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Improved Synthesis of a Terthiophene-Based Monomeric Ligand That Forms a Highly Active Polymer for the Carbon Dioxide Reduction

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Abstract:

Background: The carbon-dioxide reduction to obtain important chemicals such as fuels is a topic of high current interest. Recently, monomeric thiophenes and terthiophenes linked to a bipyridine ligand were designed and their polymeric films achieved very high turnover numbers during electrocatalytic CO_2 reduction. In this paper we improved the protocol to access the ligand that shows the best performances, in view of opening the way to a general method to obtain side-functionalized terthiophenes.

Methods: Several reactions were attempted to improve the synthetic pathway. Different approaches were attempted to convert the 3-bromothiophene into its 3-iodo analog and to brominate it to obtain the 2,5-dibromo-3-iodothiophene. The synthetic pathway was completed by using Pd-catalyzed cross-coupling reactions such as Sonogashira and Suzuki. The removal of a trimethylsilyl protection was attempted by common methods. However, with the use of a one-pot reaction, both the alkyne deprotection and the final Sonogashira coupling were performed as the key point of the pathway to obtain the final product.

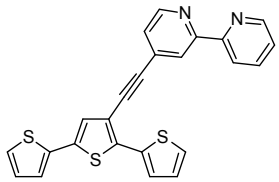
Results: The key intermediate 2,5-dibromo-3-iodothiophene was obtained by a CuI assisted electrophilic aromatic substitution, followed by a bromination with NBS in ethyl acetate This compound was reacted with TMS-acetylene to obtain the ((2,5-dibromothiophen-3-yl)ethynyl)trimethylsilane which, by a Suzuki reaction, afforded the ([2,2':5',2"-terthiophen]-3'-ylethynyl)trimethylsilane. Using a one-pot reaction for the last step, the deprotection of the TMS-protected alkyne and its coupling with 4-bromo-2,2'-bipyridine was accomplished easily. A final 52% yield was achieved over 5 steps.

Conclusion: The ligand 4-([2,2':5',2"-terthiophen]-3'-ylethynyl)-2,2'-bipyridine was prepared in a 52% yield, over 5 steps, improving the previous protocol (17% yield over 4 steps). The rhenium complex of this ligand is still under study for CO_2 reduction. This novel protocol can be used to produce a series of analog terthiophene monomers bearing side-attached ligands.

Keywords: carbon dioxide reduction, catalysis, Suzuki cross-coupling, Sonogashira cross-coupling.

INTRODUCTION

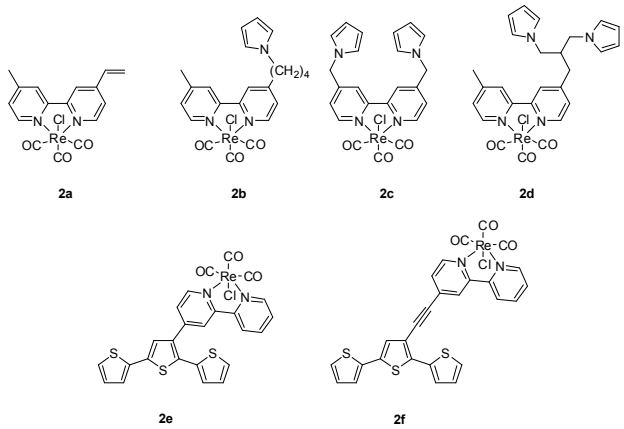
One of the most important problems of our age is connected with the overproduction of carbon dioxide, due to the enhanced exploitment of fossil fuels to obtain energy. The technological approaches to reduce carbon dioxide impact span from the use of renewable sources to produce chemicals,[1-2] to the capture and storage of CO_2,[3-4] to the attempt to reduce CO_2 in order to convert it to useful chemicals and, possibly, fuels.[5] The conversion of carbon dioxide into other compounds has been intensively studied over the last few decades, with electrochemical CO_2 reduction, giving good results.[6-7] Electrochemical CO_2 reduction was originally developed to study the activity of rhenium complexes in solution.[6-7] The immobilization of the catalyst was tried with different approaches, one of which is based on the electropolymerization of monomers having a pendant organometallic catalytically active moiety onto an electrode.[8] With the aim to give a contribution to this last topic, recently we studied the electrochemical carbon dioxide reduction to carbon monoxide, using rhenium complexes.[9] In order to facilitate the transfer of electrons from the electrode to the catalytic centers and to the CO_2 the polymer should be able to be conductive. Few cases were found in literature.[6-8] In our previous study about the preparation of thiophene-based monomers, their electrochemical-driven polymerization and their CO_2 reduction activity, we synthesized a terthiophene monomer in which the terthiophene was connected with the bipyridine ligand moiety, through an alkyne bridge (compound **1**).



1

Fig.1. Terthiophene monomer, whose synthesis was improved in this paper.

This compound was used to prepare a rhenium complex which, by electropolymerization, gave a polymeric film deposited on electrodes. The CO_2 reduction tests performed on these electrodes, gave a TON_{CO} of 519, approaching the best turnover numbers (TON) ever obtained with this approach for the production of CO with the complex **2a** (516-600) (see: Chart 1 for structures of the best performing compounds **2a-f**) and Table 1 for their TON data).[9]



2a **2b** **2c** **2d** **2e** **2f**

Chart 1. Organometallic monomers employed in literature for the preparation and immobilization of polymers onto electrodes for CO_2 reduction.[6, 8-9]

Table **1**. Comparison of the CO_2 reduction activity in CH_3CN for the polymers obtained from monomers represented in Chart 1, immobilized onto electrodes.

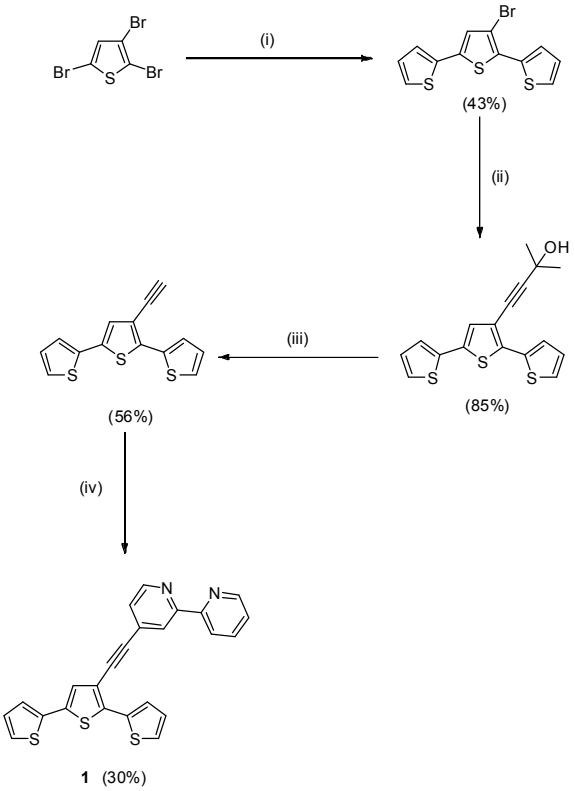
Comp.	*E*	η_{CO}	TONco	Time	Ref.
	(V)	(%)		(min)	
2a	-1.93	94	516-600	60	[6]
2b	-2.23	98.5	133-236	120	[8]
2c	-2.23	69	34	120	[8]
2d	-2.23	98	118	120	[8]
2e	-2.10	84.7	489	40	[9]
2f	-2.10	34.0	519	40	[9]

Conditions: MeCN solution (0.1 M $TBAPF_6$ as supporting electrolyte). Potentials are in V vs. Fc/Fc^+. E: potential applied to the electrode; η_{CO}: faradaic efficiency towards CO; TON_{CO}: Turnover number for CO.

As one can easily evidence, polythiophenes based on **2e**-**2f** complexes showed an important activity towards the CO_2 reduction to CO.[9] Besides, those polythiophenes seemed to reduce slightly the applied potential to obtain the reduction, with respect to polypyrroles **2b-d**. Since these monomers and the derived polymers showed very interesting results, the improvement of their synthetic pathway was an interesting topic. We recently reported about the optimized synthesis of the precursor ligand for **2e** in almost green conditions.[10] In this paper we describe an improved synthetic method for the ligand **1** from which **2f** can be easily prepared.

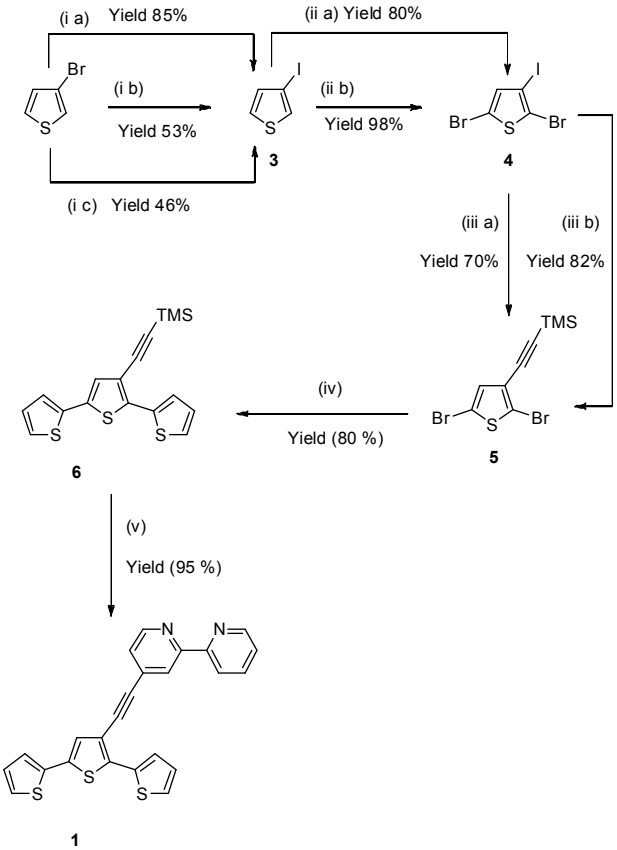
RESULTS AND DISCUSSION

The original method to prepare ligand **1** was derived from the work of Manca et al.,[11] who devised the synthesis of a similar compound (See Scheme 1). The method devised in Scheme 1 showed two low-yield steps, the first and the last one. The final total yield for **1** in the original synthesis was about 17%.[9] Since the practical importance of ligand **1** and in view of the preparation of similar terthiophene-based ligands, it seemed interesting to revise completely its preparation method.



Scheme 1. Original synthetic method for compound **1**. (i) 2-thiopheneboronic acid, $Pd(PPh_3)_4$, 1.5M $NaHCO_3$, DME, microwaves (MW), 130 °C, 30 min; (ii) 2-methyl-3-butyn-2-ol, $Pd(PPh_3)_4$, CuI, diisopropylamine (DIPA), reflux, Ar, 20 h; (iii) KOH, toluene:methanol 1:1, reflux, Ar; (iv) 4-bromo-2,2'-bipyridine, $Pd(PPh_3)_4$, CuI, DIPA, reflux, Ar, 20 h.

In the original method the first step gave a low yield that was due to the presence of three bromine atoms on the starting material, whose substitution was occurring in sequence and it was difficult to be stopped properly after the second substitution.[10-11] In order to avoid this problem, we tried to prepare the 2,5-dibromo-3-iodothiophene. This intermediate could be used to perform a Sonogashira reaction on the iodine in position 3 and a further Suzuki reaction on the bromine atoms in 2 and 5 position to give the terthiophene **6**. The preparation of the intermediate **4** has been published.[12] We used some insights taken from the literature to build a novel protocol (Scheme 2).[12-14]



Scheme 2. Novel protocol for the synthesis of **1**. (i a) NaI, CuI, N,N-dimethylethylenediamine, toluene:dioxane 4:1, 110 °C, 24 h; (i b) NaI, CuI, N,N-dimethylethylenediamine, n-butanol, 120 °C, 3 h; (i c) NaI, Cu_2O, L-Proline, ethanol, 110 °C, 21 h; (ii a) NBS, DMF, 60 °C, 24 h; (ii b) NBS, ethyl acetate, 60 °C, 30 h; (iii a) $Pd(PPh_3)_2Cl_2$, CuI, trimethylsilylacetylene (TMS-acetylene), TEA, 0 °C, 6 h; (iii b) $Pd(PPh_3)_4$, CuI, (TMS-acetylene), TEA, 0 °C, 3 h; (iv) 2-thiopheneboronic acid, $Pd(PPh_3)_4$, 1M $NaHCO_3$, DME, 80 °C, 2 h; (v) 4-bromo-2,2'-bipyridine, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), $Pd(PPh_3)_2Cl_2$, CuI, water (40% with respect to the limiting reagent), benzene, 80 °C, 18 h.

The synthetic pathway started with the transformation of the 3-bromothiophene into the 3-iodothiophene **3**. We tried a few protocols, based on two catalytic approaches. The first one is based on the Buchwald findings[15] about a sort of Finkelstein aromatic reaction. The reaction was performed following the original protocol[12] with NaI, CuI and N,N-dimethylethylenediamine using toluene:dioxane 4:1 as solvents, at 110 °C for 24 h (yield: 85%). We observed a slightly improved yield, over the literature. We also substituted the solvent with n-butanol, at 120 °C for 24 h, as reported in the literature,[16] obtaining a 53% yield. A second protocol was attempted to improve the yield, on the basis of a different green method using Cu_2O, L-proline in ethanol at 120 °C.[17] The application of this method gave a 46% yield.

The main problem to be addressed to ensure a high recovery of the product is the evaporation of the solvent, since **3** shows a high volatility.[17] We avoided as much as possible the use of common laboratory evaporators and a Claisen distillation apparatus, trying to evaporate the common solvents used to help the material transfer into the flasks, such as dichloromethane or hexane, directly at rt under the reduced pressure produced by a water pump. A further careful and slow distillation of the reaction solvent, such as xylene, not exceeding 65-70 °C, afforded the best recoveries. Ethanol could be distilled in the same way at rt, which made the Cu_2O catalyzed reaction attractive due to its simplicity, green character and easiness of work-up.

The key intermediate **4** was first obtained by bromination of **3** with NBS in DMF at 60 °C for 5 h (yield: 80%), as from the original protocol that developed part of this pathway[12]. This second step was also attempted with a similar protocol, in which the solvent was ethyl acetate. In a recent paper a fast bromination of thiophene was promoted by the use of ultrasounds in different solvents.[13] When we optimized the synthesis of the 4-([2,2':5',2''-terthiophen]-3'-yl)-2,2'-bipyridine ligand, precursor of the **2e** complex, we found that the presence of the electronwithdrawing bipyridyl substituent on the 3- position of the thiophene, prevented the reaction.[10] However, when the reaction was performed on the 4-(thiophen-3-yl)-2,2'-bipyridine with NBS in ethyl acetate at rt over 5 days (no ultrasound), the corresponding 2,5-dibromo compound was obtained in quantitative

yield.[10] The application of this bromination in EtAc at room temperature on small quantities of **3** (0.5-1.0 g.) gave 90% yield after 5 days, while by raising the temperature to 60 °C, a 92% yield was obtained in 24 h, shortening considerably the reaction time. When the reaction was performed on larger quantities (5 g.) the yield approached 98%. The simple use of a different solvent raised some important points. The yield was greatly improved, the ethyl acetate is considered a green solvent, greener than DMF,[18] and it is easier to be removed.

The difference in reactivity of the iodo- and bromo- functionalities in the thiophene **4** was exploited to insert the TMS-protected alkyne in the 3- position by a Sonogashira reaction and two thiophenes in 2,5- positions by a Suzuki reaction in two sequential steps. The compound **5** was thus obtained by a Sonogashira reaction between **4** and trimethylsilylacetylene with $Pd(PPh_3)_2Cl_2$ and CuI in TEA as a solvent, at 0 °C for 6 h (yield 70%).[12] By simple substitution of the catalyst with $Pd(PPh_3)_4$ in the same conditions the reaction completed in 3 hours , giving **4** in 82% yield. A conventional Suzuki reaction helped to obtain **6** from **5**, in 80% yield. The removal of the trimethylsilyl protective group was attempted with different protocols.[11, 19-22] However the yield was ranging between 70% and 80% and, in the best case, an impurity was still present and could not be separated, as also reported in literature.[11] In order to increase the final total yield for **1** and to reduce the number of reaction steps in the protocol, we looked for one pot protocols to perform the transformation from **6** to **1**. We were attracted by a modification of the Sonogashira coupling, designed for both symmetrical and unsymmetrical bisarylethynes[14], using TMS-acetylene, DBU as a base, $Pd(PPh_3)_2Cl_2$, CuI and water (40% with respect to the starting material) in benzene as a solvent. The method is quite general, since it can work on both iodides and bromides, can be selectively used to react iodides in the presence of bromides (iodides react at 60 °C, while bromides require higher temperature, about 80 °C) and afford excellent yields for both symmetrical and unsymmetrical alkynes. Besides, as a further key point, aryl halides bearing electronwithdrawing groups (like our reagent 4-bromobipyridine) are the compounds most prone to react. Since the protocol was originally designed to react two aryl halides in sequence with TMS-acetylene, we needed to use only the last part of it, starting with the TMS-protected heteroarylacetylene **6** and with 4-bromobipyridine. The reaction was thus performed with DBU, $Pd(PPh_3)_2Cl_2$, CuI and water in benzene at 80 °C for 18 h. The title compound **1** was obtained easily and isolated by chromatography in 95% yield. The whole process required 5 steps with a final yield of 52%. If we compare the two protocols by starting both from a trihalothiophene, the 2,3,5-tribromothiophene for the original protocol and the 2,5-dibromo-3-iodothiophene for the new method, the novel protocol requires only 3 steps (4 steps are required for the original protocol) to give **1** in a yield of 62%, about 3.5 times higher than in the original synthetic pathway.

The title product **1** was thus obtained in a fast and reasonable easy way with a good total yield over 5 steps. The rhenium complex obtained from **1** was used to prepare polymers immobilized onto electrodes for the selective carbon dioxide reduction to carbon monoxide.[9] Also, some films of these conductive polymers are showing charge separation under illumination, an interesting phenomenon that is currently under study [23].

MATERIALS AND METHOD

All chemicals were purchased from Aldrich or Fluka and were used without further purification. All reactions were performed under Argon atmosphere. The reactions were performed in 20 mL vials or 100 mL reactors that were crimped and sealed with PTFE septa caps. Some reactions were performed in a 250 ml flask. The reactions were monitored by GC-MS and/or thin layer chromatography (TLC) using silica gel as stationary phase on plastic sheets and eluents as reported for the purification in each procedure. The products were purified using a Biotage Isolera automated medium pressure purification system, equipped with UV detector (using variable/fixed wavelength and a Diode array, from 200 to 400 nm), working with silica stationary phase. The eluents used for the purifications are indicated, for every product, in the proper synthetic procedure.

NMR spectra were recorded in $CDCl_3$ with a Brüker Avance 200 NMR Spectrometer, working at 200 MHz for ^1H and 50 MHz for ^{13}C. Chemical shifts were reported in parts per million (δ) using TMS and residual solvent peaks as a reference.

GC-MS were recorded with a Thermo Finningan *Trace GC* instrument equipped with a Zebron-5MS fused silica column of Phenomenex (30 × 0.25 mm i.d., 0.25 µm film tickness), injector temperature of 250 °C, split flow of 10 mL/min, carrier gas Helium at constant flow of 1.2 mL/min.

Microanalyses were performed with a CHNS-O Analyzer Thermo flash 1112.

4-([2,2':5',2''-terthiophen]-3'-ylethynyl)-2,2'-bipyridine (1)

A 100 mL reactor was dried by keeping it in an oven overnight; it was closed with a rubber stopper and was purged with argon for 20 min. In the reactor, $Pd(PPh_3)_2Cl_2$, (44 mg., 0.063 mmol, 0.03 eq.) CuI (42 mg., 0.209 mmol, 0.10 eq.) were added and the reactor was purged with argon. Compound **6** (0.720 g., 2.089 mmol, 1 eq.) was added as a solution in benzene (10 mL). Further benzene (20 mL) was added along with TEA (1.328 g., 0.726 mL, 13.128 mmol, 6 eq.) and the solution was left to stir at rt under argon. The 4-bromo-2,2'-bipyridine, (0.540 g., 2.298 mmol, 1.10 eq.) DBU (3.82 g., 3.75 mL, 25.07 mmol, 12 eq.) and water (16 mg., 16 µl, 0.875

mmol, 0.40 eq.) were finally added and the solution was put in a pre-heated oil bath 60 °C, and left to react under vigorous stirring for 18 h. The reaction was stopped and the benzene was removed under vacuum by distillation. The residue was extracted with diethyl ether (3 × 50 mL) and water (50 mL). The organic layer was washed with 10% HCl (3 × 50 mL) and brine (1 × 50 mL) and the organic phase was dried with Na_2SO_4, filtered and evaporated under vacuum. The crude was purified by chromatography on Biotage on silica (100 g) with dichloromethane-TEA (0.5%) and after with a gradient from dichloromethane to dichloromethane:ethyl acetate 8:2. A yellow solid was finally obtained: 849.6 mg (95%).

m.p.: 153-156 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.70 (m, 2H, H6pyr and H6'pyr), 8.56 (s, 1H, H3pyr), 8.41 (d, *J* = 8.0 Hz, 1H, H3'pyr), 7.83 (td, *J* = 7.8, 1.8 Hz, 1H, H4pyr), 7.51 (dd, *J* = 3.7, 1.2 Hz, 1H, H3 or H3"), 7.44 (dd, *J* = 5.0, 1.5 Hz, 1H, H5 or H5"), 7.37 (dd, *J* = 5.1, 1.1 Hz, 1H, H5 or H5"), 7.34 – 7.29 overlapping (m, *J* = 7.5 4.8, 1.1, 1H, H5pyr or H5'pyr), 7.26 (dd, *J* = 5.1, 1.1 Hz , 1H, H3 or H3"), 7.20 (m (dd + s), 3.5, 1.2 Hz, 2H, H4' and H5pyr or H5'pyr), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H, H4 or H4").7.06 (dd, *J* = 5.1, 3.7 Hz, 1H, H4 or H4"). ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.43 (C2q-pyr), 155.65 (C2'q-pyr), 149.38 (C6-pyr or C6'-pyr), 149.27 (C6-pyr or C6'-pyr), 139.97 (C3'th), 137.09 (C5'th), 136.08 (C4'pyr), 135.54 (C2th), 134.64 (C2"th), 132.41 (C4pyr), 128.10 (C4'th), 127.51 (C5th or C5"th), 127.07 (C5th or C5"th), 126.40 (C3'pyr), 126.11 (C3"th), 125.35 (C4th or C4"th), 125.16 (C4th or C"th), 124.53 (C3pyr), 124.14 (C2th), 122.96 (C3th), 121.32 (C5pyr or C5'pyr), 116.87 (C5pyr or C5'pyr), 91.77 (C≡C), 89.69 (C≡C). MS (EI, m/z): 426.09. Elemental analysis: required for $C_{24}H_{14}N_2S_3$, C 67.57, H 3.31, N 6.57, S 22.55, found: C 67.60, H 3.28, N 6.62, S 22.50.

3-iodothiophene (3)

Method a). In a 100 mL reactor, stoppered with rubber septum and flushed with argon, CuI (0.584 g., 3.07 mmol, 0.05 eq.) and NaI (18.39 g., 123 mmol, 2 eq.) were introduced and flushed with argon. The xylene (40 mL) and the dioxane (10 mL), previously flushed with argon for 20 min, were introduced. The N,N'-dimethylethylendiamine (0.541 g., 0660 mL, 6.13 mmol, 0.1 eq.) and the 3-bromothiophene (10.00 g., 61.3 mmol, 1 eq.) were added. The suspension was degassed with argon for 10 min and it was introduced into the oil bath, warmed at 110 °C. The reaction was checked by GC and stopped after 24 h. The suspension was filtered on a Buchner, and the solid was washed with dichloromethane. The most volatile solvents were removed under vacuum with a Claisen apparatus working at rt, and the highest boiling solvent (xylene) was removed in the same apparatus by warming from rt to 65-70 °C as a maxium, to minimize product losses.

A brownish oil, was obtained, that was purified by Biotage flash chromatography on silica with petroleum ether, giving a faint yellow oil, 10.31 g. (82%).

Method b) The same reaction was performed in a 100 mL reactor, with CuI (0.584 g., 3.07 mmol, 0.05 eq.), KI (20.40 g., 123 mmol, 2 eq.), N,N'-dimethylethylendiamine (0.541 g., 0660 mL, 6.13 mmol, 0.1 eq.) and 3-bromothiophene (10.00 g., 61.3 mmol, 1 eq.) using n-butanol (40 mL) as solvent, and warming the reactor at 120 °C for 3 h. The reactor was cooled to rt and the mixture was filtered on a Buchner and washed twice with little dichloromethane. The dichloromethane was evaporated in a Claisen, under reduced pressure (water pump). The n-butanol was evaporated in the same way, warming carefully and raising the temperature step by step from 40 °C to 65 °C by 5 °C steps, until the distillation stopped. The residue was purified by flash chromatography on Biotage KP Sil 100 g. silica column, with hexane, giving a faint yellow oil: 6.80 g. (53%).

Method c) In a 250 ml reactor , previously purged with argon, the Cu_2O (878 mg., 6.13 mmol, 0.1 eq.), the L-Proline (1.41 g., 12.3 mmol, 0.2 eq.), the 3-bromothiophene (10.00 g., 61.3 mmol, 1 eq.) and the potassium iodide (30.5 g, 184 mmol, 3 eq) were introduced along with ethanol (150 mL), working under argon. The reactor was crimped. The suspension was stirred for 16 h at 110 °C. The ethanol was evaporated with Claisen apparatus at rt under reduced pressure using a water pump. The crude was purified by flash chromatography on Biotage KP Sil 100 g. silica column eluting with hexane. The collected fractions were evaporated, giving a faint yellow oil: 5.95 g (46%). The NMR spectra are in agreement with the literature.[12]

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 3.0, 1.2 Hz, 1H, H-2), 7.20 (dd, *J* = 5.0, 3.0 Hz, 1H, H-4), 7.10 (dd, *J* = 5.0, 1.2 Hz, 1H, H-5). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.87 (C-4), 128.76 (C-2), 127.43 (C-5), 77.25 (C-3). MS (EI, m/z): 209.18. Elemental analysis: required for C_4H_3IS, C 22.87, H 1.44, S 15.27, found: C 22.93, H 1.39, S 15.22.

2,5-dibromo-3-iodothiophene (4)

Method a) In a three necked Schlenk 250 mL flask the product **3** (4.77 g., 22.71 mmol, 1 eq.) was introduced as a solution in DMF (30 mL), and sparged with argon for 10 min under stirring. The NBS (19.77 g., 111 mmol, 4.89 eq.) and further 100 mL of DMF were added and the reactor was kept away from light. After 1 h of stirring at room temperature, the reactor was immersed in an oil bath warmed at 60 °C and left to react overnight. The reaction was checked by TLC and GC After 24 h, the reaction was stopped and left to cool at rt, and it was quenched with about 150 mL of water, extracted with hexane (3 × 75 mL) and the organic phase was washed

with water (2 × 75 mL) and with brine (2 × 75 mL). The organic phase was dried with sodium sulfate, filtered and evaporated, thus giving about 12.24 g of crude. The crude was purified with Biotage flash chromatography on a silica cartridge (100 gr.) with hexane. A faint yellow oil was obtained, 6.68 g (80%).

Method b). In a 100 mL reactor, purged with argon for 10 min, the compound **3** (5.00 g., mmol, 1 eq.) and NBS (12.74 g., mmol, 3 eq.) were introduced and the reactor was closed with a rubber stopper and was purged with argon for 10 min. Ethyl acetate (70 mL) was added and the reactor was introduced in an oil bath warmed at 60 °C and was left to react for 30 h. The reaction was cooled to rt and the solution was extracted with hexane and washed with water (2 × 50 mL) and brine (1 × 50 mL). The organic phase was collected, dried with sodium sulfate, filtered and evaporated, obtaining a reddish oil. The crude was purified by flash chromatography on Biotage KP Sil 100 g. silica column, eluting with hexane. The collected fractions were evaporated giving a faint pink oil: 8.54 g. (98%). The same reaction was also performed at 25 °C for 5 days, giving nearly the same yield. The NMR spectra are in agreement with the literature.[12]

^{1}H NMR (200 MHz, $CDCl_3$) δ 6.92 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.17 (C-4), 116.41 (C-2), 113.55 (C-5), 85.28 (C-3). MS (EI, m/z): 365.80. Elemental analysis: required for C_4HBr_2IS, C 13.06, H 0.27, S 8.72, found: C 13.12, H 0.31, S 8.69.

((2,5-dibromothiophen-3-yl)ethynyl)trimethylsilane (5)

Method a). A 250 mL three-necked Schlenk flask, closed with stoppers and a joint with stopcock and a balloon for gases, was purged with argon for 20 min. In the meantime triethylamine (TEA) was purged with argon for 40 min.

The Pd catalyst, $Pd(PPh_3)_2Cl_2$ (0.849 g. 0.834 mmol, 0.04 eq.) and CuI (0.2089 g, 1.097 mmol, 0.06 eq.) were added and the apparatus was continuously purged with argon for about 15 min, until 80 mL of TEA was added. The suspension was stirred and cooled with ice bath to 0 °C. The compound **4** (6.75 g., 18.34 mmol, 1 eq.) was transferred into a 20 mL vial, previously purged with argon and TEA (10 mL) was added to dissolve the oil, continuously purging with argon. Compound **4** was transferred into the reaction flask by a syringe and the vial was washed with further 2 × 5 mL of TEA, that was transferred to the reaction flask. The flask was purged with argon for further 10 min, and the trimethylsilylacetylene (1.98 g., 2.85 mL, 20.18 mmol, 1.10 eq.) was added. The reaction was run at 0 °C. The reaction was checked by GC, showing that after 3 h the residual **4** was still present in low quantity (less than 5%). The reaction was stopped after 6 h and the TEA was distilled under vacuum. The residue was taken up with 70 mL of petroleum ether, and filtered on a buchner to remove the solid, which was washed twice with petroleum ether. The organic phase was extracted with water (2 × 50 mL) and with brine (50 mL). The organic phase was dried with Na_2SO_4, filtered and evaporated, giving a reddish oil. The oil was purified by Biotage flash chromatography on silica (100 g) with petroleum ether, giving the pure product as a pale yellow oil: 4.34 g., (70%).

Method b). The reaction was carried out as in Method (a) on a slightly lower scale using 5.00 g of compound **4** (13.6 mmol, 1 eq) and replacing $Pd(PPh_3)_2Cl_2$ with $Pd(PPh_3)_4$ (0.628 g., 0.544 mmol, 0.04 eq) as the catalyst.

After Biotage flash chromatography on silica (100 g) with petroleum ether, the product was isolated giving the pure product as a pale yellow oil: 5.06 g., (82%). The NMR spectra are in agreement with the literature.[12]

^{1}H NMR (200 MHz, $CDCl_3$) δ 6.94 (s, 1H, H_{ar}), 0.25 (s, 9H, 3 CH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ 132.30, 125.35, 116.86, 110.84, 99.86, 96.93, 0.03. MS (EI, m/z): 335.91. Elemental analysis: required for $C_9H_{10}Br_2SSi$, C 31.97, H 2.98, S 9.48, found: C 13.09, H 3.02, S 9.45.

([2,2':5',2''-terthiophen]-3'-ylethynyl)trimethylsilane (6)

A 100 mL vial, closed with a rubber stopper, was purged with argon for 20 min. Compound **5** (1.4407 g., 4.26 mmol, 1 eq.), was introduced in the reactor with the Pd catalyst, $Pd(PPh_3)_2Cl_2$, (0.2461 g., 0.213 mmol, 0.05 eq.). The reactants were degassed for a few minutes and DME (44 mL), previously degassed, was added. The resulting solution was degassed for a few minutes under stirring, while the $NaHCO_3$ solution (1M in water) was degassed for at least 10-15 min. The 2-thiopheneboronic acid (2.204 g., 17.03 mmol, 4 eq.) was added and while the solution was still under argon purging, the $NaHCO_3$ solution was added (14.91 mL, 14.91 mmol, 3.5 equivalent). The degassing was continued for about 10 min and the vial was introduced into the pre-heated oil bath at 80 °C. After 2 hours, the reaction was checked by GC, showing the disappearance of the starting material. The reaction was stopped and left to cool to rt. The mixture was extracted with dichloromethane (3 ×100 mL). The organic phase was dried with Na_2SO_4, filtered and evaporated, obtaining a deep red oil with

some solid inside. The crude was purified by Biotage flash chromatography, with petroleum ether, giving a faint yellow liquid that sometimes can become solid, for which however the m.p. could not be measured, being very close to room temperature: 1.17 g (80%).

^{1}H NMR (200 MHz, CDCl3) δ 7.66 (d, J = 2.4 Hz, 1H, H-3 or H3"), 7.44 (d, J = 4.5 Hz, 1H, H-5 or H5"), 7.37 (d, J = 5.1 Hz, 1H, H-5 or H5"), 7.30 (d, J = 3.4 Hz, 1H, H-3 or H3"), 7.26 (s, 1H, H-4'), 7.17 (s, 2H, H-4 and H4"). ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.43 (C3'-C≡C), 136.34 (C5 or C5"), 135.88 (C2"), 134.04 (C5 or C5"), 128.04 (C2'), 127.48 (C4 or C4'), 127.45 (C4 or C4'), 127.29 (C2), 125.74 (C2'), 125.13 (C5'), 124.31 (C3, or C3"), 117.81 (C3, or C3"), 100.39 (C≡C), 100.31 (C≡C), -0.10 ($Si(CH_3)_3$). MS (EI, m/z): 344.06. Elemental analysis: required for $C_{17}H_{16}S_3Si$, C 59.25, H 4.68, S 27.92, found: C 59.21, H 4.75, S 27.88.

CONCLUSION

An alternative synthetic pathway to a bipyridine ligand linked to a terthiophene through an alkyne moiety was shown, obtaining a substantial yield improvement. The pathway was a modification of literature protocols and afforded the title product in a total yield of 40% over 5 steps. The compound and its rhenium complex is still under study. Preliminary results show high activity towards carbon dioxide reduction and the possible formation of photoactive polymeric films.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's web site along with the published article.

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