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Synthesis, metal complex formation, and switching properties of spiropyrans linked to chelating sites

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Abstract

The synthesis of 5-pinacolato-2,2′-bipyridine and its applicability in cross-coupling reactions is reported. The use of this framework in Suzuki type cross-coupling reactions, together with a recently published way to achieve indolization has been used to synthesize new spiropyran systems attached to two bipyridine moieties. The indolization method followed, is based on an 'in situ' hydrolysis/Fischer cyclization protocol reported by Buchwald and co-workers. The synthesis of a new phenanthroline based spirooxazine attached to a bipyridine moiety is also reported. One of the spiropyran system was used as a ligand to form a ruthenium metal complex. There photophysical properties were tested with respect to the application as sensitizer in functionalized, wire-type bridging ligands in heteronuclear metal complexes.

Keywords: Spiropyrans; Spirooxazine; Bipyridine; Ruthenium complexes; Molecular device

1. Introduction

The design and preparation of molecular-level devices shows an increasing interest in the last decade because they opens interesting applications in the field of nanotechnology [1] and molecular electronics [2]. An assembly of molecular components that can achieve new specific functions such as light-induced energy or electron transfer processes [3], conformation changes or bond breaking–making processes composes a molecular-level device. A special care must be devoted in the design of new systems able to perform light-induced functions, since they can find applications in signal generation, processing and storage [4]. We have focused our investigations in the preparation and study of heteronuclear metal complexes, which are connected by a wire-type bridging ligand. The bridging ligand itself contains a switchable function that changes after an external stimulus the properties of the bridging ligand. Especially a change in conductivity for electrons across the wire is of great interest (Fig. 1). A rutheniumtrisbipyridine type sensitizer who can induce the light driven energy or electron transfer processes is one of the components of our system. As acceptor unit we have planned to use osmium complexes since their photophysical properties with respect to the easy detection of the transmitted energy or electrons are well studied [5]. We have chosen as bridging ligand a spiropyran or spirooxazine unit modified by covalently bounded 2,2′-bipyridine and/or 1,10-phenanthroline ligands.

The photochromism of spiropyrans is well known since the pioneering work of Fischer and Hirshberg back in 1952 [6]. These compounds have been widely studied due to their applicability in the field of optical filters and optical recording [7]. The performance of such systems is based on the reversible heterolytic cleavage of a C–O bond, in the spiro form, to generate a highly colored merocyanine form which reverts spontaneously to the closed 'spiro' form (Fig. 2). The reversibility of these systems is strongly influenced by the substituents attached to both sides of the structure, hence electronic and steric factors have been extensively studied [8]. In this sense, several modifications have been introduced in the basic spiropyran skeleton oriented to the fine rate tuning of the photochemical opening/closing processes

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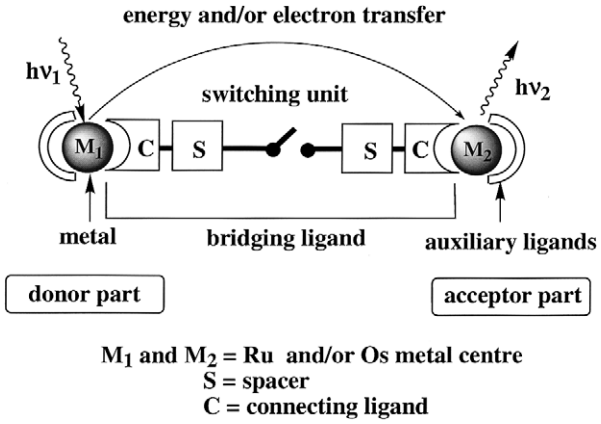


Fig. 1. A model compound to study energy- and/or electron transfer processes.

and to improve fatigue resistance [8]. Nevertheless the inclusion of transition metals in such a skeleton in order to study effects like energy-transfer processes, or the influence of the different states of the spiropyran system on the conductibility for electrons, or metal based sensitized opening/closing processes remain still an open field. Recently Moore and co-workers have reported a porphyrin–spiropyran dyad where the spiropyran behavior tunes the lifetime of the porphyrin first excited state [9]. On the other hand the sensitized opening through a triplet state mechanism of a spirooxazine has also been suggested [10]. To the best of our knowledge in spite of these two examples and the work of Hurst with phenanthroline based spirooxazines coordinated to a ruthenium center [11], no suitable structures to link the spiropyran moiety to well known metal complex sensitizers like rhenium, ruthenium or osmium complexes have been developed. The aim of this paper is to shed a bit of light in the synthetic development of spiropyran structures covalently linked to bipyridine moieties and the preparation of there metal complexes as well as a preliminary study of the switching properties of the free ligands and there complexes.

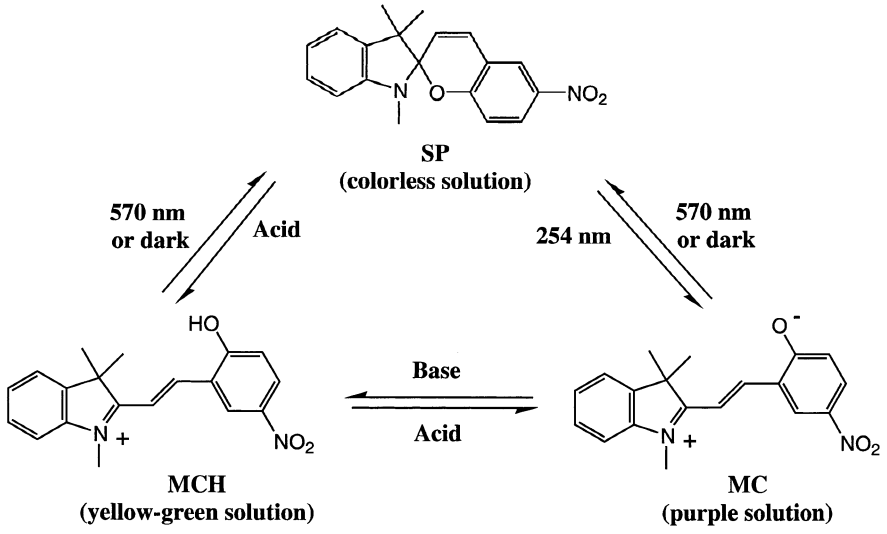
This paper shows the synthesis of three new bipyridine substituted spiropyran derivatives. The first one bearing a bipyridine moiety attached to the pyran part of the spiropyran skeleton, the second one bearing the bipyridine moiety attached to the indoline part and the last one bearing a bipyridine moiety on each end of the spiropyran skeleton. The paper also shows, the preparation of a phenanthroline based spirooxazine attached to a second bipyridine chelating center. Finally the spiropyran system bpy-spNO_2 was used as bidendate ligand forming a ruthenium complex with $Ru(bpy)_2Cl_2$ as precursor.

The photoinduced switching properties of the spiropyran system and its metal complex were studied.

2. Results and discussion

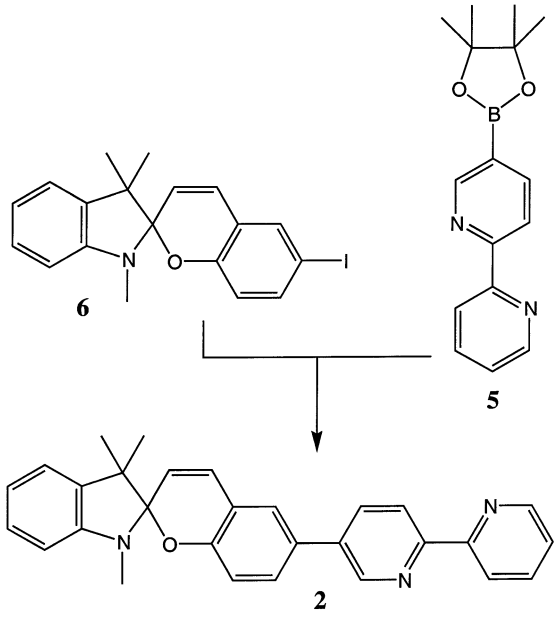
2.1. Preparation of the ligand systems

The functionalization of the basic spiropyran moiety with 2,2′-bipyridine, was attempted in two different ways depending on the indoline/pyran side of this structure. The first approach attempted, consisted in the introduction of the bipyridine moiety at the 6-position of the spiropyran (sp-bpy). The reaction was carried out by means of a direct C–C bond formation using a Suzuki type cross-coupling reaction (Scheme 1) [12]. This choice was taken due to the easy synthetic



SP = spiropyran; MC = merocyanine; MCH = protonated form of merocyanine

Fig. 2. The spiropyran system bpy-spNO_2.

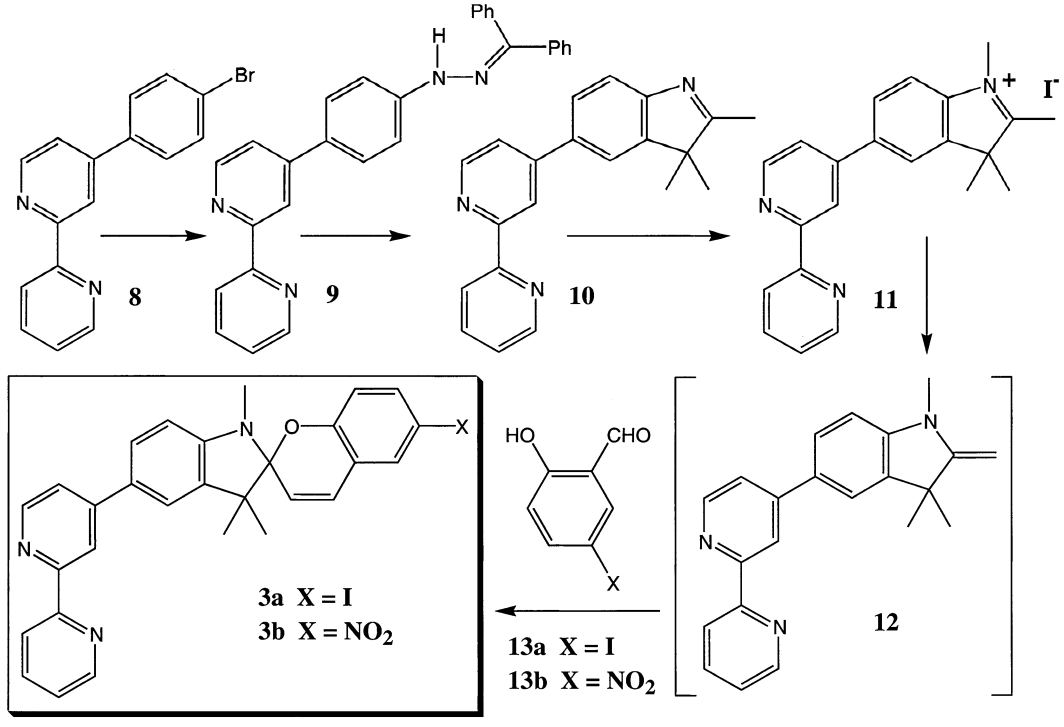


Scheme 1. Synthesis of the spiropyran **2** (sp-bpy).

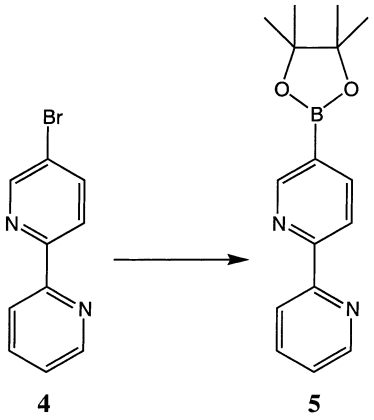
accessibility of the 6-iodo substituted spiropyran **6** [13]. On the other hand, to introduce the bipyridine moiety in the 5′ position of the spiropyran, compounds **3a** and **3b** (bpy-spI and bpy-spNO_2, respectively), the strategy was based on the formation of the already functionalized Fischer's salt with the 2,2′-bipyridine. The scheme was followed by condensation of Fischer's salt **12** generated 'in situ'' with the appropriate salicylaldehyde (Scheme 2).

These two different approaches, were combined to obtain compound **1** were the bipyridine moieties are located both sides of the spiropyran central framework (bpy-sp-bpy) in para position to the heteroatoms N, O (Scheme 4). The choice of these two different approaches was mainly based on the recently published work of Yoon in where it is stated that strategies based on the preparation via Suzuki coupling of the salicylaldehydes substituted with aromatic moieties afford always these compounds in very low yields [14]. In any case we were interested in testing the use of a synthetic building block like 5-boronicacid-pinacolatoester-2,2′-bipyridine which to the best of our knowledge has never been previously reported.

This framework can open new strategies toward the functionalization of photochromic materials with chelating sites able to hold in built-in fashion metallic sensitizers. The synthesis of compound **2** (Scheme 1) began with the preparation of the boronate ester **5**. This compound was prepared following a Suzuki–Miyaura [15] coupling between the 5-bromo-2,2′-bipyridine **4**, obtained following literature procedures [16], and the corresponding bis-pinacolato-boronicacid using potassium acetate as base and $Pd(dppf)Cl_2$ as catalyst (Scheme 3). In this way the desired boronate was readily synthesized using DMSO as solvent. The use of stronger bases promote further reactions of the already formed boronate with the unreacted aryl bromide 2-(2,2′; 5′,3″; 6″,2″) quaternion pyridic **7**. The yield of the reaction, after purification, was 74%. In our early attempts to prepare compound **5**, this was always isolated together



Scheme 2. Synthesis of spiropyrans **3** (**a**, bpy-spI; **b**, bpy-spNO_2).



Scheme 3. Synthesis of the bipyridine boronate **5**.

with some unreacted starting materials. Several attempts to recrystallize this mixture were always unsuccessful. After this observation, column chromatography was attempted. In this new case, using a short plug of silica and *n*-hexane as eluent, the boronate precursor was finally removed. Compound **5** was isolated by flushing the column with a mixture dichloromethane/methanol (1/1). This last experiment shows that compound **5** can overlife silica based chromatography in contrast with the terpyridine homologous compounds [17]. Compound **6** was synthesized following standard literature procedures [13]. The cross-coupling reaction depicted in Scheme 1 to obtain compound **2** was carried out by heating compounds **6** and **5** in DMF at 100 °C using Na_2CO_3 as base and $Pd(PPh_3)_4$ as catalyst. The yield of this reaction, after two chromatographic purification steps, was 45%.

The synthesis of compounds **3a** and **3b** bearing a bipyridine moiety in the indoline part of the spiropyran system, was achieved as it is depicted in Scheme 2. In this approach the 'key compound' was the bipyridine substituted Fischer's salt **12** obtained via an 'in situ' hydrolysis/Fisher cyclization protocol. The synthesis of this compound was attempted following a new approach, introduced by Buchwald and co-workers [18]. The preparation of indol rings takes as starting material the 4(4-bromophenyl)-[2,2′]bipyridine compound **8** (Scheme 2). Following Scheme 2, compound **8** was reacted with benzophenone hydrazone to afford the stable hydrazone **9** which was purified by column chromatography. The reaction was carried out using sodium-*tert*-butoxide as base and $Pd(acetate)_2/\pm$BINAP as catalyst. The following reaction was the indolization step. This was achieved by refluxing the hydrazone **9** in EtOH in presence of TsOH as acidic catalyst and the appropriate ketone. This approach is based on the fact that the hydrolysis of hydrazones can be promoted by trapping the liberated hydrazine with an excess of an aldehyde or ketone. This can produce an *N*-arylhydrazone which can undergo Fischer indolization under acidic conditions [17]. The reaction was tested under different conditions. The use of three equivalents of acid and 50 h yielded 76%. However when the reaction was carried out using two equivalents of acid and reflux over the same period of time, the yield was 44%. In all these attempts the amount of enolizable ketone was changed from 1.2 equivalents up to 2 equivalents without significative changes. The methylation of this indol-type system was achieved using a slightly excess of MeI. Compounds **3a** and **3b** were obtained by 'in situ' generation of the Fischer's salt **12** using Et_3N as base and further condensation with the corresponding 4-substituted salicylaldehydes **13a** and **13b**.

The synthesis of compound **8** was achieved by a modified literature procedure. This compound has been previously synthesized using and approach based on a Kröhnke reaction between 3-(4-bromo-phenyl)-acrylic acid and the corresponding pyridinium salt to afford 4-(4-bromophenyl)-[2,2′]bipyridinyl-6-carboxylic acid which can be readily decarboxylated by sublimation [19]. In our case this last reaction was not yielding properly.

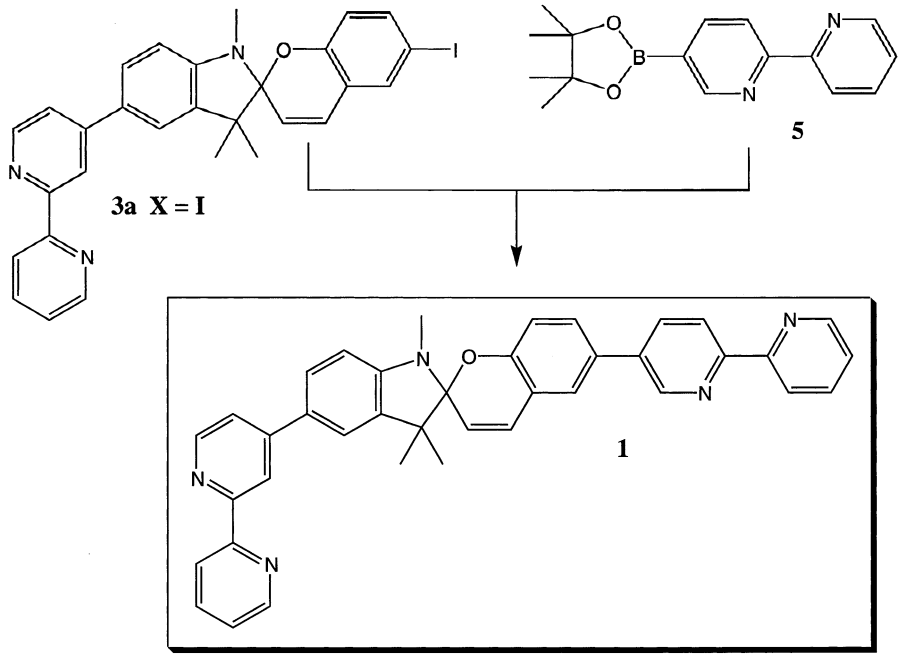
We attempted this last step using microwaves. In this new approach, the 4-(4-bromo-phenyl)-[2,2′]bipyridinyl-6-carboxylic acid was dissolved in ethylene glycol and was heated for three periods of 2 min using a standard microwaves oven (750 W).

The ditopic compound **1** was synthesized following Scheme 4. This scheme involves the synthetic methodologies underlined previously for the preparation of compounds **2** and **3**. The cross-coupling reaction between compounds **5** and **3a** was carried out in a similar manner as it has been shown for the synthesis of compound **2**. Flash chromatography purification using CH_2Cl_2/MeOH (98/2) as eluent afforded compound **1** in 30% yield.

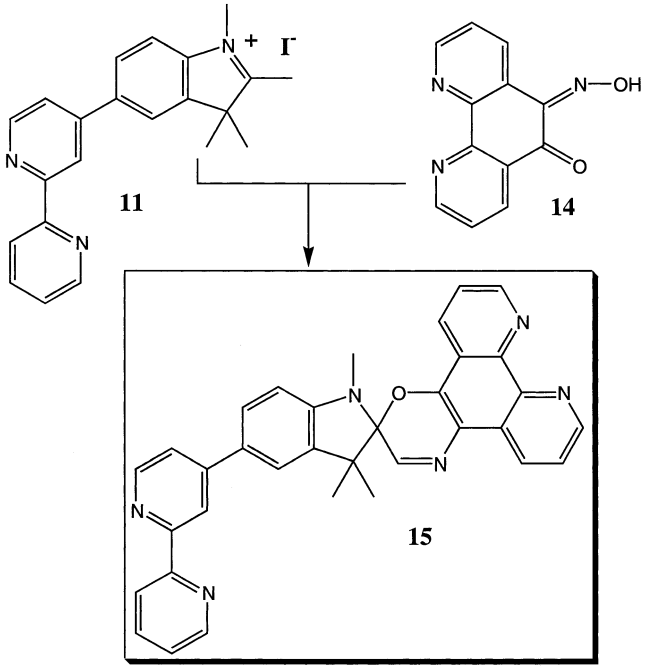
The last ligand system of our series, was synthesised as shown in Scheme 5. Condensation of compound **11** with the already published phenanthroline derivative **14** [20] in boiling ethanol afforded the desired spirooxazine **(15)** (bpy-ox-phen) in 62% yield after chromatographic purification.

2.2. Preparation of the metal complex

$[Ru(bpy)_2(bpy\text{-}spNO_2)](PF_6)_2$ was prepared by refluxing the ligand bpy-$spNO_2$ with the appropriate metal source $(Ru(bpy)_2Cl_2\cdot 2H_2O$ for 3.5 h using methoxyethanol as solvent [21]. The metal complex was purified, after counterion exchange, by preparative plate chromatography and recrystallization from a mixture acetone/water/NH_4PF_6 yielding 53.6% of an orange powder.



Scheme 4. Synthesis of the spiropyran **1** (bpy-sp-bpy).



Scheme 5. Synthesis of the spirooxazine **15** (bpy-spox-phen).

2.3. Irradiation experiments

Preliminary irradiation experiments were performed with the free ligand **3b** (bpy-spNO_2) and the ruthenium complex $[Ru(bpy)_2(\mathbf{3b})](PF_6)_2$. All compounds show during irradiation with a 365-nm light source the formation of a steady state band at about 570 nm corresponding to the merocyanine form (open form; MC). Under acidic conditions the molecule can be transferred into the stable yellow, protonated merocyanine form (MCH) which has an absorption band at 410 nm (Figs. 2 and 3). In the dark, the MC is not stable and undergo a fast backreaction to the closed form (spiropyran; SP) with a rate constant of about 1×10^{-3} s. The backreaction is depending on the polarity of the used solvent. In methanol as the more polar solvent versus acetone is the closing reaction much slower due to stabilization of the polar MC form by the solvent molecules. Fig. 4 show the decay curves of MC form of the free ligand and the ruthenium complex. It seems to be that the backreaction from the MC to the SP form is much faster if the ligand is complexes by the metal centre. In such a case the MC form can only be observed at low temperatures.

In a further experiment we have irradiated the ruthenium complex to check the ability of an energy transfer from the excited metal centre to the switching unit. Fig. 5 shows clearly, that after irradiation of the metal complex with a 365-nm light source the merocyanine molecule is formed. By a 450-nm irradiation of the same solution the metal complex remain unchanged. Therefore the metal centre in the excited state is not able to induce a photochemical reaction to transfer the SP into MC. The different spin states of the excited metal centre (triplet state) and the spin state of the photochemical reaction (singlet state) are not compatible to induce the photochemical reaction.

If the present system is incorporated in a heteronuclear, bridged metal complex (Ru-switch-Os) an ideal molecular device can be observed. The switching unit can be opened (365 nm) independently from the sensitizer unit. An irradiation of the sensitizer (450

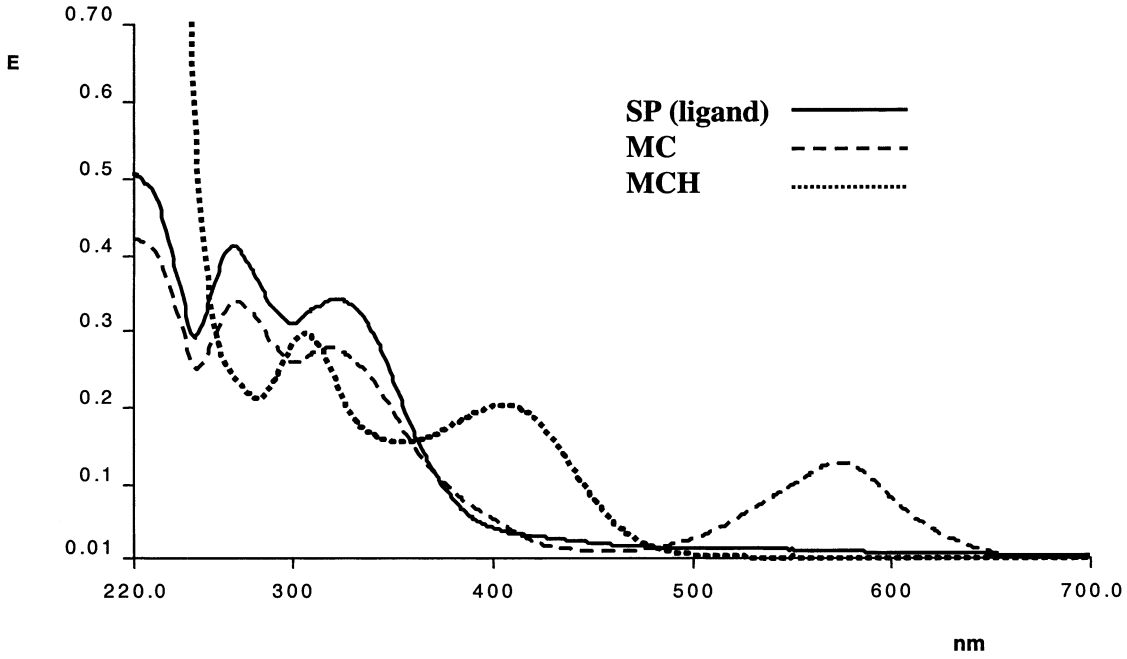


Fig. 3. Irradiation experiments with the spiropyran bpy-spNO$_2$. SP (ligand) corresponds to the spiropyran form of the ligand, MC to the merocyanine form, and MCH to the protonated merocyanine form.

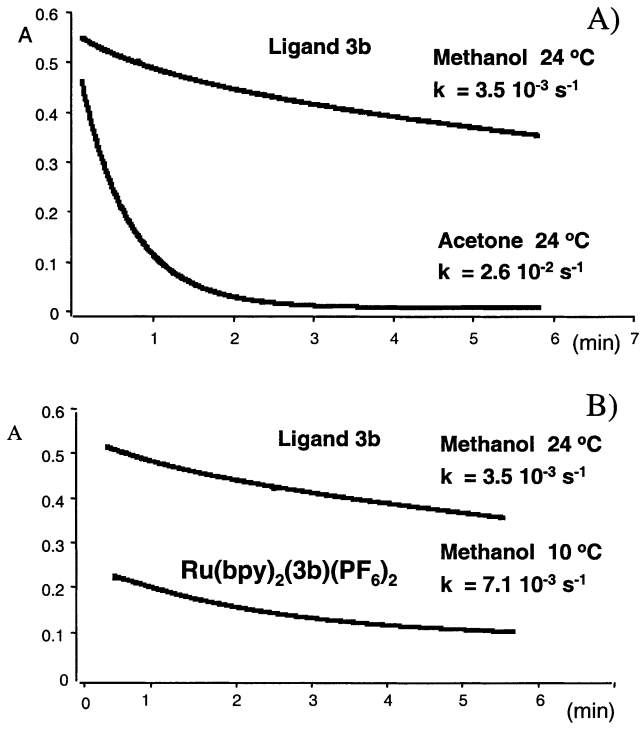


Fig. 4. Decay of the MC-form under different conditions: (A) methanol versus acetone solutions (24 °C); (B) ligand 3b (24 °C) versus the ruthenium complex (10 °C) in methanol solution.

nm) does not affect the switching unit and an energy transfer process from the ruthenium to the osmium centre can occur. Furthermore, the rate of the energy transfer process is dependent on the state of the switching unit.

3. Conclusions

Suzuki type cross-coupling reaction has been proved to be an excellent synthetic tool to introduce bipyridine

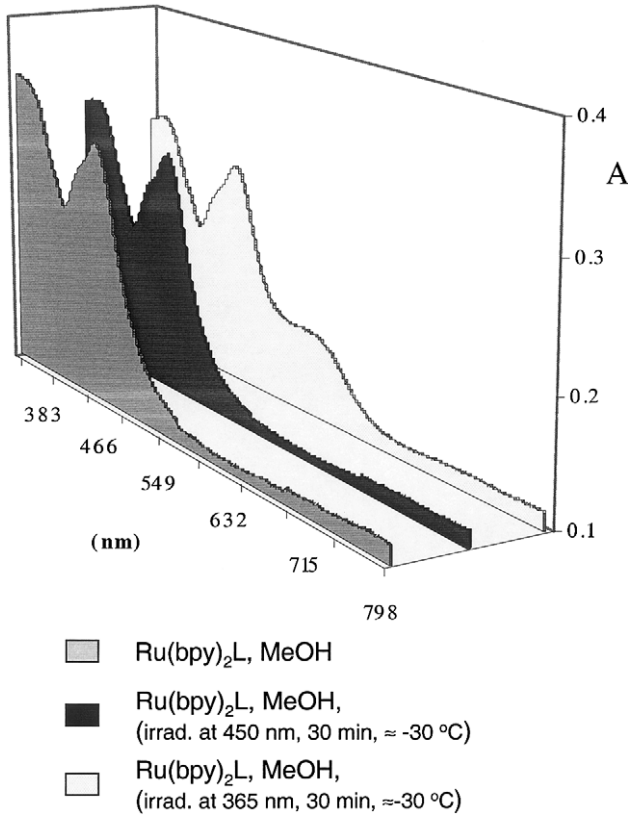


Fig. 5. Irradiation experiment on the ruthenium complex.

moieties in 6-iodo substituted spiropyrans. On the other hand the 'in situ' hydrolysis/Fisher cyclization protocol reported by Buchwald has been successfully applied to generate an indol ring already functionalized with a bipyridine moiety. This new framework has led straightforward to the formation of spiropyran skeletons with good yields. The combination of both techniques leads, in an easy way, to the preparation of new ditopic ligands with potential applications as functionalized molecular wires. Irradiation experiments show that no energy transfer occur after irradiation into the 450 nm MLCT band of the sensitizer. In the metal complex, the SP form can easily be transferred into the MC form by irradiation into the 365 nm band of the SP unit.

4. Experimental

4.1. General details

All reactions were run in ovendried glassware under a slight positive pressure of argon unless otherwise stated. Solvents were distilled following literature procedures. Sodium-*tert*-butoxide was purchased from Aldrich Chemical Co.; the bulk of this material was stored under nitrogen in a vacuum atmospheres glove box. Small portions (1–2 g) were removed from the glove box in glass vials, stored in a desiccator with anhydrous calcium sulfate for periods of up to 2 weeks, and weighted in the air. Benzophenone hydrazone was purchased from Aldrich Chemical Co. and used as received. Et_3N was distilled under vacuum from KOH and stored under Ar. The catalysts used in the Suzuki type reactions were purchased from Strem Chemicals and were kept under argon, small amounts were taken for every reaction and the flask was recapped and flushed with argon before the storage. When the catalyst turned into a dark brown color (originally yellow crystals) it was avoided and fresh one was used. All other reagents were commercially available and used without further purification unless otherwise noted. Preparative chromatography was performed using Silica Gel, 230–400 or 400–600 mesh. All products were characterized by ^{1}H NMR and ^{13}C NMR. NMR spectra were obtained in $CDCl_3$ on a Varian Gemini-300 MHz, or Bruker ADVANCE 400 MHz spectrometer. All ^{1}H NMR spectra are reported in ppm units, ppm downfield from tetramethylsilane as an internal standard. All ^{13}C NMR spectra are reported in ppm relative to the central line of the triplet for $CDCl_3$ at 77 ppm. Coupling constants are given in Hertz. New compounds were further characterized by C, H, N analysis performed at the Fribourg Engineering School, 1700 Fribourg, Switzerland. Electron spray ionisation (ESI) mass spectra were measured with a Bruker FTMS 4.7 T Bio APEXII spectrometer. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 2 spectrometer. Band positions are in nm indicated and band intensities (ε) in parenthesis.

4.1.1. 4-(4-Bromophenyl)-[2,2′]bipyridine (**8**)

4-(4-Bromophenyl)-[2,2′]bipyri-dinyl-6-carboxylic acid (3 g, 0.85 mmol) was suspended in 25 ml of ethylene glycol and the suspension was repeatedly heated three times for 2 min., allowing to cool down between heating periods, in a standard microwaves oven (750 W). After these cycles, the solvent was removed under reduced pressure and the black mixture was filtered through a short plug of silica using as solvent a mixture 3/1 of CH_2Cl_2/AcOEt. Yield 1.8 g, (68%).^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 7.34 (ddd, $^1J = 9.0$, $^2J = 4.9$, $^3J = 1.1$, 1H), 7.80 (dd, $^1J = 4.9$, $^2J = 1.6$, 1H), 7.63 (s, 4H), 7.84 (td, $^1J = 7.7$, $^2J = 1.6$, 1H), 8.45 (brd, $J = 8.2$, 1H), 8.64 (d, $J = 1.6$, 1H), 8.69–8.74 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 118.83, 121.36, 121.42, 123.64, 124.01, 128.75, 132.27, 137.14, 148.26, 149.13, 149.73, 155.77, 156.66. *Anal*. Calc.: C, 61.76; H, 3.56; N, 9.00 Found: C, 61.43, H, 3.61, N, 9.04. MS/ES: 312 [M+H].

4.1.2. 4-(4-benzophenone-hydrazone)-2,2′-bipyridine (**9**)

(0.724 g, 4.0 mmol), $Pd(AcO)_2$ (0.036 g, 0.16 mmol), (±) BINAP (0.15 g, 0.18 mmol), *t*-ButONa (0.5 g, 5.2 mmol) and the bromophenyl derivative **8** (1 g, 3.2 mmol) were suspended in 10 ml of freshly distilled toluene. The reaction mixture was purged during 10 min with argon before being heated at 100 °C for 36 h under argon. After this period the crude reaction, was filtered through a short plug of celite to afford a dark oil after removal of the solvent under reduced pressure. This oil was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 98/2) to yield 1.170 g (87%) of compound **9** as a yellow flaky solid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 7.18 (s, 6H), 7.26–7.37 (m, 6H), 7.45–7.64 (m, 5H), 7.68 (d, $J = 6.1$, 1H), 7.71 (d, $J = 8.2$, 2H), 7.80 (td, $^1J = 7.7$, $^2J = 1.6$, 1H), 8.42 (d, $J = 9.2$, 1H), 8.62–8.66 (m, 2H), 8.69 (brd, $J = 4.9$, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 113.25, 117.85, 120.56, 121.20, 123.576, 126.57, 127.97, 128.18, 128.23, 129.02, 129.29, 129.33, 129.68, 132.49, 136.81, 138.07, 145.28, 145.40, 148.81, 149.02, 149.05, 149.46, 149.48, 156.35, 156.40. *Anal*. Calc.: C, 81.66; H, 5.20; N, 13.14. Found: C, 81.71, H, 5.17, N, 13.08. MS/ES: 427 [M+H]. MP = 68–70 °C.

4.1.3. Compound ***10***

Hydrazone **9** (1 g, 2.4 mmol), TsOH (1,4 g, 7.2 mmol) were heated together in 3 ml of freshly distilled ethanol under argon. After a period of 20 min, 0.4 ml of isopropylmethylketone was added through syringe and the mixture was refluxed for a period of 72 h. After cooling down, the solvent was removed in vacuum and the dark oil was purified by column chromatography

(SiO_2, CH_2Cl_2/MeOH, 98/2) to yield 0.565 g (75%) of indol **10** as a yellow flaky solid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.34 (s, 6H), 2.28 (s, 3H), 7.29 (ddd, $^1J = 7.1$, $^2J = 4.4$, $^3J = 1.1$, 1H), 7.52 (dd, $^1J = 4.9$, $^2J = 1.6$, 1H), 7.61 (t, $J = 8.2$, 1H), 7.64–7.60 (m, 2H), 7.80 (td, $^1J = 7.7$, $^2J = 2.6$, 1H), 8.43 (brd, $^1J = 7.7$, 1H), 8.63–8.70 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 15.63, 23.19, 53.99, 118.93, 120.24, 120.34, 121.39, 121.73, 123.82, 127.05, 135.40, 137.00, 146.66, 149.17, 149.57, 149.64, 154.74, 156.27, 156.64, 189.45. *Anal*. Calc.: C, 80.48; H, 6.11; N, 13.41. Found: C, 80.39, H, 6.07, N, 13.49. MS/ES: 314 [M+H]. MP = 139–140 °C.

4.1.4. Compound *11*

MeI (0.11 ml, 1.7 mmol) was added over the indol **10** (0.26 g, 0.8 mmol) dissolved in acetonitrile. Then the mixture was heated overnight at 55 °C, after this time the solvent was removed in vacuo and the crude mixture was chromatographically purified through a short plug of silica using CH_2Cl_2/MeOH/Et_3N (97/3/1) to afford 0.16 g (44%) of the salt **11** as a clear oil which underwent reddish after fridge storage. ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.39 (s, 6H), 3.07 (s, 3H), 3.92 (s, 3H), 6.61 (d, $J = 8.2$, 1H), 7.29 (ddd, $^1J = 7.1$, $^2J = 4.4$, $^3J = 1.1$, 1H), 7.46–7.54 (m, 2H), 7.58 (dd, $^1J = 8.2$, $^2J = 1.6$, 1H), 7.81 (td, $^1J = 7.7$, $^2J = 1.6$, 1H), 8.41 (brd, $J = 7.1$, 1H), 8.57 (d, $J = 1.6$, 1H), 8.61 (d, $J = 5.5$, 1H), 8.7 (dm, $J = 5.5$, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 28.87, 30.01, 44.14, 74.69, 105.25, 117.94, 120.51, 120.75, 121.40, 123.68, 127.09, 128.31, 136.97, 138.62, 147.54, 149.13, 149.51, 156.45, 156.54, 162.51. *Anal*. Calc.: C, 58.03; H, 4.87; N, 9.23 Found: C, 58.12, H, 4.79, N, 9.19. MS/ES: 328 [M−I].

4.1.5. Spiropyran formation (*3a, 3b*)

General method for compounds **3a** and **3b**. Compound **11** (0.2 g, 0.44 mmol) and the corresponding salicylaldehyde (0.44 mmol), were heated under argon at 80 °C in a two necked round bottom flask. To the boiling solution, Et_3N (0.1 ml) were added through a septum and the refluxing was maintained until TLC (SiO_2, CH_2Cl_2/MeOH/Et_3N = 99/1/0.5) did not show further changes (4–6 h). After this period the solvent was removed in vacuo and the crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 99/1) to yield compound **3a** (0.16 g, 68%) and **3b** (0.15 g, 70%).

4.1.6. *3a (bpy-spI)*

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 1.21 (s, 3H), 1.36 (s, 3H), 2.77 (s, 3H), 5.72 (d, $J = 10.1$, 1H), 6.50 (d, $J = 9.1$, 1H), 6.61 (d, $J = 7.1$, 1H), 6.80 (d, $J = 10.1$, 1H), 7.29–7.38 (m, 3H), 7.50 (d, $J = 1.5$, 1H), 7.53 (dd, $^1J = 5.5$, $^2J = 2.0$, 1H), 7.64 (dd, $^1J = 8.1$, $^2J = 2.0$, 1H), 7.84 (td, $^1J = 7.6$, $^2J = 2.5$, 1H), 8.46 (d, $J = 8.1$, 1H), 8.64 (d, $J = 2.0$, 1H), 8.66 (d, $J = 5.0$, 1H), 8.72 (brd, $J = 4.5$, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 20.21, 25.93, 28.95, 30.97, 52.01, 81.75, 104.63, 107.15, 117.41, 118.22, 120.02, 120.40, 120.48, 120.92, 121.17, 121.50, 123.82, 127.33, 128.57, 129.02, 135.13, 137.05, 136.64, 138.40, 149.17, 149.29, 150.04, 154.17, 156.122. *Anal*. Calc.: C, 62.49; H, 4.34; N, 7.54; Found: C, 62.22, H, 4.29, N, 7.51. MS/ES: 558 [M+H].

4.1.7. *3b (bpy-spNO$_2$)*

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 1.24 (s, 1H), 1.37 (s, 3H), 2.80 (s, 3H), 5.87 (d, $J = 11.1$, 1H), 6.65 (d, $J = 8.1$, 1H), 6.79 (d, $J = 8.1$, 1H), 6.95 (d, $J = 10.1$, 1H), 7.32–7.35 (m, 1H), 7.51–7.55 (m, 2H), 7.66 (d, $J = 7.1$, 1H), 7.83–7.87 (m, 1H), 8.01–8.04 (m, 2H), 8.46 (d, $J = 8.1$, 1H), 8.64 (s, 1H), 8.67 (d, $J = 5.0$, 1H), 8.71 (d, $J = 4.0$, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 20.88, 25.58, 29.73, 29.80, 51.89, 99.73, 107.63, 118.29, 119.47, 120.56, 120.85, 121.01, 121.42, 122.98, 123.61, 123.82, 126.82, 127.67, 130.18, 130.48, 137.05, 138.88, 142.68, 148.35, 148.57, 149.14, 149.56, 151.07, 156.52. *Anal*. Calc.: C, 73.09; H, 5.08; N, 11.76; Found: C, 73.17, H, 5.17, N, 11.68. MS/ES: 477 [M+H].

4.1.8. *5-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-[2,2′] bipyridinyl (5)*

5-Bromo-2,2′-bipyridine **4** (0.20 g, 0.86 mmol), oven-dried AcOK (0.25 g, 2.57 mmol) and bispinacolatoboronicacid (0.26 g, 1.03 mmol) were mixed in a two necked round bottom flask. One of the necks was sealed via septum and the other one was adapted to a reflux condenser connected to the argon/vacuum line. Oxygen was removed from the closed system by evacuation and argon backfilling (three times). Over this system freshly distilled and degassed DMSO 2 ml was added through the septum and then the system was opened and the catalyst (0.02 g, 3 mol%) was quickly added. The system was recapped and the oxygen elimination procedure was repeated three more times. After this, the reaction mixture was heated at 105 °C for 12 h. After this period, the crude reaction was partitioned between a mixture H_2O/CH_2Cl2 (20/60) and the organic phase was collected and evaporated under reduced pressure to afford a black solid. Addition of hexane to this solid, solubilized the desired compound which was used without further purification. For analytical purposes, this last compound was further purified using a short plug of silica and hexane as eluent to remove the pinacolato derivatives and a mixture CH_2Cl_2/MeOH (1/1) to flush off the desired compound. ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.35 (s, 12H), 7.29 (dd, $^1J = 7.7$, $^2J = 5.0$, 1H), 7.80 (td, $^1J = 7.7$, $^2J = 2.2$, 1H), 8.10 (dd, $^1J = 7.7$, $^2J = 2.2$, 1H), 8.35 (d, $J = 8.0$, 1H), 8.42 (d, $J = 8.0$, 1H), 8.67 (d, $J = 5.0$, 1H), 8.99 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 24.92, 84.25, 120.25, 121.63, 123.97, 136.96, 143.33, 149.25, 155.08, 156.14, 157.99, 165.20.

Anal. Calc.: C, 68.11; H, 6.79; N, 9.93; Found: C, 69.14, H, 6.72, N, 9.89. MS/ES: 283 [$M+H$].

4.1.9. Cross-coupling reaction (**1, 2**)

General method: 5-pinacolatoboronic acid-2,2′-bipyridine (0.15 g, 0.52 mmol), the corresponding Iodo derivative (0.43 mmol) and $Na_2CO_3 \times 10\ H_2O$ (2.38 g, 8.33 mmol) were mixed together in a two necked round bottom flask. The reaction flask was adapted to a condenser linked to the argon/vacuum line. The oxygen was removed from the sealed system by evacuation and argon was backfilled (three times). Over this system freshly distilled and degassed DMF 3 ml was added through the septum and then the system was opened and the catalyst (0.05 g, 0.04 mol%) was quickly added. The system was recapped and the oxygen elimination procedure was repeated three more times. The reaction mixture was heated a 105 °C for a period of 6–8 h. After that, water (10 ml) was added and the whole crude mixture was evaporated under reduced pressure. The black crude mixture was suspended in CH_2Cl_2 (50 ml) and filtered through celite. The liquid was collected, evaporated and purified using column chromatography (SiO_2, CH_2Cl_2/MeOH-99/1).

4.1.10. bpy-sp (**2**)

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 1.20 (s, 3H), 1.35 (s, 3H), 2.77 (s, 3H), 5.77 (d, $J = 10.1$, 1H), 6.55 (d, $J = 8.1$, 1H), 6.83–6.89 (m, 2H), 6.95 (d, $J = 10.1$, 1H), 7.09 (d, $J = 7.1$, 1H), 7.20 (t, $J = 8.1$, 1H), 7.30–7.36 (m, 2H), 7.40 (brd, $J = 7.6$, 1H), 7.84 (brt, $J = 7.6$, 1H), 7.97 (brd, $J = 7.1$, 1H), 844 (dd, $^1J = 8.1$, $^2J = 5.5$, 2H), 8.70 (d, $J = 4.5$, 1H), 8.88 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 20.21, 25.95, 29.00, 51.96, 104.78, 106.92, 115.87, 119.32, 119.43, 120.36, 121.24, 121.58, 123.76, 125.26, 127.70, 128.43, 129.22, 129.28, 134.83, 136.27, 136.67, 137.27, 146.93, 148.17, 149.06, 155.02. *Anal*. Calc.: C, 80.72; H, 5.84; N, 9.74; Found: C, 80.65, H, 5.77, N, 9.69. MS/ES: 431 [$M+H$].

4.1.11. bpy-sp-bpy (**1**)

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 1.28 (s, 3H), 1.45 (s, 3H), 2.86 (s, 3H), 5.82 (d, $J = 10.4$, 1H), 6.67 (d, $J = 8.1$, 1H), 6.89 (d, $J = 8.4$, 1H), 7.01 (d, $J = 10.1$, 1H), 7.31–7.37 (m, 2H), 7.39 (d, $J = 2.0$, 1H), 7.44 (dd, $^1J = 8.3$, $^2J = 2.2$, 1H), 7.55 (d, $J = 7.8$, 2H), 7.58 (dd, $^1J = 5.3$, $^2J = 1.76$, 1H), 7.69 (dd, $^1J = 7.8$, $^2J = 1.7$, 1H), 7.83–7.90 (m, 2H), 7.99 (dd, $^1J = 8.3$, $^2J = 1.3$, 1H), 8.46 (dd, $^1J = 16.4$, $^2J = 8.3$, 2H), 8.67–8.70 (m, 2H), 8.73 (dd, $^1J = 12.9$, $^2J = 4.0$, 2H), 8.89 (d, $J = 2.3$, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 20.27, 24.49, 25.99, 29.00, 52.00, 104.80, 107.14, 115.83, 118.22, 119.26, 119.78, 120.51, 120.92, 121.01, 121.48, 123.63, 123.77, 125.33, 127.32, 128.44, 128.57, 129.02, 129.52, 129.76, 132.19, 134.61, 135.99, 135.96, 137.02, 137.76, 147.15, 149.17, 149.26, 149.39, 150.03, 154.42, 154.68, 155.99, 156.20. *Anal*. Calc.: C, 79.98; H, 5.33; N, 11.96; Found: C, 80.11, H, 5.24, N, 11.90. MS/ES: 586 [$M+H$].

4.1.12. bpy-spox-phen (**15**)

Compound **14** (0.087 g, 0.4 mmol) and compound **11** (0.16 g, 0.35 mmol) were dissolved in freshly distilled EtOH. The mixture was refluxed under argon for 5 h. After this period the solvent was removed in vacuo and the dark blue crude product was purified 3 times by column chromatography (SiO_2, CH_2Cl_2/MeOH, 99/1) to afford the desired compound as a bright blue flaky solid. 0.12 g, 62%. ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 1.46 (s, 3H), 1.48 (s, 3H), 2.86 (s, 3H), 6.71 (d, $J = 8.1$, 1H), 7.33–7.36 (m, 1H), 7.54–7.58 (m, 3H), 7.68–7.72 (m, 2H), 7.84–7.88 (m, 2H), 8.44 (dd, $^1J = 8.1$, $^2J = 1.5$, 1H), 8.50 (d, $J = 8.1$, 1H), 8.66–8.73 (m, 3H), 8.95 (dd, $^1J = 8.1$, $^2J = 1.5$, 1H), 9.10 (dd, $^1J = 4.5$, $^2J = 1.5$, 1H), 9.15 (dd, $^1J = 4.5$, $^2J = 2.0$, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 20.88, 25.57, 29.73, 30.94, 51.89, 99.73, 107.64, 118.36, 119.47, 120.58, 121.02, 121.21, 121.50, 122.98, 123.61, 123.88, 126.82, 127.71, 130.20, 130.49, 136.76, 137.12, 138.88, 142.65, 146.69, 148.42, 148.55, 149.13, 149.38, 149.69, 150.99, 151.07, 155.09, 156.32. *Anal*. Calc.: C, 81.18; H, 5.30; N, 10.52; Found: C, 81.26, H, 5.19, N, 10.61.

4.1.13. [Ru(bpy)$_2$(3b)](PF$_6$)$_2$

A mixture of $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (0.057 g, 0.150 mmol) and the spiropyran **3b** (0.078 g, 0.150 mmol) in 2-methoxyethanol/H_2O (10 ml, 95:5, v/v) was heated at 120 °C under an Argon atmosphere for 3.5 h. The solvent was removed under reduced pressure. After adding of 2 ml of H_2O a saturated solution of NH_4PF_6 (2 ml) was added and the orange precipitate filtered off. The crude product was purified by preparative plate (SiO_2, eluent: AN:H_2O:MeOH:KNO_3 = 40:10:10:1). The scratched strip of silica was washed with acetone/1% NH_4PF_6. After evaporation of acetone the precipitated solid was redissolved in water/acetone, and a saturated aqueous solution of NH_4PF_6 was added. After evaporation of the acetone, the precipitated solid was filtered off, washed with water and dried (45 °C) to yield $[Ru(bpy)_2(3b)](PF_6)_2$ (0.095 g, 53.7%) as an orange solid. ESI-MS: m/z: 1034 $[M-PF_6]^+$, 445 $[M-2PF_6]^+/2$. UV–Vis: (acetonitrile; λ_{max} (ε)): 495 (5000), 454 (6000), 370 (7700), 295 (20 600), 245 (13 000).

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