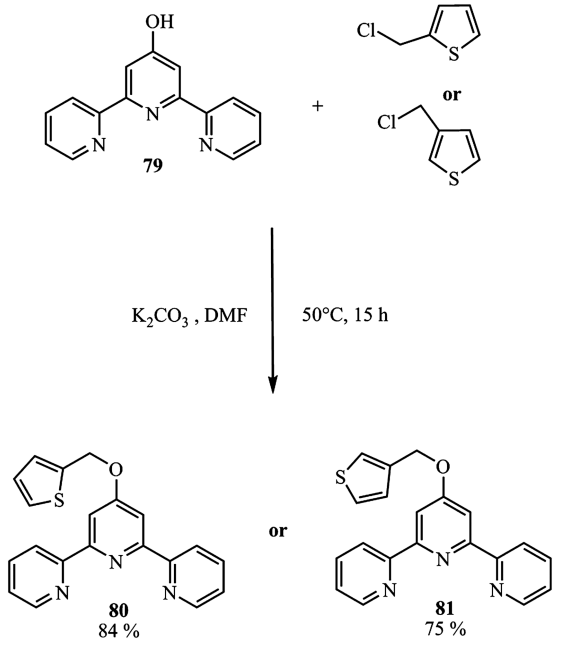
The same methodology was used for the preparation of terpyridine **44**, under slightly different conditions [38] (Scheme 18).

Bis-terpyridines **45**–**49**, in which the two tpy units were connected through a thiophene spacer (Th), were also prepared using Suzuki cross-coupling reactions. The boronate functionality was present either on the terpyridine unit [63] (thus requiring bromo-thiophene derivatives for coupling)

Scheme 27



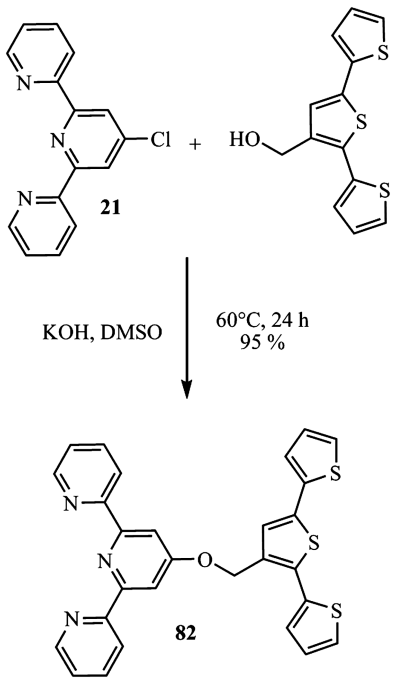
Scheme 29



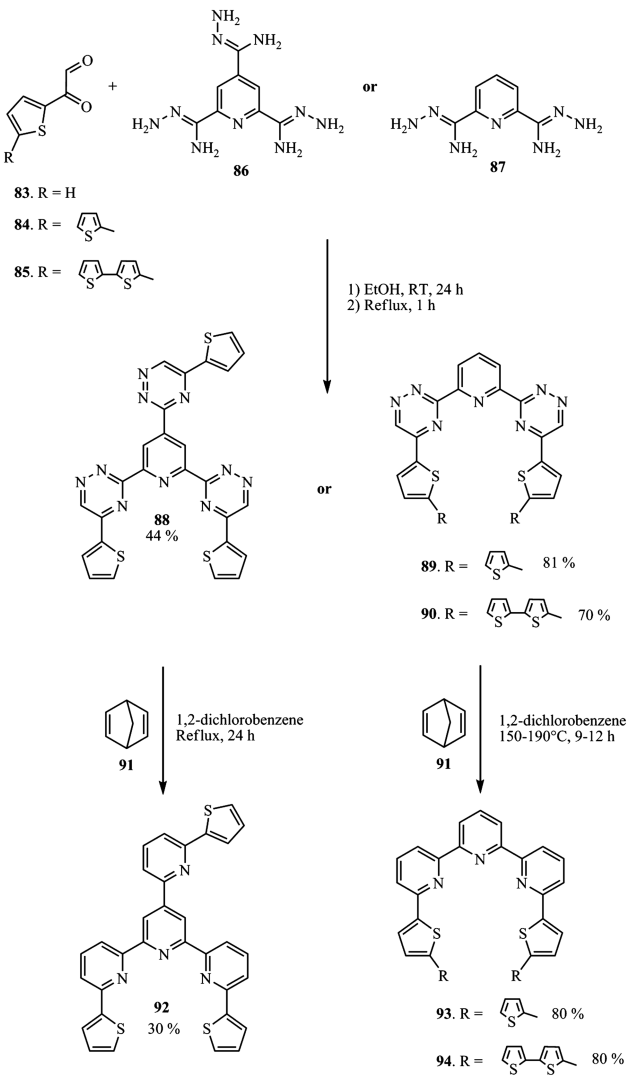
or on the thiophene unit [64,65] (thus requiring halogeno-tpy) (Scheme 19, Table 5).

2.2.3 Sonogashira coupling. The Sonogashira coupling is a C—C bound formation based on the catalytic reaction between an alkyne and an halogenated compound [66]. Using this methodology, alkynyl-tpy **50** was coupled to a dibromo derivative [67] or a bithiophene unit [68] to afford terpyridines **51** and **52** (Scheme 20).

Scheme 30



Scheme 31

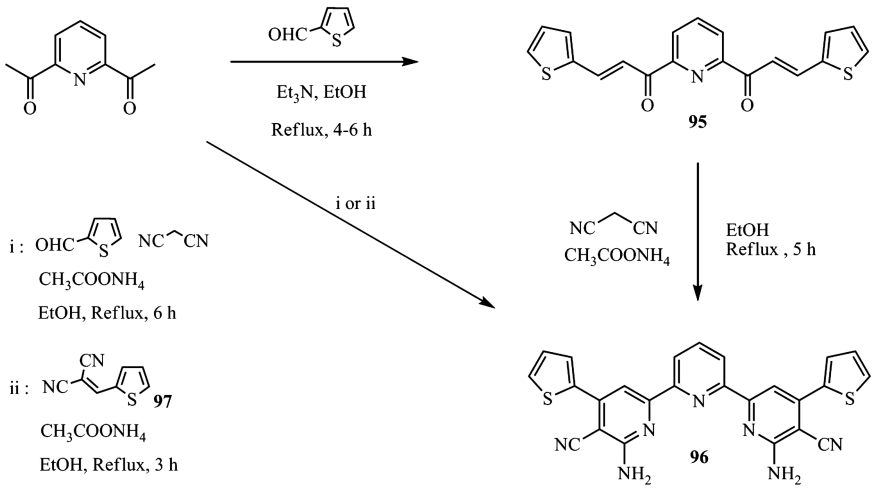


Treatment of 2 equiv of terpyridine **53** with dibromothiophene derivative **54** gave rise to the ditopic ligand [69] **55** (Scheme 21).

Multitopic ligand **56** was obtained via a "one-pot" procedure involving two Sonogashira reactions between terpyridine **50**, an alkynyl-thiophene, and dibromoanthracene [70] (Scheme 22).

Despite the possibility of formation of side products by bis-coupling of thienyl-alkyne or tpy-alkyne to anthracenyl unit, the isolated main compound was terpyridine **56**. The preferred selectivity toward this compound was explained by initial coupling of the tpy unit to the anthracene moiety, resulting in an enhanced reactivity of the second bromide substituted position. Terpyridines bearing oligo-thiophenes were also obtained by a sequential Sonogashira coupling-deprotection sequence as depicted in Scheme 23. Reaction of terpyridine **50** with thiophene derivative **57** using a first

Scheme 32



Sonogashira reaction afforded the coupling-product **58**, which has the peculiarity of being functionalized with a protected alkyne. Deprotection of the latter resulted in formation of terminal alkyne **59** that could be reacted again in the same fashion thus increasing the length of oligo-thiophene pendant chain [71,72]. Final coupling with triflate terpyridine [49] **60** or 2,5-diiodo-3,4-dibutylthiophene **61** afforded terpyridines **62–65**.

Scheme 33

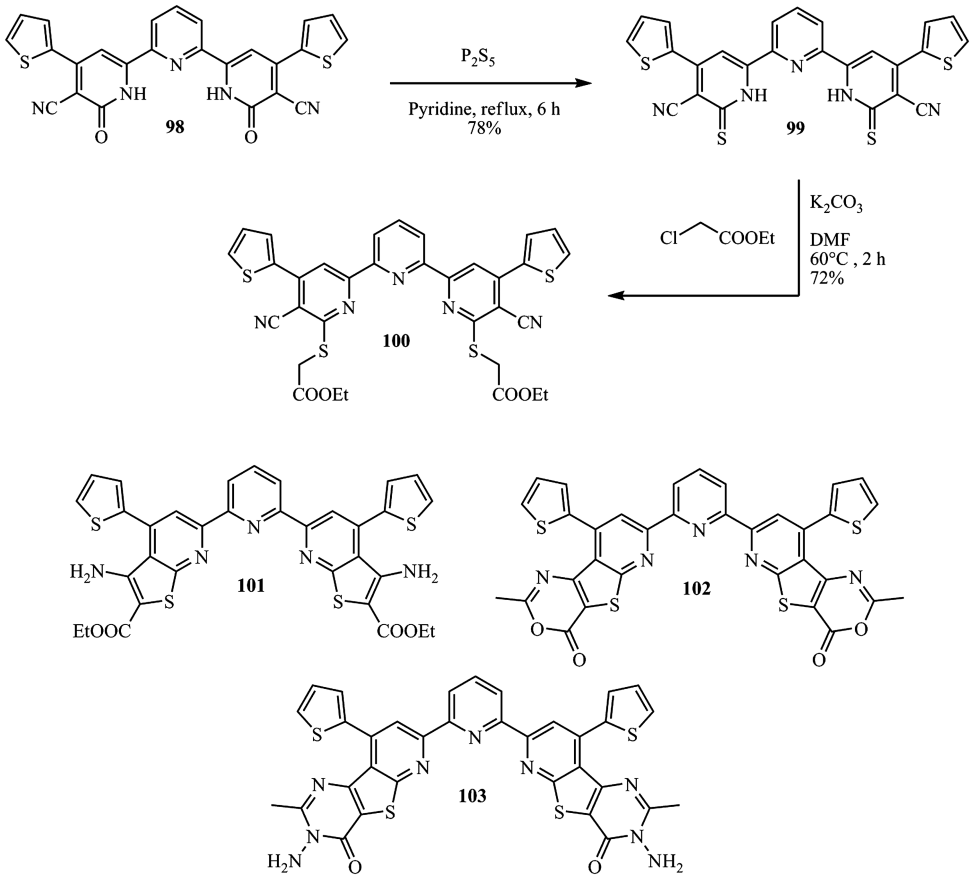
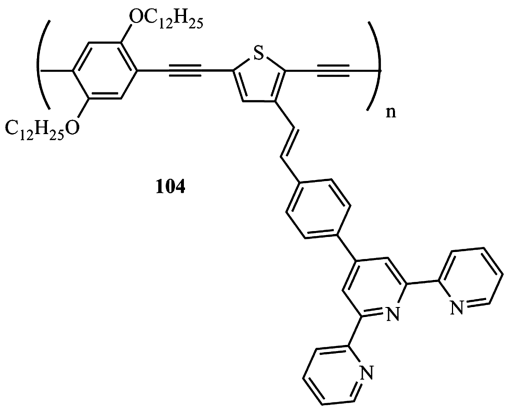


Figure 5. Structures of compounds **101–103**.



104

Figure 6. Terpyridine-substituted poly(arylene ethynylene) including a thienyl ring.

Triflate terpyridine **60** was also used in a Sonogashira reaction to assemble compound **66** (Scheme 24) [73].

Although in the afore-mentioned examples the reaction was carried out on the free ligand, it was demonstrated that it is also possible to functionalize a terpyridine already ligated on the octahedral Ru(II) complex (**67**) using the Sonogashira reaction [74] (Scheme 25). This coupling afforded the alkynyl-terthiophene chelate complex **68** in 40% yield.

2.3 Wittig reaction. Creation of a double bond by the reaction of a phosphonium salt derivative via an ylide with a carbonyl function of ketones or aldehydes is known as the Wittig reaction [75]. Anchoring a thiophene unit to a terpyridine was thus achieved. Treatment of salt **69** with dialdehyde **70** afforded a mixture of terpyridines **71** and **72**. Both *E* and *Z* isomers were obtained. Isomerisation in refluxing toluene in the presence of iodine afforded finally the *E* isomer as the sole product (Scheme 26) [76].

The Horner–Wadsworth–Emmons reaction [77], which is quite similar to the Wittig reaction in its mechanism, was also used to prepare tpys bearing thiophene rings. Phosphonate ester **73** was reacted with different aldehyde-containing thiophenes in the presence of a base

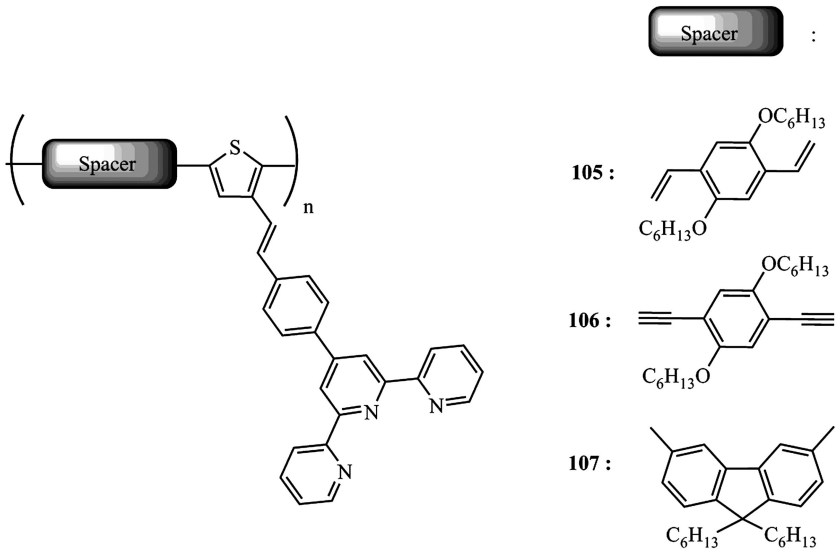
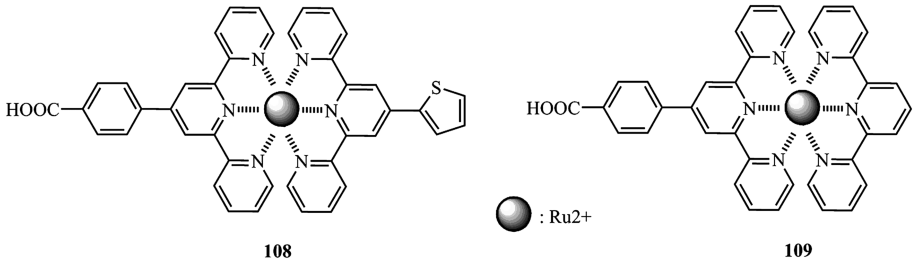


Figure 7. Conjugated polymers with a thiophene ring in the backbone and a pendant terpyridine unit.



108 **109**

Figure 8. Structure of a thienyl-functionalized sensitizer and its analogue lacking a thiophene ring.

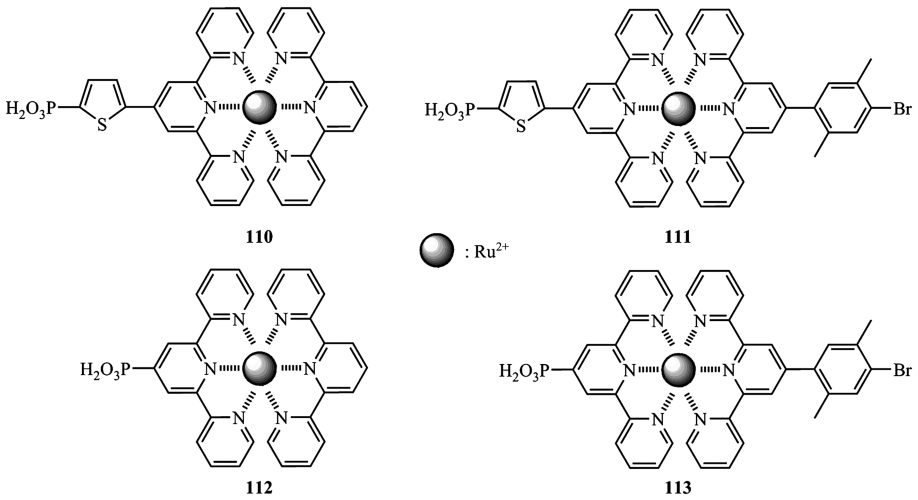


Figure 9. Phosphonate-functionalized terpyridine sensitizers.

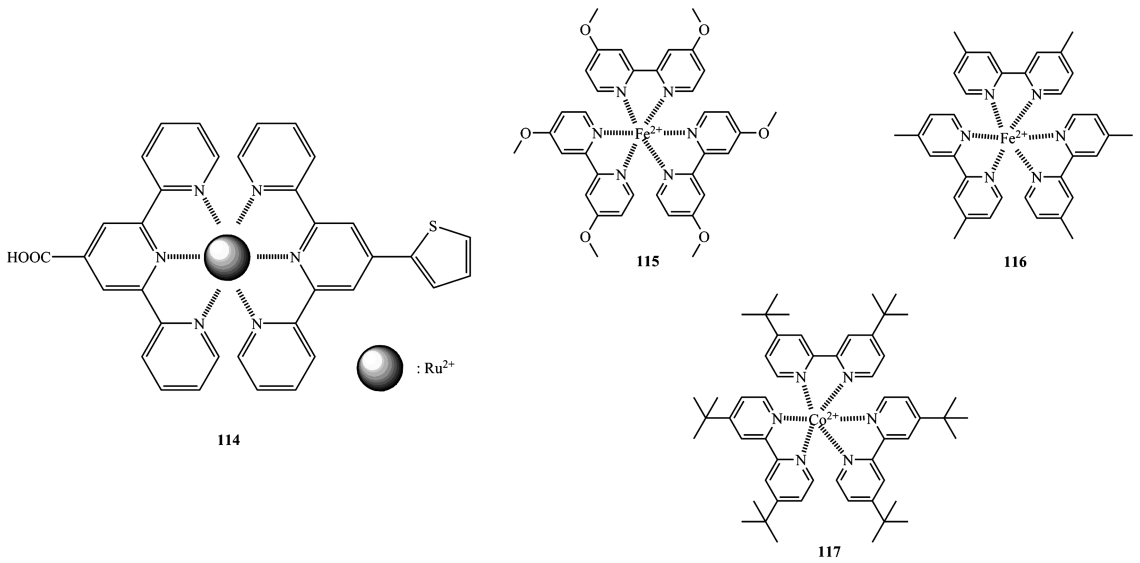


Figure 10. Structures of sensitizer **114** and redox shuttles **115–117**.

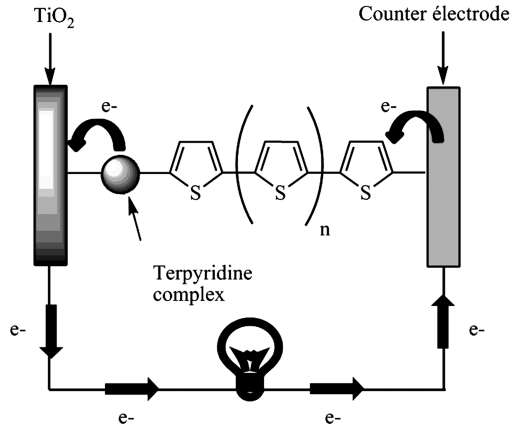


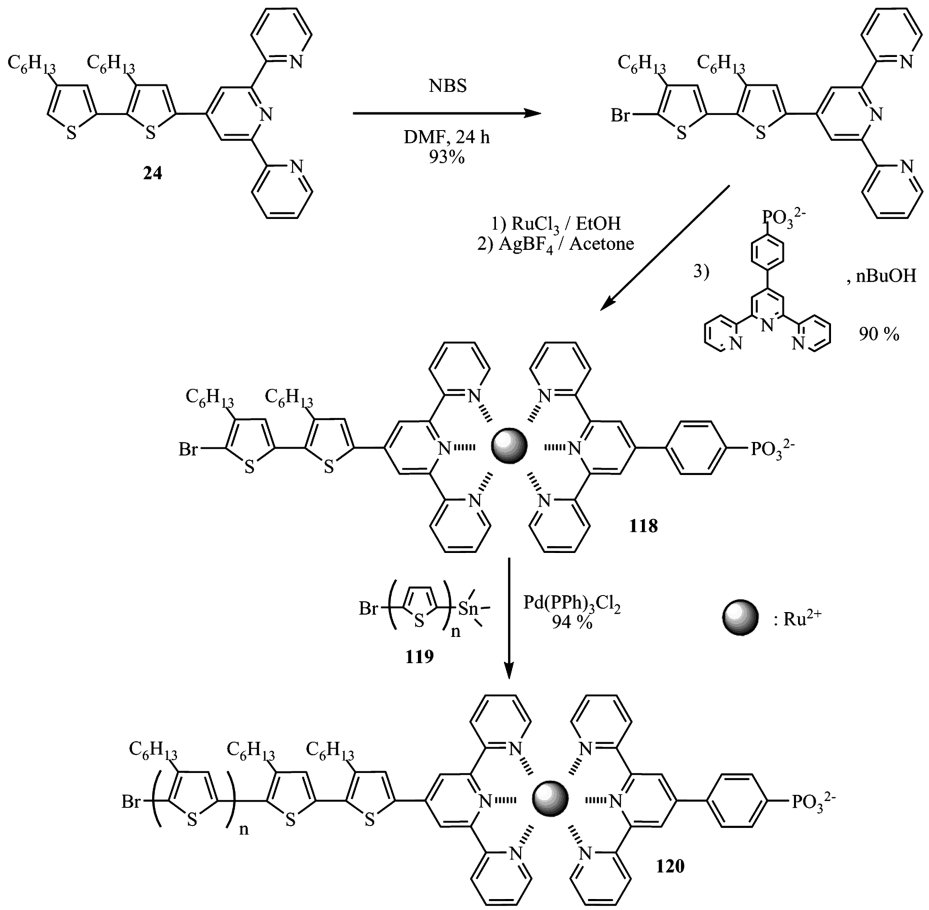
Figure 11. Schematic representation of a solid state DSSC based on a polythiophene conducting material and a terpyridine sensitizer.

thus producing terpyridines **74** and **75** (Scheme 27) [78,79].

2.4 Ether bond formation. Linking a tpy unit to a thiophene moiety via an ether bond was applied for the synthesis of a series of tpy ligands. The Williamson reaction [80] involving reaction between a halogen derivative and an alkoxide was primarily used. Treatment of bromomethyl derivative **76** with (2,5-dibromothiophen-3-yl)-methanol **77** in the presence of sodium hydride as a base (to generate the alcoholate) in THF allowed preparation of terpyridine **78** in 60% yield [78] (Scheme 28).

Reaction of 2- and 3-chloromethylthiophene with the alkoxide of 4″-hydroxy-2,2′:6′,2″-terpyridine [49,81] **79** in DMF afforded terpyridines **80** and **81** in 84 and 75% yield, respectively, [82] (Scheme 29).

Scheme 34



Another method reported in the literature to prepare 4″-terpyridinoxy-derivatives is the utilization of nucleophilic aromatic substitution S_{NAr}. Because of the electron-deficient behavior of the pyridine ring of 4″-chloro-2,2′:6′,2″-terpyridine **21**, this substitution at the activated C—Cl bond by an alcoholate could be performed using a polar aprotic solvent. The thienyl-functionalized terpyridine **82** was obtained by this manner [83] (Scheme 30).

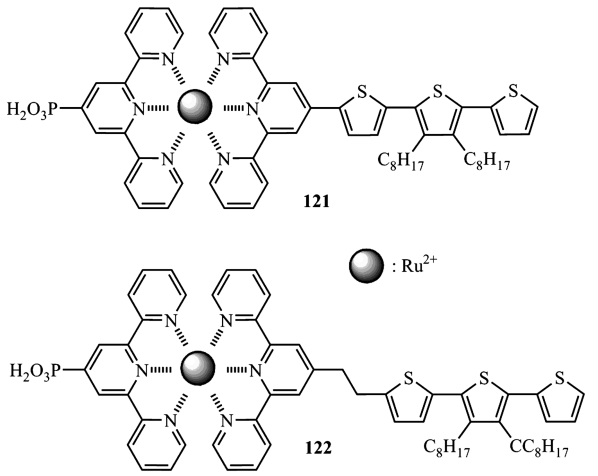


Figure 12. Structure of complexes **121** and **122** tested in a solid state DSSC device.

2.5 Cycloaddition. 1,2,4-Triazines are versatile building blocks for the synthesis of pyridine derivatives. The triazine nucleus can act as electron-poor diene component in inverse Diels–Alder reaction with electron-rich dienophiles thus affording a pyridine ring [84] after extrusion of N_2. Reaction of thienyl glyoxals **83–85** with carboxamidrazones **86** and **87** generates triazines **88–90**. The latter were then reacted with norborna-2,5-diene **91** to afford terpyridines [85,86] **92–94** (Scheme 31).

Table 6

Comparison of solar cells efficiencies using complex **116** and **117** as sensitizers.

Complex	Solar cell efficiency η (%)	
	Classical device	Solid-state device
121	0.21	0.038
122	0.46	0.047

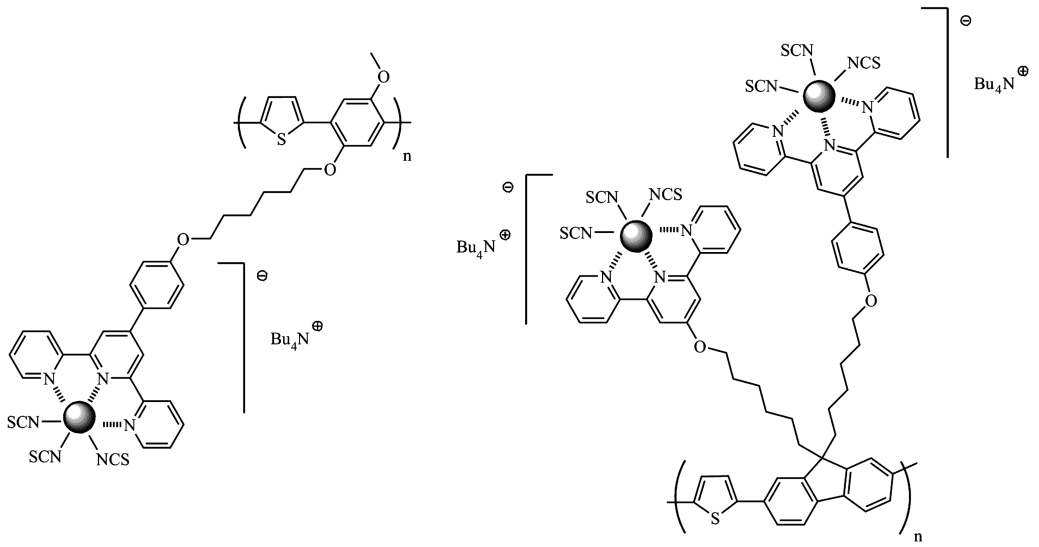
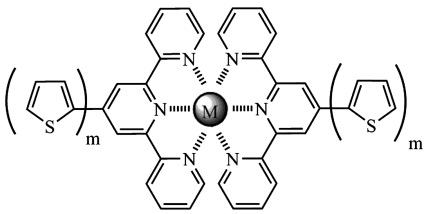


Figure 13. Structure of polythiophene-functionalized with terpyridine-ruthenium complexes.

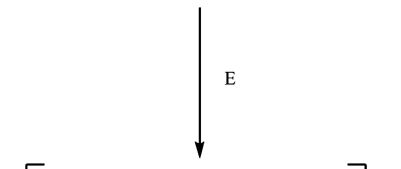
2.6 Miscellaneous. Like 2-acetylpyridine, 2,6-diacetylpyridine is also a versatile precursor for the preparation of variously substituted terpyridines. Treatment of 2,6-diacetylpyridine with thiophene-2-carboxaldehyde in a Knoevenagel reaction with triethylamine afforded the α-β-unsaturated diketone **95**. By reacting the latter with malononitrile in the presence of ammonium acetate as ammonia source the thienyl-substituted tpy **96** was obtained, which also bears cyano and amino groups [87] (Scheme 32). The synthesis can even be conducted in a one-pot fashion by directly reacting 2,6-diacetylpyridine with malononitrile and thiophene-2-carboxaldehyde or by the treatment of 2,6-diacetylpyridine with 1,1-dicyano-2-(2-thienyl)ethylene **97**.

Oxo-derivative **98** was prepared similarly except that ethylcyanoacetate was used instead of malononitrile. Compound **98** was used as a starting material for the preparation of a terpyridine in a two step synthesis [88]. First, it was converted into thioamide derivative **99**. Reaction of the latter with ethylchloroacetate yielded the thiophene-containing terpyridine **100** (Scheme 33).

Scheme 35



123. m = 1; M = Ru^{2+}
124. m = 1; M = Os^{2+}
125. m = 2; M = Ru^{2+}
126. m = 2; M = Os^{2+}
127. m = 3; M = Os^{2+}



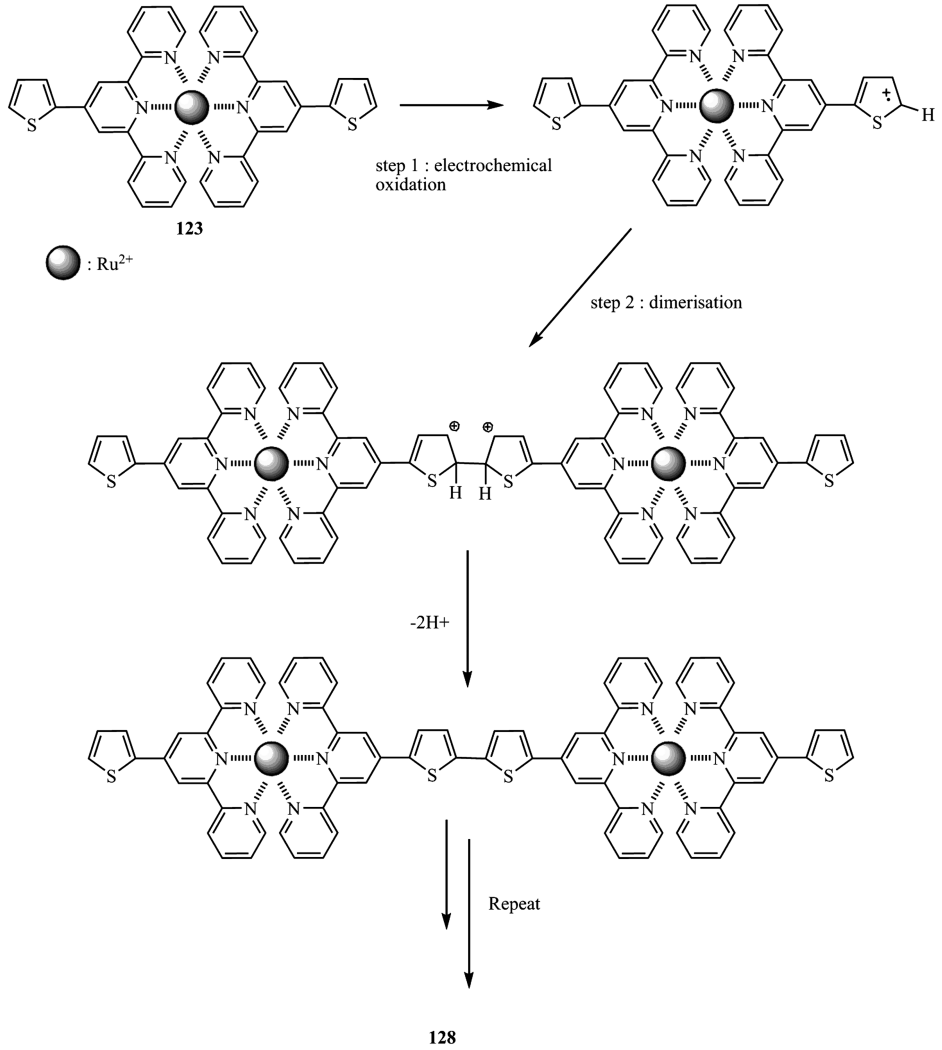
128. x = 2; M = Ru^{2+}
129. x = 2; M = Os^{2+}
130. x = 4; M = Ru^{2+}
131. x = 4; M = Os^{2+}
132. x = 6; M = Os^{2+}

3. UTILIZATION OF THIOPHENE-FUNCTIONALIZED TERPYRIDINES

3.1 Chemotherapeutic agents. Simple terpyridines **1** and **2** were tested against eight different tumor cell lines. These compounds were in many cases more efficient than anti-tumor agent doxorubicin [13]. Unfortunately they also displayed renal cytotoxicity thus precluding their use *in vivo*.

Compounds **101**, **102**, and **103** (Fig. 5) were prepared using tpy **100** as starting material. They were tested for their biological activities as analgesic, anticonvulsant, and anti-Parkinsonian agents [88]. To assess their potencies, comparisons were made with reference products currently

Scheme 36. Postulated mechanism for the formation of polymer **128**. Formation of polymers **129–132** proceed analogously.



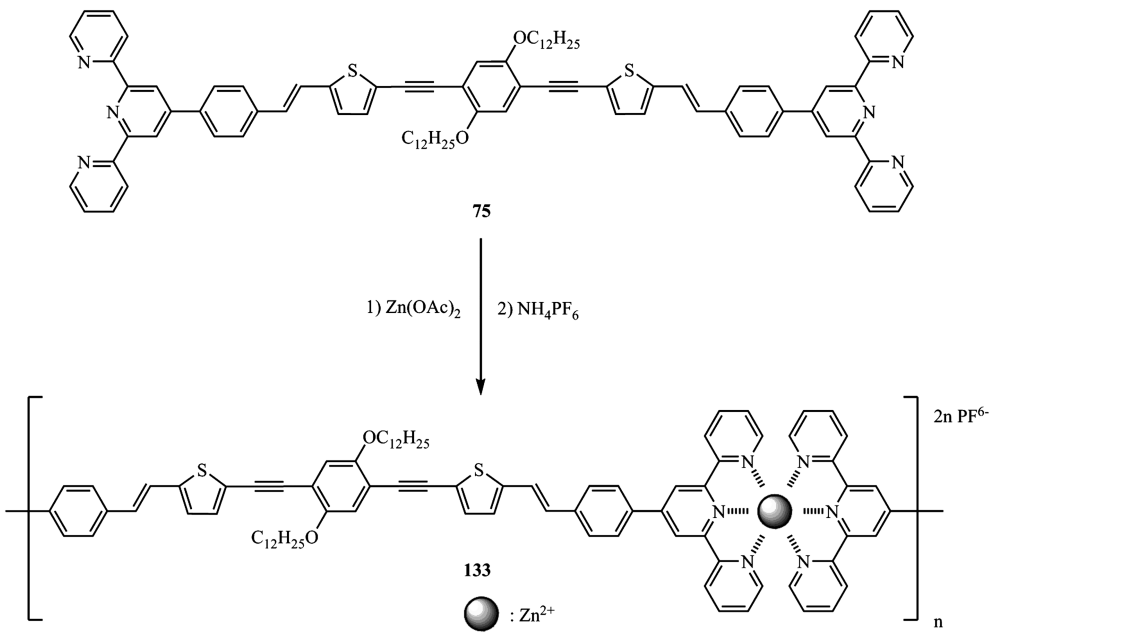
marketed such as Voltarene® (analgesic), Carbamazepine® (anticonvulsant), and Benzotropene® (antiparkinsonian). Terpyridine **101** exhibited analgesic properties similar to the reference because its activity after 120 min in mice was 91% of reference, whereas the two others showed activities around 50 %. Compounds **101** and **102** showed no anticonvulsant activity, but **103** exhibited potent activity (193% of reference compound). The same order was observed concerning anti-Parkinsonian activity, because compounds **101** and **102** exhibited 12 and 16% potency, respectively. The activity of compound **103** reached nearly 80% compared with that of Benzotropene®.

3.2 Sensors. Chemosensory materials are generally based on the modification of electrochemical or photophysical properties on binding to the analyte to be detected [89]. Owing to the complexing properties of terpyridine derivatives toward many metallic cations, the terpyridine moiety was used as a binding unit in metal-sensors. Conjugated polymer **104** (Fig. 6) [76] was prepared by Sonogashira coupling of terpyridine **74** with a diyne derivative.

The conjugated polymer backbone acts at the signalling unit because it is fluorescent. On binding of metals to the terpyridine unit, fluorescence of the polymer is efficiently quenched. Therefore, this material is a "turn-off" sensor for metal cations [90]. The efficient quenching effect was attributed to energy transfer along the polymer backbone resulting in extinction of many repeating units on complexation of one binding site. Such behavior has been reported for many conjugated polymer-based sensors [91–93]. The same methodology was used in the design of a NO sensor [94]. Different conjugated polymers (**105–107**) including pendant tpy ligands were prepared using Heck, Sonogashira, or Suzuki cross-coupling reaction involving compound **74** (Fig. 7).

Initially the system is fluoresecent. On complexation with Cu^{2+}, luminescence is extinguished as described above. In the presence of NO, Cu^{2+} is reduced to Cu^{+}, and luminescence

Scheme 37



Scheme 38

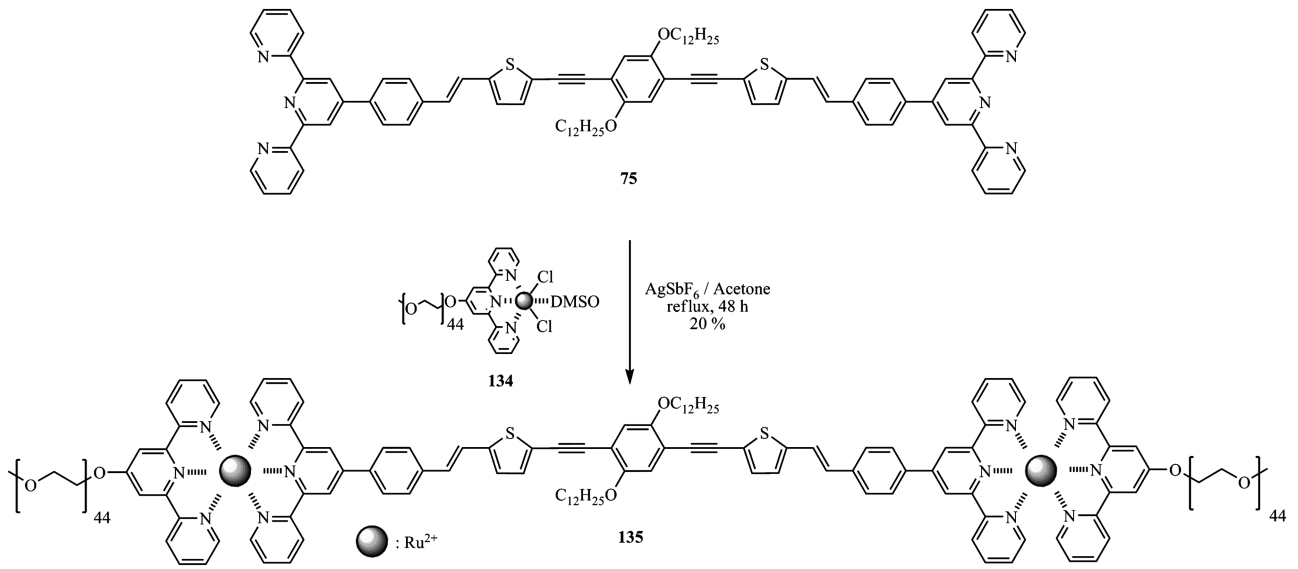
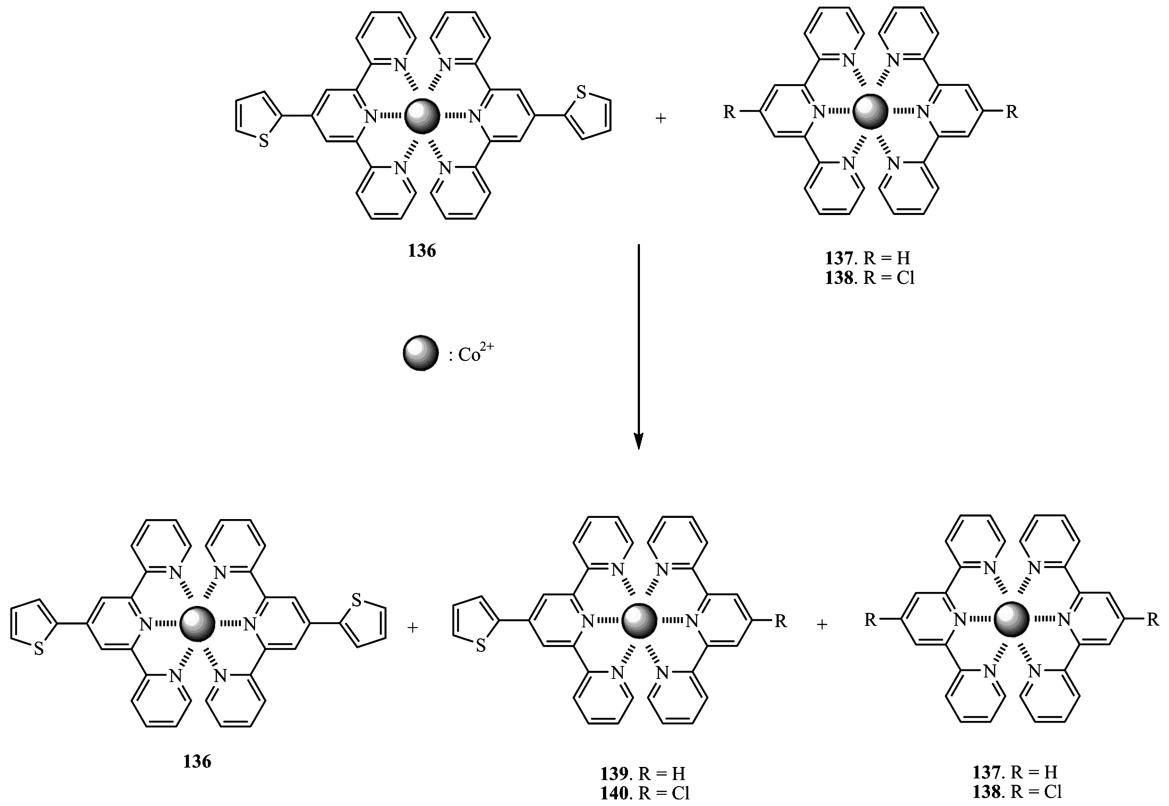


Table 7

Variation of K^+ transport capability of **66** under different conditions.

Receiver phase	Light conditions	K^+ flux (mol/sm^2)
Aqueous citric acid 1 M	Dark	1.53×10^{-8}
	50% visible light	1.92×10^{-8}
	100 % visible light	2.02×10^{-8}
Aqueous sulfobenzo-18-crown 6 (7.85×10^{-4} M)	Dark	3.3×10^{-8}
	50% visible light	4.86×10^{-8}
	100 % visible light	5.68×10^{-8}
Aqueous sulfobenzo-18-crown 6 (1.57×10^{-3} M)	Dark	5.25×10^{-8}
	50% visible light	4.47×10^{-8}
	100 % visible light	7.26×10^{-8}

Scheme 39



is restored. Therefore, materials **105**–**107** are considered as "turn-on" NO sensors.

The use of terpyridine ligand **66** as potential sensor for zinc cations in biological media was also investigated [95]. The elegant idea was to use the pyrene unit to anchor the ligand to DNA thanks to intercalation of the pyrene between base pairs. The modified DNA should allow transportation of the sensing molecule into biological media. There, on complexation with Zn^{2+}, the fluorescence of the terpyridine is modified allowing detection.

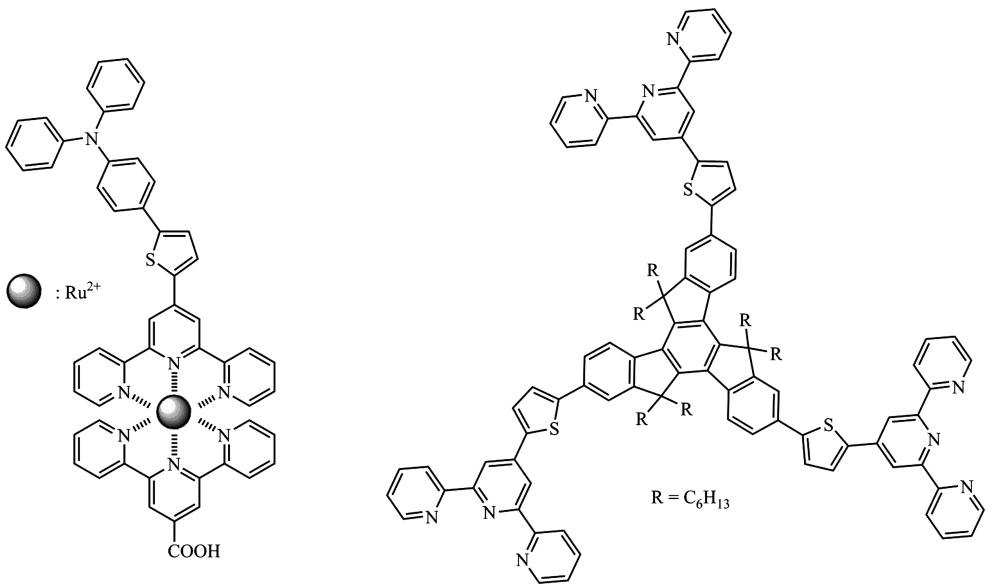


Figure 14. Two recent examples of structures containing a thiophene-functionalized terpyridine.

Unfortunately, according to the authors, such process is not easy to handle due to the complexity of calibration of this probe.

3.3 Solar cells. Dye-sensitized solar cells (DSSC) are photoelectrochemical cells that allow conversion of solar light into electricity. The principle of these cells relies on the use of a sensitizer generally adsorbed onto a wide band gap semi-conductor [96] (e.g., TiO_2). One of the best sensitizer to date is a terpyridine-ruthenium complex also known as "Black Dye" [97]. Many research groups developed terpyridine complexes with the goal of improving cell efficiency. Taking this into account, complexes prepared from thiophene-containing terpyridines were tested as sensitizers.

Complex **108** was obtained from terpyridne **1**. This complex was tested in DSSC and compared with similar complex **109** (Fig. 8) lacking an attached thiophene ring [98].

Results clearly demonstrated crucial influence of the thiophene cycle. Introduction of the latter leads to the localization of the LUMO mainly onto the thiophene containing ligand, as demonstrated by calculations and electrochemical measurements. As a consequence, the excited electron to be injected onto TiO_2 is located at the thiophene-functionalized ligand rather than the COOH-functionalized tpy (which ensure anchorage onto the semi-conductor). Therefore, this electron is more distant from TiO_2 compared with the unfunctionalized complex, and **108** was less efficient than complex **109** for this purpose. The importance of the thiophene ring on Frontier orbitals and photophysical properties of terpyridine complexes was further demonstrated by other studies [99–102]. Taking this into account, dyes **110** and **111** were prepared by functionalization of ligand **6** followed by complexation. These two sensitizers were compared [42] with analoguous complexes **112** and **113** (Fig. 9).

Best efficiencies were obtained with **110** and **111** because the thiophene ring was connected with the ligand grafted to the semiconductor surface (via phosphonic acid moiety). As a consequence, the excited electron is now closer to the semiconductor surface and therefore easier injected.

A necessity for the device to operate properly is bringing back the electron to the dye. This is generally affected by using a liquid electrolyte such as I^-/I_3^- in an organic solvent, as in the above-mentioned examples. It was recently shown that electrolyte nature also plays a crucial role [103]. Using complex **114** as sensitizer (Fig. 10) and iron and cobalt complexes **115**, **116**, or **117** as redox mediators provided a cell with better efficiency compared with the use of I^-/I_3^-.

Nevertheless, the use of liquid electrolytes can lead to problems such as leakage or breakage of the solar cell due to overpressure of the liquid. To prevent this, solid state DSSC were designed [104] using a conducting polymer such as polythiophene to bring back the electron to the dye as depicted in Figure 11.

Complex **118** was prepared in two steps, namely NBS bromination and subsequent complexation, from terpyridine **24**. Coupling with stannylated polythiophene **119** using Stille conditions allowed the assembly of polythiophene-appended dye **120** (Scheme 34).

The latter was tested in a solid state DSSC, but unfortunately device efficiency was very low (<0.01%) [53].

As mentioned above, thiophene rings directly linked to the terpyridine core result in worst results. To circumvent this problem and keeping nevertheless a thiophene ring allowing linkage to a polythiophene polymer, deconjugation of the thiophene from the terpyridine by introducing a spacer was probed. Complexes **121** and **122** (Fig. 12) were tested as sensitizers in a classical device and in a solid state device (using polyoctylthiophene as electron transporting material) [74,105].

Indeed, deconjugation of the thiophene ring resulted in an increased efficiency of the cell, complex **122** being the most efficient sensitizer in both cases (Table 6).

Organic solar cells are another kind of device for converting light into electricity. The architecture of such cells is a bit different compared with DSSC. Photosensitizers used are generally conjugated polymers, and electron acceptor is generally a C_{60} derivative [106] (instead of TiO_2 in DSSC). Recently, the two concepts were mixed by using conjugated polymers containing thiophene, appended with tpy complexes [107] (Fig. 13).

Efficiencies of such cells were near 0.1%, independently of the polymer chain used.

To date, solar cells using terpyridine-thiophene sensitizers are far to be the optimal devices. Nevertheless, the reported results may be helpful to improve dye design and solid-state architecture.

3.4 Macromolecular assemblies. Metallopolymers are macromolecular assemblies containing a metal centre some-where in their structures. Combination of terpyridine complexing properties and thiophene ability to undergo oxidative coupling was used to prepare metallopolymers. Complexes **123–127**, being the monomers, were electropolymerized [34,108,109] to obtain polymeric materials **128–132** (Scheme 35).

The polymerization rely on the fact that thiophene can undergo electrochemical oxidation [20] to generate a radical cation. Two of the latter can undergo coupling, and after loss of two protons a dimer is formed with pendant thiophene rings. The cycle can be repeated again and again and complex monomers are linked one to another thus producing a polymer (Scheme 36).

Another possibility to construct terpyridine-based coordination polymers is to use their complexing properties to assemble monomers together. Ligands bearing two terpyridines heads such as **75** can be linked on complexation with a metallic cation, the latter acting as "glue" between terpyridine units. Polymer **133** was obtained from **75** using this methodology with Zn^{2+} cations [110] (Scheme 37).

Complexation of **75** with Ru^{2+} and terpyridine end-capped polyethylene glycol **134** allowed formation of **ABA**-type triblock polymer **135** (Scheme 38) [111].

Even if no applications are yet reported for these materials, such polymers could find applications in optoelectronic devices, OLED, or sensors.

3.5 Cations carrier. The transport of cations is an important process involved in many biological systems. Terpyridine **66** was tested as a K^+ carrier through a supported liquid membrane [112]. This membrane consist of a saturated solution of **66** in 1-decanol, sandwiched between two Teflon seals and placed in a cell containing a K^+ source phase (aqueous solution of potassium picrate) and a receiver phase (aqueous solution of citric acid or a crown ether). The possibility of **66** to act as a photoresponsive carrier was investigated owing to photophysical properties of this ligand and its complexes [113]. As depicted in Table 7, it appeared that light may be used to modulate transport properties of **66** toward K^+. Nevertheless, the mechanism involved is not clearly elucidated.

3.6 Dynamic combinatorial libraries. The homoleptic Co^{2+} complex **136** was prepared from terpyridine **1**. This complex was then mixed with complexes **137** or **138** and ligand exchange occurred leading to a mixture of complexes **136**, **137**, or **138** and heteroleptic complexes **139** or **140** (Scheme 39) [114].

The final equilibrium mixture was close to the statistical distribution 1:2:1 (homoleptic:heteroleptic:homoleptic). This methodology is a way to prepare heteroleptic Co^{2+}-terpyridine complexes.

4. CONCLUSIONS

This review showed that meanwhile there are numerous methods available for the attachment of a thiophene ring somewhere on a terpyridine ligand. An impressive number of these derivatives has been synthesized and, due to the complexing properties of the terpyridine, many coordination compounds have been prepared. The latter find various interesting applications. With the vast chemistry tools available for the functionalization of both the pyridine or thiophene heterocycle, the preparation of many other derivatives is conceivable in next future. This prospective is illustrated by two examples that appeared in the recent literature [115,116] (Fig. 14).

5. NOTE ADDED IN PROOF

During the submission and review process of this article, a number of relevant articles appeared in the literature. Using the Sonogashira coupling reaction, highly luminescent terpyridine ligands were obtained [117]. These ligands feature a dithieno[3,2-*b*:2',3'-*d*]phosphole. Other luminescent polythienyl-functionalized tpys and their complexes were also described recently [118,119]. They were prepared using method 8 in combination with Suzuki or Stille cross-coupling reactions. Finally, compound **1** has been recently used to prepare Ni and Cu complexes useful as catalysts for the oxidation of sulfides [120].

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