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An Approach to Long and Unsubstituted Molecular Wires: Synthesis of Redox-Active, Cationic Phenylethynyl Oligomers Designed for Self-Assembled Monolayers

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Various oligo(phenyleneethynylene)s (OPEs) have been synthesized in the past, as they are considered as prototypes of molecular wires. When the oligomers are capped by a redox site at one end and a thiol at the other end, the resulting molecules can be grafted as a self-assembled monolayer on a gold electrode and fully studied by electrochemical techniques. Unfortunately, such molecules are usually poorly soluble and require the incorporation of solubilizing pendant groups. In this paper, we show that the replacement of the classically used redox group ferrocene by a cationic organometallic ruthenium complex, namely, $[Ru(bipy)_2(ppH)]^+$ (bipy, 2,2′-bipyridine; ppH, 2-(2′-yl-phenyl)pyridine), allows a concise synthesis of an unsubstituted thioacetate-capped OPE up to four repetitive units long. The positive charge does not interfere with the conventional organic chemistry used to elongate, purify, or characterize the hexafluorophosphate salts of the molecules. To our knowledge, this represents the first family of long, poorly substituted OPEs designed for self-assembly.

Introduction

Molecular wires are of critical interest in the developing field of molecular electronics.[1−3] Both the conductivity and its decay with length are crucial characteristics of such molecules. For a tunneling process, this decay is thought to follow an exponential law, but if several theoretical calculations are available, few experimental data exist.[4−6] It remains a challenge to address a *single* molecule with two metallic electrodes;[5,7−9] thus, most of the experiments are based on the average response of a group of molecules, possibly arranged in a self-assembled "nanoarchitecture".[10,11] On the other hand, since electron tunneling is also used to describe electron transfer processes (either a light-induced, intramolecular one or a chemically driven one), chemical approaches such as spectroscopy and kinetics have also being extensively used.[2,12] Among the last, ultrafast electrochemical techniques have been reported, allowing one to study the behavior of a small number of active molecules.[6,13−18] Experimentally, the molecules probed are embedded in a self-assembled monolayer (SAM), either pure or made of a dilute solution of the redox-active molecule in an inert diluent. By recording the rate constant of the interfacial electron transfer for various molecule lengths, one can characterize the distance dependence of the tunneling parameter. This electrochemical approach has the advantage of being rapid, and the technique itself remains simple.

Thus, suitable molecules for such an experiment must be rigid, rod-shaped, and asymmetrical with a redox site at one end and a connecting atom at the other end, the "molecular wire" being the portion comprised between the redox site and the connecting atom anchoring the electrode. Thiol groups are commonly used along with

(1) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541−548.
(2) Launay, J.-P. *Chem. Soc. Rev.* **2001**, *30*, 386−397.
(3) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; Campbell, I. *Chem. Eur. J.* **2001**, *7*, 5118−5134.
(4) Sikes, H. D.; Smalley, J. F.; Dudek, S. P.; Cook, A. R.; Newton, M. D.; Chidsey, C. E. D.; Feldberg, S. W. *Science* **2001**, *291*, 1519−1523.
(5) Langlais, V. J.; Schlittler, R. R.; Tang, H.; Gourdon, A.; Joachim, C.; Gimzewski, J. K. *Phys. Rev. Lett.* **1999**, *83*, 2809−2812.
(6) Creager, S.; Yu, C. J.; Bamdad, C.; O'Connor, S.; MacLean, T.; Lam, E.; Chong, Y.; Olsen, G. T.; Luo, J.; Gozin, M.; Kayyem, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1059−1064.
(7) Cui, X. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science* **2001**, *294*, 571−574.
(8) Weber, H. B.; Reichert, J.; Weigend, F.; Ochs, R.; Beckmann, D.; Mayor, M.; Ahlrichs, R.; von Lohneysen, H. *Chem. Phys.* **2002**, *281*, 113−125.
(9) Reichert, J.; Ochs, R.; Beckmann, D.; Weber, H. B.; Mayor, M.; von Lohneysen, H. *Phys. Rev. Lett.* **2002**, *88*, 176804/1−176804/4.
(10) Holmlin, R. E.; Haag, R.; Chabinyc, M. L.; Ismagilov, R. F.; Cohen, A. E.; Terfort, A.; Rampi, M. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **2001**, *123*, 5075−5085.
(11) Holmlin, R. E.; Ismagilov, R. F.; Haag, R.; Mujica, V.; Ratner, M. A.; Rampi, M. A.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2316−2320.
(12) Launay, J.-P.; Coudret, C. In *Electron Transfer in Chemistry*; Wiley: New York, 2001; Vol. 5, pp 3−47.
(13) Weber, K.; Creager, S. E. *Anal. Chem.* **1994**, *66*, 3164−72.
(14) Weber, K.; Hockett, L.; Creager, S. *J. Phys. Chem. B* **1997**, *101*, 8286−8291.
(15) Forster, R. J. *Inorg. Chem.* **1996**, *35*, 3394−3403.
(16) Forster, R. J.; Figgemeier, E.; Loughman, P.; Lees, A.; Hjelm, J.; Vos, J. G. *Langmuir* **2000**, *16*, 7871−7875.
(17) Finklea, H. O.; Hanshew, D. D. *J. Am. Chem. Soc.* **1992**, *114*, 3173−81.
(18) Brevnov, D. A.; Finklea, H. O.; Van Ryswyk, H. *J. Electroanal. Chem.* **2001**, *500*, 100−107.

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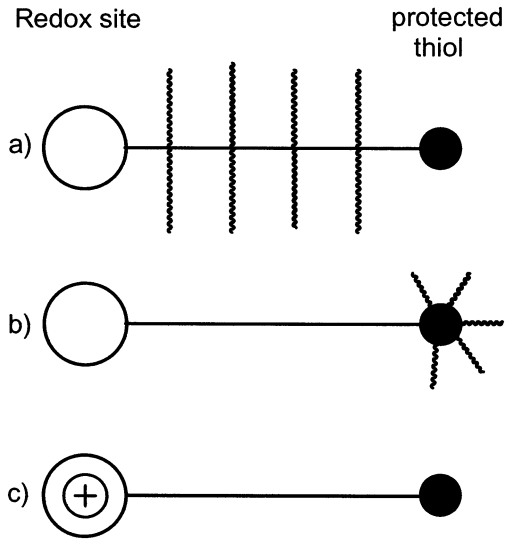
SCHEME 1. Improvement of the Solubility of Asymmetrical Oligomers: (a) Flexible Chains Added on the Conjugated Spacer, (b) Bulk Protecting Group of the Thiol, and (c) Charge Effect

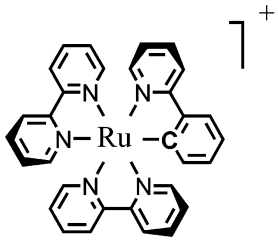


conjugated spacers such as oligo(phenylenevinylene) (OPV) and oligo(phenylethynyl) (OPE).[19,20] Whatever the repetitive unit chosen, the bottleneck that the synthetic chemist has to go through is the necessary solubility required throughout all the synthetic steps *and* the geometrical constraints due to the desired rodlike shape of the molecular wire.

In a seminal paper, Sita and co-workers reported the preparation of unsubstituted rigid OPE capped at one end by a ferrocene and at the other end by a thiophenol masked either as a thioacetate or as a methyl thioether (or its sulfoxide and sulfone derivative).[21] Unfortunately, the solubility was found to depend strongly on the substituent carried by the sulfur atom. Indeed, the longest soluble molecule described was a methyl thioether-capped wire of 31 Å, the cleavage of which was not attempted. Since gold−thioethers interactions are weaker than thiol−gold ones,[22] such capping groups are hardly interesting for the formation of stable mixed SAM.

Classically, the solubility is improved by grafting saturated chains (alkyl, alkoxy...) on the repetitive units of the conjugated skeleton (Scheme 1a).[19,20] Despite its efficiency, this approach could present the following disadvantages: (i) it requires additional steps of synthesis to prepare the suitable monomeric units, and (ii) the solubilizing groups may disturb the packing of the SAM and influence the electron transfer. Grafting the solubilizing groups at one or both ends of the OPE is a way to bypass the first impediment: a single triisopropylsilyl group seems to be enough to solubilize an OPE made of five repetitive phenylene−ethynylene units.[23] In the case

SCHEME 2. $[Ru(bipy)_2(ppH)]^+$



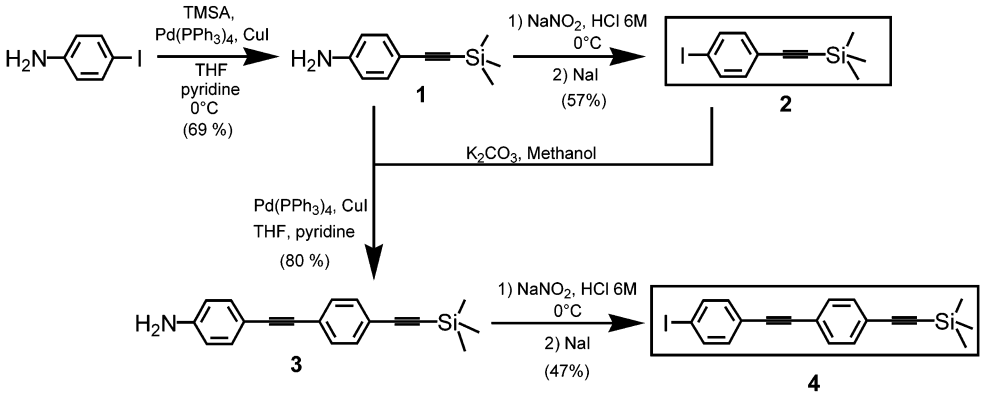
of arenethiol-terminated molecular wires, one can think of combining the solubilizing group with the protective one necessary to avoid oxidation into disulfide (Scheme 1b), as proposed in a general route to symmetrical double thiol-capped OPV. However, the solubility is lost at the thiol deprotection step just before the formation of the SAM. A third strategy, albeit limited to the "electrochemical approach", is to improve the solubility via the redox site, by charge effect for instance (Scheme 1c), which to our knowledge has been applied only to prepare water-soluble but nonredox active OPE.[24] In this case, the solubility is maintained even after the thiol deprotection step and, since the redox site will not be buried within the SAM, no dramatic structural consequences should be expected.

Ferrocene has been extensively used and proved to be more suitable than the other possible redox centers described in the literature.[4,6,13,25] However, it does not improve the global solubility and its persubstitution requires specific routes of synthesis.[26] In our group, the chemical potentialities of the remarkably robust organometallic complex $[Ru(bipy)_2(ppH)]^+$ (Scheme 2), easily accessible in two steps from commercially available products, have been investigated.[27−30] Compared to its N_6 analogue $[Ru(bipy)_3]^{2+}$, the N_5C donor set around the ruthenium(II) lowers dramatically the first metal-centered oxidation redox potential, down to ca. 0.5 V vs SCE, a value comparable to that of the ferrocene derivative. Moreover, it allows the regiospecific introduction of various functionalities such as bromine on the metalated phenyl ring in an *electrophilic* way. Thus, the readily accessible brominated complex $[Ru(bipy)_2(ppBr)]^+$ can be used as a building block in palladium-catalyzed cross-coupling reactions, the main reactions to build OPE and OPV. The cationic character of those complexes makes them soluble in various polar organic solvents, and the use of hexafluorophosphate as counteranions allows purification via conventional chromatographic techniques.

In a recent report, we have shown that the electrochemical properties of this redox site (standard potential,

(19) Dudek, S. P.; Sikes, H. D.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2001**, *123*, 8033−8038.
(20) Yu, C. J.; Chong, Y.; Kayyem, J. F.; Gozin, M. *J. Org. Chem.* **1999**, *64*, 2070−2079.
(21) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808−15.
(22) Li, X.-M.; de Jong, M. R.; Inoue, K.; Shinkai, S.; Huskens, J.; Reinhoudt, D. N. *J. Mater. Chem.* **2001**, *11*, 1919−1923.
(23) Anderson, S. *Chem. Eur. J.* **2001**, *7*, 4706−4714.
(24) Anderson, S.; Aplin, R. T.; Claridge, T. D.; Goodson, T., III; Maciel, A. C.; Rumbles, G.; Ryan, J. F.; Anderson, H. L. *J. Chem. Soc., Perkin Trans.* **1998**, *1*, 2383−2397.
(25) Creager, S. E.; Wooster, T. T. *Anal. Chem.* **1998**, *70*, 4257−4263.
(26) Hradsky, A.; Bildstein, B.; Schuler, N.; Schottenberger, H.; Jaitner, P.; Ongania, K.-H.; Wurst, K.; Launay, J.-P. *Organometallics* **1997**, *16*, 392−402.
(27) Coudret, C.; Fraysse, S. *Chem. Commun.* **1998**, 663−664.
(28) Fraysse, S.; Coudret, C.; Launay, J.-P. *Tetrahedron Lett.* **1998**, *39*, 7873−7876.
(29) Fraysse, S.; Coudret, C.; Launay, J.-P. *Eur. J. Inorg. Chem.* **2000**, 1581−1590.
(30) Monchaud, D.; Lacour, J.; Coudret, C.; Fraysse, S. *J. Organomet. Chem.* **2001**, *624*, 388−391.

SCHEME 3



kinetics) were compatible with the general requirements of an electrochemical screening of molecular wires embedded in SAMs.[31] We wish to present in this paper that the remarkable solubility of these complexes, combined with efficient palladium-catalyzed ethynylation reactions, allows a concise synthesis of conjugated redox active thiols containing *unsubstituted* OPE from simple starting materials, easily purified by column chromatography.

Results and Discussion

Synthesis. Most of the different routes developped to prepare unsymmetrical phenylethynyl oligomers rely on palladium-catalyzed ethynylation reaction and involve either the dissymmetrization of an existing OPE, a stepwise growth of the oligomeric chain, or a combination of the two, especially for the smaller terms. Since no pendant group has to be included on the aromatic moieties, the strategy is greatly simplified. The ruthenium organometallic building block is used as a stopper and the elongation of the chain is achieved by the repetition of a Sonogashira coupling followed by a terminal alkyne unmasking. As noticed by Sita and co-workers, this synthesis suffers from its linearity, due to the iterative process, and the convergence can be improved by preparing two types of organic units for the wire's elongation, containing one (**2**) or two phenylene (**4**) nuclei (Scheme 3) (the synthesis of analogous molecules with more units would have led to a loss of solubility).[32−35] Iodine has been preferred to bromine, since it is known to give better yields in Sonogashira cross-coupling and it allows one to work at room temperature, which can be beneficial since it has been shown recently that cuprous chloride catalyzed desilylation was readily observed for trimethylsilyl protected alkyne upon heating with DMF as solvent.[36]

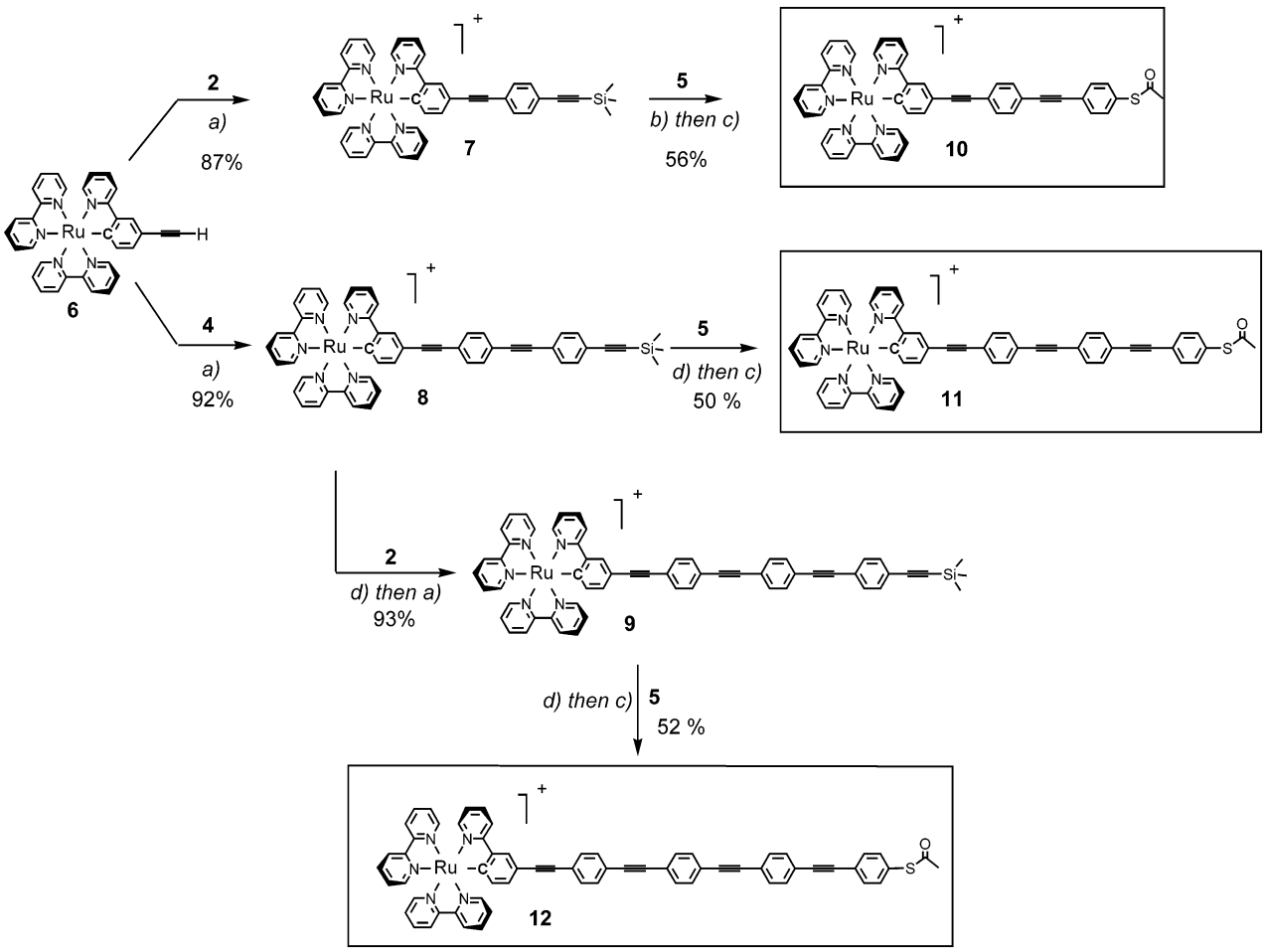
We have shown recently that the ethynylated complex **6** was a readily accessible synthon.[29] Thus, the elongation of the growing wire is rather straightforward. All the syntheses start with a coupling between complex **6** and compound **2** or **4** (Scheme 4)**.** The molecules **7** and **8** are obtained, with respectively 87% and 92% yield. The best results have been obtained, at room temperature, using $Pd(PPh_3)_4$, CuI, and diisopropylamine (DIPA). Since the ruthenium moiety is not soluble in DIPA, DMF is added as a cosolvent. The three-benzene-ring complex **9**, ended with a trimethylsilyl group, is also obtained following an analogous procedure. Starting from **8**, the TMS group is removed under standard conditions by use of a carbonate salt (namely potassium carbonate) in a 1:1 mixture of methanol/dichloromethane. This provides a terminal alkyne, which is not isolated and used under the same conditions of cross coupling, as described above, with the derivative **2** to give **9** with 93% yield.

Synthesis is terminated by capping the chain with a derivative of thiophenol, the 1-iodo-4-thioacetylbenzene **5**, prepared in one step following the protocol described by Tour and co-workers (Scheme 5).[37]

Despite their known lability, thioesters such as thioacetate are protecting groups known to be compatible with palladium-catalyzed cross-couplings, but the use of a 1:1 mixture of anhydrous THF and diisopropylethylamine (Hunig's base) is critical for obtaining high yields.[32] Unfortunately, the derivatives **7**−**9** are not soluble in such a mixture. Our first attempt was to replace DIPA by Hunig's base under the same conditions as those used to obtain **7**−**9**. The desired molecules **10**−**12** have been obtained, albeit in moderate yields (40%). Addition of THF as cosolvent (2:1:1 DMF:THF:diisopropylethylamine) increases the yield only up to 50%. Despite this low yield in the last stage of this strategy, unsubstituted asymmetric molecular wires of various lengths are easily obtained by the right combination of only four synthons, without any problem of solubility for the synthesis, thanks to the cyclometalated ruthenium redox site. The introduction of the sulfur atom at the very end of the strategy also enables the use of the simple and rather labile thioacetate as protective group. However, a clear decrease in solubility is noticeable by comparison to the TMS-capped molecules of similar length, and we

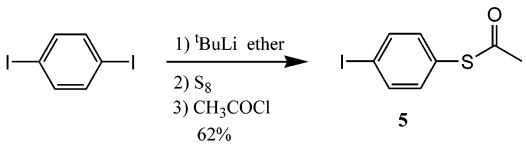
(31) Hortholary, C.; Minc, F.; Coudret, C.; Bonvoisin, J.; Launay, J.-P. *Chem. Commun.* **2002**, 1932−1933.
(32) Hsung, R. P.; Babcock, J. R.; Chidsey, C. E. D.; Sita, L. R. *Tetrahedron Lett.* **1995**, *36*, 4525−8.
(33) Aujard, I.; Baltaze, J.-P.; Baudin, J.-B.; Cogné, E.; Ferrage, F.; Jullien, L.; Perez, E.; Prévost, V.; Qian, L. M.; Ruel, O. *J. Am. Chem. Soc.* **2001**, *123*, 8177−8188.
(34) Lavastre, O.; Ollivier, L.; Dixneuf, P. H.; Sibandhit, S. *Tetrahedron* **1996**, *52*, 5495−5504.
(35) Mongin, O.; Papamicaël, C.; Hoyler, N.; Gossauer, A. *J. Org. Chem.* **1998**, *63*, 5568−5580.
(36) Nishihara, Y.; Ikegashira, K.; Hirabayashi, K.; Ando, J.-i.; Mori, A.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 1780−1787.
(37) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376−1387.

SCHEME 4[a]



[a] Reagents and conditions: (a) $Pd(PPh_3)_4$, CuI, DIPA, DMF, rt, 10 h; (b) K_2CO_3, MeOH, rt, 2 h; (c) $Pd(PPh_3)_4$, CuI, Hunig's base, DMF, THF, rt, 12 h; (d) K_2CO_3, MeOH−CH_2Cl_2, rt, 2 h.

SCHEME 5



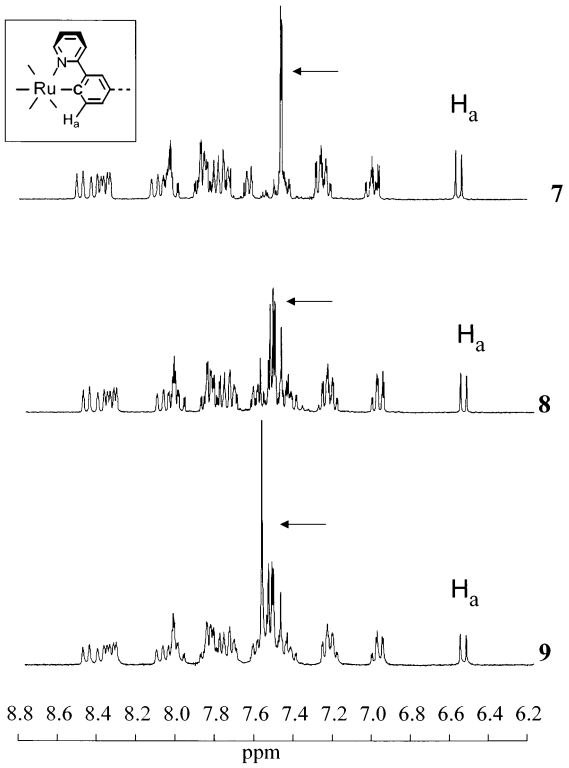
have been compelled to change the NMR solvent (vide infra). Nevertheless, the solubilizing properties of the ruthenium complex are sufficient to allow the handling of these molecules with conventional techniques. To our knowledge, this represent the first family of such poorly substituted OPEs designed for self-assembly.

Purification of Oligomers. The chromatographic behavior of cyclometalated derivatives is strongly dependent on the associated counteranion. We have shown in the past that easy purifications, comparable to classical organic compounds, were achieved with common solvents on silica with the readily available hexafluorophosphate ion.[29] The elution of such species is mainly controlled by the global charge of the molecule. In the present case, all the oligomers are purified by silica gel using the same eluent (98:2 dichloromethane:acetonitrile). Indeed, the mass increase after one coupling is not sufficient enough to counterbalance the charge effect, and the complexes exhibit almost the same behavior during the purification. This could be a drawback of our strategy, if we had to separate a mixture of two same-charged complexes, but this never happened. We can explain this as follows. The desilylation step is quantitative (**7**−**9** are not found in the analysis of **10**−**12**). The nonprotected alkyne can react following two paths: the cross-coupling with the iodo derivative or the oxidative dimerization called Glaser coupling. This second competitive way of reaction provides a dinuclear complex with two positive charges. It is thus easily separated from the required mononuclear complex, since the elution is controlled by charge effect. The formation of this dinuclear species can be limited by the use of well degassed solutions.

Characterization and Properties. All the complexes are characterized by ^1H NMR, ^{13}C NMR, and mass spectroscopy. We have reported in Scheme 6 the ^1H NMR spectra (recorded in acetonitrile, concentration 0.02 mol/L) for molecules **7**−**9**, focusing on the aromatic region. The peaks remain narrow and well-resolved, whatever the length of the wire, proving the very good solubilities of these complexes in this solvent.

The behavior of the molecules **10**−**12** (terminated by a thioacetate group) is quite different. Indeed, at a concentration of 0.02 mol/L in acetonitrile the peaks broaden when the length of the wire is increased (from **10** to **12**), showing the decrease of solubility. Well-

SCHEME 6. Aromatic Region of the ^{1}H NMR Spectra between 6.2 and 8.8 ppm, Recorded in Acetonitrile, for Molecules 7, 8, and 9[a]



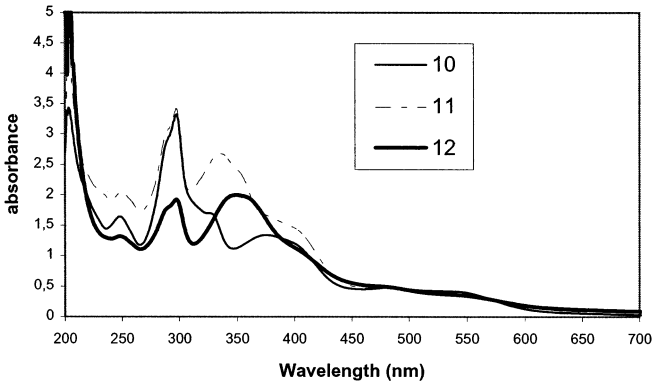
[a] The inset shows the attribution to the most shielded proton H_a; the arrow indicates the quasidegenerated signal for all the protons of the OPE part.

resolved spectra are achieved by the use of more polar solvents such as DMF or DMSO. Nevertheless, these molecules remain soluble in ethanol in the range of concentration classically used for the formation of SAMs (from 10^{-6} to 10^{-4} mol/L).[6,14]

A comparison of the ^{1}H NMR spectra reported in Scheme 6 shows small differences between them. It appears that the main modification occurs between 7.4 and 7.6 ppm. For this family of silylated complexes, we have recorded 2D ^{1}H−^{1}H and ^{1}H−^{13}C correlation spectra. Starting from the attribution of the signals already reported by Constable for the $[Ru(bipy)_2ppH]^+$ moiety, we have assigned the signals to the conjugated wire.[38] This shows that the chemical shifts of the OPE part are quasidegenerate in the 7.4−7.6 ppm region. Thus, ^{1}H NMR analysis is not the best way of analyzing the elongation of the wire. A similar feature is observed in the ^{13}C NMR spectra: the shielding influence of the complex vanishes quickly and chemical shifts of the triple bond carbons tend to be degenerate. Unambiguous characterization of the complexes has been achieved by mass spectroscopy. All of the complexes behave well under electrospray mass spectrometry, giving a typical peak attributed to a monocharged, PF_6^--free molecular ion. As previously observed, no starting material could be detected.

From the ^{1}H NMR and UV−visible spectra, one can also estimate the degree of interaction between the redox

SCHEME 7. UV−Visible Spectra, Recorded in Ethanol, of Molecules 10 (5×10^{-5} mol/L), 11 (5×10^{-5} mol/L), and 12 (3×10^{-5} mol/L)



site and the oligomeric rod. It has been stressed previously that the very shielded proton H_a on the cyclometalated ring was an efficient probe of the electronic influence of the substituent of the complex.[38] In the present case, no significant drift could be observed, indicating a moderate influence of the length of the spacer on the redox site. Cyclic voltammogramms, recorded in acetonitrile, led to the same conclusion, since the length of the spacer affects neither the half-wave potential $E_{1/2}$ nor the potential peak difference between the anodic and the cathodic waves.

The UV−visible electronic absorption spectra of molecules **10**−**12**, recorded in ethanol, are shown in Scheme 7 and display typically two features: a complex group of transitions in the region between 200 and 400 nm, corresponding to the absorption of the conjugated ligands, and a group of less intense transitions in the visible region centered around 450−600 nm, where the ruthenium complex is supposed to absorb. As the first group depends, as expected, on the number of monomeric units, since it contains intraligands transitions, the second one is remarkably insensitive to the extension of the pendant conjugated phenylpyridine substituent. To explain these rather surprising results, since charge transfer transition are commonly invoked to explain this part of the electronic absorption spectrum, we have performed calculations at the ZINDO/S level of approximation. The results fit the experimental data well between 450 and 600 nm, and calculations confirm that this region of the spectrum is due to the MLCT transitions but *only* to those of the ancillary bipyridine ligands, as shown by a closer analysis of the involved orbitals. However, calculated spectra do not reproduce the experimental ones for the 200−400-nm region. This mismatch can be rationalized by keeping in mind that the geometry of the oligomeric chain has been arbitrary chosen as coplanar for our calculations. It was shown recently that the absorption spectrum of such type of molecule strongly depends on the torsion angle between adjacent phenylene moieties.[39] Because of the very weak rotational barrier (estimated to ca. 0.5 kcal/mol), a considerable disorder is thus expected. Since all the conformations are available in solution, a calculation taking into account all these conformations should be performed to improve the result in this region.

(38) Constable, E. C.; Holmes, J. M. *J. Organomet. Chem.* **1986**, *301*, 203−208.

(39) Levitus, M.; Schmieder, F.; Ricks, H.; Shimizu, K. D.; Bunz, U. H. F.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 4259−4265.

TABLE 1

	7	8	9
δ (ppm) H_a	6.55	6.55	6.55
λ_{max} (nm)	485, 539	481, 540	480, 540
$E_{1/2}$ (V)	0.51	0.51	0.51

The same behavior is also observed for the molecules **7**−**9** ended with a trimethylsilyl group (namely, no change in the 450−600-nm region), but no calculation has been performed, since the ZINDO parameters are not available for silicon. However, we can reasonably suggest that this behavior could be explained in a similar manner.

All these results (summarized in Table 1) indicate that the oligomer chain and the complex are not strongly coupled. Hence, further electrochemical measurements should characterize the oligomer itself and allow the determination of the decay parameter along it.

Conclusion

In this paper we have presented the advantages of capping oligo(phenylethynyl) by a cationic cyclometalated ruthenium complex, for the synthesis of rodlike, conjugated molecules. The presence of the charged center on the molecule is sufficient to allow the molecule elongation by conventional palladium-catalyzed cross-couplings up to 35 Å without any appreciable loss of solubility. And, since no additional solubilizing group is necessary, their syntheses require less organic synthons and fewer steps. Furthermore, the resulting charged species are easily purified and characterized by standard techniques. Since several charged organometallic or coordination building blocks are now available,[40−42] we believe that this strategy should provide a convenient access to long, conjugated, rigid molecules designed for various purposes such as light-emitting devices.[43]

Since they carry no substituent, we anticipate that these molecules should have a limited impact on their environment: in our case fewer disruptions of self-assembled monolayers are expected. This should facilitate their coadsorption as a SAM on a gold electrode for further electrochemical studies.

Experimental Section

General Instrumentation and Materials. FID were analyzed using the MestRE-C 2.3a program.[44] Two-dimensional COSY NMR experiments were performed by the Service de RMN of the Laboratoire de Chimie de Coordination in Toulouse. ES-MS spectra were recorded by the Service de Spectrométrie de Masse of the Université Paul Sabatier and FAB−HRMS by the CESAMO in Bordeaux. Reagents and anhydrous DMF were all commercially available and were used as received; other solvents were distilled from the appropriate drying agent (THF from sodium/benzophenone, amines from potassium hydroxide, and dichloromethane from calcium hydride). All experiments were carried out under an argon atmosphere using standard Schlenck tube techniques, except otherwise mentioned.

Physicochemical Measurements and Calculations. The working electrode for cyclic voltammetry esperiments was a 1 mm platinium button, and the reference electrode an aqueous saturated calomel electrode with a double frit system. The solvent was DNA-synthesis-grade acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate.

Molecular geometry was optimized using the Cerius2 package.[45] The force field was Universal with Ru−N and Ru−C bonds defined by Kb = 350 kcal mol^{-1} $Å^{-2}$ and R_o = 2.05 Å (N) or 2.02 Å (C). The ZINDO/S calculations were performed in the Hyperchem environment,[45] using the ruthenium bases of Krogh-Jespersen but with Ruβ(4d) = −26.29 eV.[46,47]

4-(Trimethylsilylethynyl)aniline (1) was prepared by following the procedure described in the litterature. Yield: 69%. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.26 (d, J = 8.6 Hz, 2H), 6.56 (d, J = 8.6 Hz, 2H), 3.76 (s, 1H), 0.21 (s, 9H). MS (CI, NH_3) m/z: 190.0 ($M + H^+$).

4-iodo-(trimethylsilylethynyl)benzene (2): prepared by following the procedure described in the litterature. Yield: 57%. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.63 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 0.23 (s, 9H). MS (CI, NH_3) m/z: 301.0 ($M + H^+$), 318.0 ($M + NH_4^+$).

4-{[4-(Trimethylsilylethynyl)phenyl]ethynyl}aniline (3). To a solution of 4-(trimethylsilylethynyl)aniline (**1**) (378 mg, 2 mmol) in 10 mL of methanol is added 1.3 g of potassium carbonate in one portion (9.4 mmol). After stirring at room temperature for 2 h, 10 mL of dichloromethane and 20 mL of water are added. The aqueous layer is extracted twice with dichloromethane, and the combined organic layers are dried over magnesium sulfate. After evaporation, the crude product is not purified but solubilized in 6 mL of THF and added, under argon, to 2 mL of a piperidine solution containing the 4-iodo-(trimethylsilylethynyl)benzene (**2**) (630 mg, 2.1 mmol), Pd-$(Ph_3)_4$ (36 mg, 0.03 mmol), and CuI (18 mg, 0.09 mmol). The resulting mixture is stirred overnight under argon. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer is extracted twice with dichloromethane. The combined organic layers are washed with a diluted solution of hydrochloric acid (0.5 M) and dried over magnesium sulfate. After evaporation, the crude product is purified by silica gel flash chromatography (eluent, cyclohexane:diethyl ether 1:1) to provide 460 mg of a pale yellow solid. Yield: 80%. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.40 (s, 4H), 7.31 (d, J = 8.6 Hz, 2H), 6.62 (d, J = 8.6 Hz, 2H), 3.84 (s, 2H), 0.24 (s, 9H). MS (CI, NH_3) m/z: 290.0 ($M + H^+$), 307.0 ($M + NH_4^+$).

1-(Trimethylsilylethynyl)-4-[(4-iodophenyl)ethynyl]-benzene (4). To a solution of **3** (820 mg, 2.8 mmol) in hydrochloric acid (6 M, 40 mL), cooled at 0 °C, is added sodium nitrite (246 mg, 3.6 mmol) in one portion. After 1 h at 0 °C, this solution is added dropwise to an ice-cold solution of sodium iodide (750 mg, 5 mmol), and 40 mL of dichloromethane is poured in this solution. The resulting mixture is allowed to reach room temperature and is stirred for 4 h. The aqueous phase is extracted twice with dichloromethane. The combined organic layers are washed with a saturated solution of sodium thiosulfate and dried over magnesium sulfate. The solvents are removed, and the crude product is purified by silica gel flash chromatography with hexane as eluent, to provide 526 mg of a white solid. Yield: 47%. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.68 (d, J = 8.7 Hz, 2H), 7.43 (s, 4H), 7.22 (d, J = 8.7 Hz, 2H), 0.24 (s, 9H). MS (CI, NH_3) m/z: 401.0 ($M + H^+$), 418.0 ($M + NH_4^+$).

(40) Chodorowski-Kimmes, S.; Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **1996**, *37*, 2963−2966.
(41) Tor, Y. *Synlett* **2002**, 1043−1054.
(42) Xu, B.; Yongge, W.; Barnes, C. L.; Peng, Z. *Angew. Chem., Int. Ed.* **2001**, *40*, 2290−2292.
(43) Glussac, K. D.; Jiang, S.; S., S. K. *Chem. Commun.* **2002**, 2504−2505.
(44) Cobas, J. C.; Cruces, J.; Sardina, F. J. *MestRe C 2.3*, a freeware program for NMR data processing.
(45) *Cerius2*; Molecular Simulations Inc: San Diego, CA.
(46) Krogh-Jespersen, K.; Westbrook, J. D.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 7025−7031.
(47) Anderson, W. P.; Cundari, T. R.; Zerner, M. C. *Int. J. Quantum Chem.* **1991**, *39*, 31.

1-Iodo-4-(acetylthio)benzene (5). To a solution of 1,4-diiodobenzene (3 g, 9.1 mmol) in dry ether (100 mL), cooled at −78 °C, is added dropwise *tert*-butyllithium (1.7 M in hexane, 10 mL, 17 mmol). The solution is vigorously stirred at this temperature for 10 min. Then the solution is allowed to warm, and sulfur is added (290 mg, 1.1 mmol), as soon as the temperature reaches −10 °C. The reaction is kept at 0 °C for 30 min and then cooled again at −78 °C before the addition of acetyl chloride in one portion (0.9 g, 11.4 mmol). The solution is allowed to warm to room temperature overnight. After hydrolysis, the mixture is extracted with dichloromethane. The combined organic layers are washed with a dilute solution of sodium hydrogenocarbonate and dried over magnesium sulfate. The crude product is purified by silica gel flash chromatography (eluent, hexane:ether 25:1) and then recrystallized in pentane to provide 1.58 g of a white solid. Yield: 62%. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.73 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.6 Hz, 2H), 2.42 (s, 3H). MS (CI, NH_3) *m/z*: 279.0 ($M + H^+$), 296.0 ($M + NH_4^+$), 313.0 ($M + N_2H_7^+$).

General Procedure for the Deprotection of the Trimethylsilyl Group (7−9). To a solution of 0.2 mmol of the silylated complex either in methanol (12 mL) (**7**) or in a 1:1 dichloromethane:methanol mixture (6 mL/6 mL) (**8** and **9**) is added 270 mg (2.0 mmol, 10 equiv) of potassium carbonate. The solution is stirred at room temperature for 2 h under argon. After evaporation of the solvents, the excess potassium carbonate is eliminated by filtration in dichloromethane. The crude product is not purified.

General Procedure for Sonogashira Cross-Coupling (7−9). To 2 mL of a DMF solution containing the deprotected alkyne (typically 0.2 mmol) are added the required *p*-iodo derivative **2** or **4** (2 equiv), $Pd(PPh_3)_4$ (0.05 equiv), CuI (0.1 equiv), and 1 mL of distilled diisopropylamine. The solution is stirred at room temperature under argon for 10 h. After evaporation of the solvents, the crude product is purified by silica gel chromatography (eluent, dichloromethane:acetonitrile 98:2).

General Procedure for Sonogashira Cross-Coupling (10−12). To 3 mL of a 2:1 mixture of DMF:THF containing the deprotected alkyne (typically 0.2 mmol) are added the S-protected derivative **5** (2 equiv), $Pd(PPh_3)_2Cl_2$ (0.05 equiv), CuI (0.1 equiv), and 1 mL of distilled diisopropylethylamine (Hunig's base). The solution is stirred at room temperature under argon for 12 h. After evaporation of the solvents, the crude product is purified by silica gel chromatography (eluent, dichloromethane:acetonitrile 98:2).

Complex 7: 87% yield from **7**. ^{1}H NMR (400 MHz, CD_3CN) δ: 8.48 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.33−8.37 (m, 2H), 8.10 (d, J = 8.4 Hz, 1H), 8.06 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 8.02 (d, J = 1.6 Hz, 1H), 8.01 (td, J_1 = 6 Hz, J_2 = 1.6 Hz, 1H), 7.81−7.89 (m, 3H), 7.79 (d, J = 6 Hz, 1H), 7.73−7.77 (m, 3H), 7.63 (d, J = 5.6 Hz, 1H), 7.43−7.47 (m, 5H), 7.22−7.28 (m, 3H), 7.00 (pseudo td, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H), 6.98 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 1H), 6.56 (d, J = 8 Hz, 1H), 0.26 (s, 9H). ^{13}C NMR (400 MHz, CD_3CN) δ: 199.43, 166.80, 158.02, 157.29, 157.10, 155.42, 154.49, 150.85, 150.70, 150.53, 149.46, 146.78, 136.95, 136.29, 136.15, 135.63, 134.57, 134.48, 132.22, 131.51, 130.63, 127.44, 126.84, 126.75, 126.59, 124.60, 123.87, 123.61, 123.47, 123.44, 123.21, 122.52, 119.57, 114.49, 104.89, 96.37, 93.69, 87.31, 62.71, −0.75. ES-MS: 764.1 ($M - PF_6^-$). HRMS calcd for $RuC_{44}N_5SiH_{36}$ ($M - PF_6^-$): 764.17835. Found: 764.17881.

Complex 8: 92% yield from **6**. ^{1}H NMR (400 MHz, CD_3CN) δ: 8.48 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.33−8.37 (m, 2H), 8.10 (d, J = 8 Hz, 1H), 8.06 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H), 8.03 (d, J = 1.6 Hz, 1H), 8.01 (td, J_1 = 8 Hz, J_2 = 1.6 Hz, 1H), 7.81−7.89 (m, 3H), 7.79 (d, J = 5.6 Hz, 1H), 7.73−7.78 (m, 3H), 7.63 (d, J = 5.6 Hz, 1H), 7.43−7.57 (m, 9H), 7.22−7.28 (m, 3H), 7.00 (pseudo td, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H), 6.98 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 1H), 6.56 (d, J = 8 Hz, 1H), 0.26 (s, 9H). ^{13}C NMR (400 MHz, CD_3CN) δ: 199.59, 166.75, 157.98, 157.24, 157.06, 155.38, 154.49, 150.87, 150.70, 150.54, 149.48, 146.78, 136.97, 136.31, 136.17, 135.65, 134.59, 134.50, 132.28, 132.07, 131.96, 131.61, 130.63, 127.46, 126.87, 126.79, 126.62, 126.60, 124.58, 123.89, 123.63, 123.49, 123.46, 123.41, 123.26, 122.30, 119.59, 114.44, 104.65, 96.83, 93,80, 91.26, 90.62, 87.44, −0.76. ES-MS: 864.4 ($M - PF_6^-$). HRMS calcd for $RuC_{52}N_5SiH_{40}$ ($M - PF_6^-$): 864.20965. Found: 864.21120.

Complex 9: 93% yield from **8**. ^{1}H NMR (400 MHz, CD_3CN) δ: 8.48 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.33−8.37 (m, 2H), 8.11 (d, J = 8 Hz, 1H), 8.07 (dd, J_1 = 6 Hz, J_2 = 1.2 Hz, 1H), 8.03 (d, J = 1.6 Hz, 1H), 8.01 (td, J_1 = 8 Hz, J_2 = 1.6 Hz, 1H), 7.82−7.89 (m, 3H), 7.80 (d, J = 6 Hz, 1H), 7.73−7.78 (m, 3H), 7.63 (d, J = 6 Hz, 1H), 7.43−7.57 (m, 13H), 7.22−7.28 (m, 3H), 7.00 (pseudo td, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H), 6.98 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 1H), 6.56 (d, J = 8 Hz, 1H), 0.26 (s, 9H). ^{13}C NMR (400 MHz, CD_3CN) δ: 199.49, 166.81, 158.02, 157.29, 157.10, 155.42, 154.49, 150.85, 150.70, 150.53, 149.47, 146.79, 136.96, 136.30, 136.17, 135.64, 134.58, 134.49, 132.27, 132.09, 132.06, 132.03, 131.99, 131.62, 130.65, 127.44, 126.84, 126.76, 126.60, 124.62, 123.87, 123.62, 123.55, 123.52, 123.47, 123.44, 123.30, 123.22, 122.36, 119.59, 114.51, 104.67, 96.89, 93.81, 91.33, 91.07, 90.97, 90.76, 87.47, − 0.77. ES-MS: 964.2 ($M - PF_6^-$). HRMS calcd for $RuC_{60}N_5SiH_{44}$ ($M - PF_6^-$): 964.24095. Found: 964.24143.

Complex 10: 56% yield from complex **7**. ^{1}H NMR (250 MHz, CD_3CN) δ: 8.46 (d, J = 8.20 Hz, 1H), 8.38 (d, J = 8.20 Hz), 8.32 (dd, J = 3.4 Hz, 7.7 Hz, 2H), 8.03 (m, 4H), 7.79 (m, 7H), 7.49 (m, 10 H), 7.23 (m, 4H), 6.96 (m, 2H), 6.53 (d, J = 7.7 Hz, 1H), 2.41 (s, 3H).^{13}C NMR (250 MHz, CD_3CN) δ: 200.17, 194.27, 167.17, 158.43, 157.69, 157.50, 155.82, 154.91, 151.38, 151.16, 151.01, 149.97, 147.24, 137.46, 136.79, 136.64, 136.12, 135.52, 135.07, 135.00, 132.87, 132.61, 132.12, 131.11, 129.81, 127.94, 127.38, 127.27, 127.12, 125.07, 124.73, 124.35, 123.94, 123.76, 122.68, 120.07, 114.84, 94.31, 91.26, 90.84, 87.90, 30.49. FAB-MS: 842($M - PF_6^-$). HRMS calcd for $RuC_{49}N_5SOH_{34}$ ($M - PF_6^-$): 842.15276. Found: 842.15384.

Complex 11: 50% yield from complex **8**. ^{1}H NMR (250 MHz, DMF-d_7) δ: 8.88 (d, J = 8.2 Hz, 1H), 8.80 (d, J = 8.2 Hz, 1H), 8.74 (m, 2H), 8.39 (d, J = 8.2 Hz, 1H), 8.17 (m, 3H), 7.89 (m, 4H), 7.65 (m, 16H), 7.46 (m, 4H), 7.16 (m, 1H), 7.02 (dd, J = 1.6 Hz, J = 7.8 Hz, 1H), 6.60 (d, J = 7.6 Hz, 1H), 2.49 (s, 3H). ^{1}H NMR (250 MHz, DMSO-d_6) δ: 8.77 (d, J = 8.2 Hz, 1H), 8.69 (d, J = 8.2 Hz, 1H), 8.63 (dd, J = 3.3 Hz, J = 8.2 Hz, 2H), 8.29 (d, J = 8.7 Hz, 1H), 8.09 (m, 2H), 7.77 (m, 3H), 7.58 (m, 18 H), 7.39 (m, 4H), 7.10 (m, 1H), 6.94 (dd, J = 1.2 Hz, J = 7.6 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H) 2.45 (s, 3H). ^{13}C NMR (250 MHz, DMF-d_7) δ: 200.36, 193.46, 167.07, 158.38, 157.67, 157.42, 155.74, 154.70, 151.13, 150.96, 150,88, 149.78, 147.16, 137.48, 136.77, 136.26, 135.25, 135.10, 134.98, 132.82, 132.53, 132.44, 132.01, 130.90, 129.88, 129.47, 128.09, 127.46, 127.28, 127.15, 127.09, 124.93, 124.53, 124.21, 124.05, 123.80, 123.43, 122.46, 120.11, 114.51, 84.53, 91.88, 91.25, 91.06, 87.84. ES-MS: 942.3 ($M - PF_6^-$). HRMS calcd for $RuC_{57}N_5SOH_{38}$ ($M - PF_6^-$): 942.18406. Found: 942.18340.

Complex 12: 52% yield from complex **9**. ^{1}H NMR (250 MHz, DMF-d_7) δ: 8.88 (d, J = 8.4 Hz, 1H), 8.80 (d, J = 8.4 Hz, 1H), 8.74 (m, 2H), 8.39 (d, J = 8.1 Hz, 1H), 8.17 (m, 3H), 7.89 (m, 4H), 7.65 (m, 20H), 7.45 (m, 4H), 7.16 (m, 1H), 7.02 (dd, J = 1.4 Hz, J = 7.7 Hz, 1H), 6.59 (d, J = 7.7 Hz, 1H), 2.49 (s, 3H). ^{1}H NMR (250 MHz, DMSO-d_6) δ: 8.76 (d, J = 8.5 Hz, 1H), 8.68 (d, J = 8.5 Hz, 1H), 8.63 (dd, J = 3.0 Hz, J = 8.5 Hz, 2H), 8.29 (d, J = 8.5 Hz, 1H), 8.10 (m, 2H), 7.77 (m, 3H), 7.59 (m, 22 H), 7.38 (m, 4H), 7.09 (m, 1H), 6.93 (d, J = 8.5 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H).^{13}C NMR (250 MHz, DMF-d_7) δ: 200.36, 193.45, 167.07, 158.38, 157.67, 157.41, 155.73, 154.70, 151.12, 150.95, 150.88, 149.81, 147.16, 137.48, 136.77, 136.26, 136.17, 135.25, 135.11, 134.98, 133.85, 132.82, 132.50, 132.01, 130.90, 129.88, 128.09, 127.47, 127.28, 127.14, 127.09, 124.93, 124.52, 124.21, 124.05, 123.80, 123.71, 123.61, 123.56, 123.49, 122.46, 120.11, 114.51, 94.53, 94.44, 91.87, 91.61, 91.24, 91.07,

87.84. ES-MS: 1042.3 ($M - PF_6^-$). HRMS calcd for $RuC_{65}N_5SOH_{42}$ ($M - PF_6^-$): 1042.21536. Found: 1042.21741.

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Supporting Information Available: ^1H NMR spectra, ^{13}C NMR spectra, and UV−visible absorption spectra for all new molecules, 2D-NMR spectra (COSY 45) and attributions of the protons in the aromatic region for complexes **7**−**9**, and representation of the molecular orbitals involved in MLCT transitions for complexes **10**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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