Novel fullerene platinum alkynyl complexes with high second-order nonlinear optical properties as a springboard for NLO-active polymer films.

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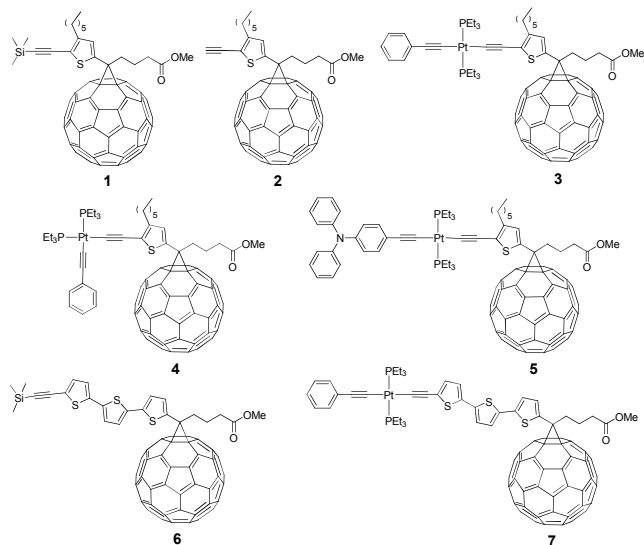
ABSTRACT: The synthesis and second-order nonlinear optical (NLO) properties of seven novel fullerene-C_{60} derivatives are reported. In these Donor-bridge-Acceptor systems, the fullerene unit (Acceptor) is connected through a cyclopropane group to an ethynyl thienyl fragment (bridge) which binds a trimethylsilyl or platinum alkynyl fragment (Donor). All derivatives are NLO-active, as determined by the Electric Field Induced Second Harmonic generation technique, but the fullerene platinum alkynyl complexes are characterized by a particularly large second-order NLO response. Substitution of the thienyl fragment by a terthiophene leads to an increase of the NLO performance by using trimethylsilyl as Donor group whereas no effect is observed in the case of platinum derivatives. Remarkably, fullerene platinum alkynyl complexes can be dispersed in polymethylmethacrylate or polystyrene affording NLO-active polymer films.

INTRODUCTION

Compounds with second-order nonlinear optical (NLO) properties are of great interest as molecular building block materials for optical communications, optical data processing and storage, or electro-optical devices.[1] Very early in the search for second-order NLO-phores it was recognized that molecules consisting of donor and acceptor groups linked with an unsaturated bridge possessing polarizable π-electrons are particularly NLO-efficient. Among them, metal complexes are fascinating because they can offer additional flexibility, when compared to organic compounds, due to the presence of NLO-active charge-transfer transitions between the metal and the ligands, usually at relatively low energy and of high intensity, tunable by virtue of the nature, oxidation state and coordination sphere of the metal center and even by the number of f electrons.[2] In the last decade, metal σ-acetylides has been a widely investigated class of second-order NLO-phores, mainly developed by Humphrey et al.,[3] where the metal acts as the donor group of a donor-acceptor system connected by a π-linker. A few years ago an Electric Field Second Harmonic generation (EFISH)[4] study showed that dipolar alkynyl ruthenium complexes with a phenyleneethynylene or phenylenevinylene bridge between a donor "ClRu" moiety and a nitro acceptor group are characterized by high second-order NLO properties.[5] Also, recently, some of us reported that a "phenylalkynyl-Ru" moiety behaves as a good donor in various NLO-efficient push-pull architectures bearing an acceptor group such as methyl-cyanoacrylate or 2,1,3-benzothiadiazole.[6] Besides the photophysical properties of various Pt(II) acetylide complexes have been investigated,[7] some of them being characterized by interesting third-order NLO properties such as two.photon absorption cross-sections[8] or strong reverse saturable absorption.[9] In addition some terpyridyl and cyclometal-

lated (dipyridyl)benzene platinum(II) complexes with a phenyl-alkynyl ancillary ligand are characterized by a high, second-order NLO response, as determined by the Hyper-Rayleigh Scattering and EFISH techniques, where the "phenylalkynyl-Pt" moiety and the tridentate ligand act as a donor and an acceptor, respectively.[10] Based on the fact that platinum alkynyls are good donors in NLO-active systems, the idea of a related hybrid with a C_{60}-fullerene is highly intriguing because fullerene is an electron deficient compound with exceptionally strong π-aromaticity.[11] As a matter of fact it was shown that C_{60}-fullerene is an excellent building block for NLO materials due to its strong acceptor properties and large polarizability.[12] However, although elegant studies of the photoinduced electron transfer reactions in both platinum(II) bis(N-(4-ethynylphenyl)carbazole)bipyridine fullerene[13] and platinum(II) bis(N-(4-ethynylphenyl)phenothiazine)bipyridine fullerene[14] complexes, of particular interest for the preparation of organometallic photovoltaic cells,[15] have been reported, to the best of our knowledge, the second-order NLO properties of a push-pull system containing both a donor metal σ-acetylide moiety and a fullerene have never been investigated. These observations prompted us to prepare novel fullerene derivatives (**1-2** Chart 1) where the C_{60} unit is connected through a cyclopropane group, which allows a facile electronic communication (periconjugation),[16] to an ethynyl thienyl fragment chosen as π -delocalized bridge for binding the fullerene to the platinum center. Its second-order NLO properties are presented here along with those of related platinum phenylalkynyl complexes. Besides, it is known that an increase of the π-delocalized bridge between the acceptor and donor groups can lead to an enhanced second-order NLO response[2] and that terthiophene is an interesting π-conjugated electron-releasing unit.[17] Therefore the effect of the substitution of the thienyl fragment by a terthiophene was investigated, and the results are reported.

Complex **7** was prepared in a similar manner from the new methanofullerene (**6**, Scheme 2, see Experimental Section).

Scheme 2. Synthesis of the methanofullerene derivative 6 and of the platinum complex 7.Ale:Scrivere 6 invece di 9 nella fig
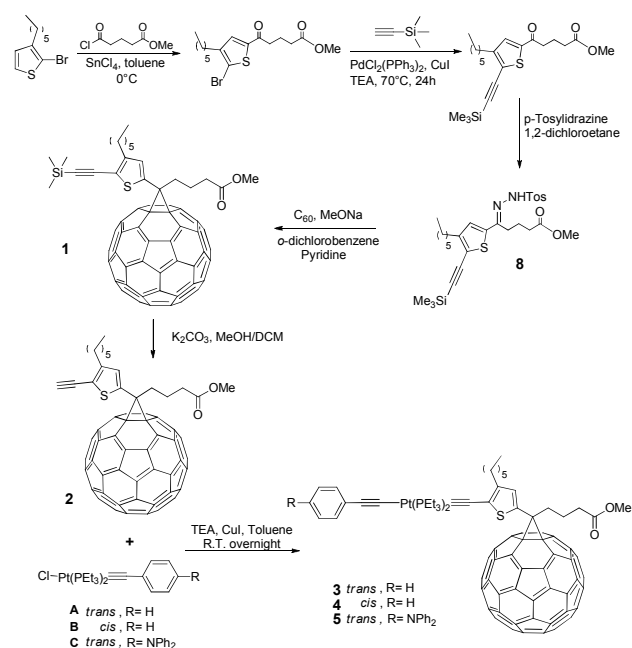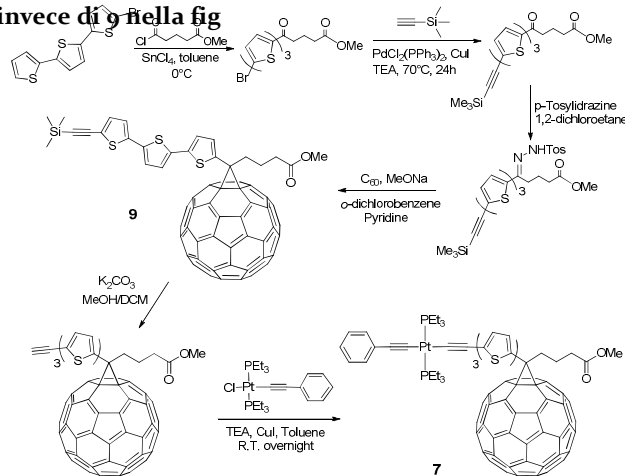

RESULTS AND DISCUSSIONS

The novel thiophene-substituted methanofullerenes **1** and **2** were prepared following the procedure reported for other methanofullerenes,[18-20] by reaction of the suitable p-tosylhydrazone derivative with sodium methoxide and C_{60}-fullerene. (Scheme 1) .

The platinum derivatives **3-5** were synthesized by deprotection of **1** and reaction with the opportune platinumacetylide complex in the presence of CuI and triethylamine (TEA) in dry toluene.

Scheme 1. Synthesis of the methanofullerene derivatives 1,2 and of the platinum complexes 3,4,5.

Table 1 Photophysical data and second-order NLO properties of compounds 1-7

Sample	Absorption[a] λ_{max} / nm (ε / M^{-1} cm^{-1})	$\mu\beta_{EFISH}$[b] ($\times 10^{-48}$ esu)	μ[c] ($\times 10^{-18}$ esu)	β_{EFISH}[d] ($\times 10^{-30}$ esu)
1	259 (95515), 329 (33683)	-350	4.22	-83
2	260 (94597) 327 (35867)	570	4.27	133
3	259 (74672), 332 (34045), 356 (33794)	-3100	5.75	-539
4	259 (72220), 331 (33320), 355 (30600)	-3200	13.33	-240
5	259 (73100), 327 (30114), 482 (1530)	-2700	5.92	-456
6	260 (89900), 330 (35462), 375 (23215)	-1400	3.61	-388
7	255 (87500), 276 (74432), 296 (65910), 301 (64839), 402 (1557)	-3200	5.14	-623

(a) In CH_2Cl_2 (b) in DMF at 1.907 μm; estimated uncertainty in EFISH measurements is ±10%. (c) computed dipole moments in DMF. (d) the zero-frequency static quadratic hyperpolarizability β_o is -71, 114, -459, -205, -391, -331 and -547 $\times10^{-30}$ esu for **1**, **2**, **3**, **4**, **5**, **6**, and **7**, respectively, as calculated using the expression $\beta_o = \beta_{EFISH}(1- (2\lambda_{max}/1907)^2)(1-(\lambda_{max}/1907)^2)$.[2c]

Absorption data of compounds **1-7** in solution are presented in Table 1. All compounds show bands in the range 255-332 nm as expected for thienyl fullerene derivatives,[17] the platinum complexes having an additional band at lower energy (355-482 nm) due to the alkynyl platinum moiety.[6] **6** is also characterized by a band at 375 nm, typical of the terthiophene moiety.[21]

We applied the EFISH method to study the NLO response in solution of compounds **1-7**. This technique[4] can provide direct information on the intrinsic molecular NLO properties, through

$$\gamma_{EFISH} = (\mu\beta_{EFISH}/5kT) + \gamma(-2\omega; \omega, \omega, 0) \qquad (1)$$

where $\mu\beta_{EFISH}/5kT$ is the dipolar orientational contribution to the molecular nonlinearity, and $\gamma(-2\omega; \omega, \omega, 0)$, the third order polarizability, is a purely electronic cubic contribution to γ_{EFISH} which can usually be neglected when studying the second-order NLO properties of dipolar compounds. To obtain β_{EFISH}, the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, it is necessary to know the dipole moment, μ. In the present study we used the theoretical dipole moments calculated in DMF as described in the Experimental section (see also Supporting Information).

We found that **1**, which has the trimethylsilyl fragment as weak inductive donor group,[22] is characterized by a fair value of $\mu\beta_{EFISH}$ (-350 x 10^{-48} esu, see Table 1) working in DMF with a non-resonant incident wavelength of 1.907 μm. The negative value of $\mu\beta_{EFISH}$ suggests a decrease of the excited state dipole moment with respect to the ground state.[23] The NLO response increases by a factor of ca 9 upon formation of complexes **3** ($\mu\beta_{EFISH}$ = -3100 x 10^{-48} esu) and **4** ($\mu\beta_{EFISH}$ = -3200 x 10^{-48} esu), due to an increase of both the dipole moment and the quadratic hyperpolarizability (see Table 1). However since the dipole moment of **3** is about half that of **4** a higher value of β_{EFISH} (-539x10^{-30} esu) is reached when the two alkynyl moieties are in *trans* position, in agreement with a more efficient "push-pull" system. A slightly lower response is obtained by functionalization of the phenyl ring with a diphenylamino substituent (complex **5**), suggesting that the observed overall NLO response is the result of negative and positive contributions due to different NLO-active charge transfer transitions as previously observed for other platinum(II) complexes.[10b] This is confirmed by the effect of the trimethylsilyl removal from **1** to give **2** which changes the value and the sign of the β_{EFISH} from -83 to 133 x10^{-30} esu. The negative sign observed for **1** can reasonably be explained by the electron acceptor properties of the Si atom, through the low lying *d* orbitals,[24] which can behave both as a donor or acceptor like the platinum center.

Interestingly, in the presence of the trimethylsilyl fragment, substitution of the thiophene by a terthiophene leads to a fourfold increase of the second order NLO response (compare **1** and **6**, Table 1) whereas a less significant increase is observed with the *trans*-(triethylphosphine)₂phenylacetilyde platinum moiety (compare **3** and **7**).

The huge values of $\mu\beta_{EFISH}$ observed in the present work for the fullerene platinum alkynyl derivatives are remarkable for neutral metal complexes. Indeed, to our knowledge, complex **3** is characterized by the highest absolute value of $\mu\beta_{EFISH}$ reported for a platinum alkynyl complex. Such a high value was reached for a fullerene ruthenium derivative, *cis*-Cl,*trans*-PPh₃-[Ru(9-fulleriden-4,5-diazafluorene)(PPh₃)₂Cl₂], only.[12b] Various attempts to prepare second-order NLO-active polymer films with this ruthenium complex failed. This observation prompted us to produce composite films of complexes **3** and **5** dispersed both in polymethylmethacrylate (PMMA) and polystyrene in order to study the Second Harmonic Generation (SHG) signal of the resulting poled host-guest systems (see Experimental Section).

The corona wire poling (65°C and 9.5 kV) of a PMMA film containing complex **3** (4-6 wt % complex/PMMA) leads to a fair SHG signal, due to the orientation of the dipolar NLO-phores, which decreases rapidly when the electric field is switched off. By using **5** instead of **3** as NLO-phore, a twofold SHG signal is ob-

served. Substitution of PMMA by polystyrene as matrix for complex **5** allows to double the SHG signal which however drops by a factor of 6 upon removal of the electric field with a final χ^2_{33} value of ca 0.5 pm/V.

These preliminary data confirm the important role of the matrix whose specific functionalities can lead to host-guest and host-host interactions and affect the stability of the organized NLO molecules.[25] Clearly, the novel fullerene platinum alkynyl complexes presented here, in particular **5**, are good candidates for the preparation of efficient second-order NLO-active polymer films. The next step will be to stabilize the NLO response for example by anchoring covalently the NLO-phores to the matrix in order to inhibit their movement and therefore the loss of their orientation upon removal of the electric field. In fact, the progressive fading of the NLO signal with time due to the loss of molecular orientation within the material is a quite general drawback of NLO-active molecular materials that needs to be solved.

CONCLUSIONS

In summary, this work has confirmed the great potential of fullerene as acceptor group in the design of second-order NLO-phores. Remarkably, its combination with a platinum alkynyl fragment as donor group leads to a huge second-order nonlinear optical response. These novel fullerene platinum alkynyl complexes are of particular interest as molecular building blocks for NLO devices because they can be easily dispersed and oriented in a polymethylmetacrylate or polystyrene matrix to give NLO-active thin films.

EXPERIMENTAL SECTION

General comments

Solvents were dried by standard procedures: toluene was freshly distilled from Na/benzophenone under nitrogen atmosphere and triethylamine (TEA) was freshly distilled over KOH. All reagents were purchased from Sigma-Aldrich and were used without further purification. Reactions requiring anhydrous or oxygen-free conditions were performed under nitrogen. Thin-layer chromatography (TLC) was carried out using pre-coated Merck F254 silica gel plates. Flash chromatography was carried out with Macherey-Nagel silica gel 60 (230-400 mesh).

¹H and ¹³C spectra were recorded at 400 MHz on a Bruker AVANCE-400 instrument. Chemical shifts (δ) for ¹H and ¹³C spectra are expressed in ppm relative to internal Me₄Si as standard. Signals are abbreviated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Elemental analyses were performed using an Exeter Analytical E-440 analyser. All the derivatives **1-7** were also characterized by UV-visible spectroscopy.

Synthesis of 1 and 2(Scheme 1)

The new methanofullerene **1** was prepared following procedures reported for related compounds (see Scheme 1 of "Results and discussion").[18-20] A mixture of the *p*-tosylhydrazone derivative (376.6 mg, 0.67 mmol, 1.2 equiv.), sodium methoxide (36.18 mg, 0.67 mmol, 1.2 equiv.), and dry pyridine (6.7 mL) was stirred at room temperature for 30 min. Then a solution of C_{60}-fullerene (396 mg, 0.55 mmol, 1 equiv.) in *o*-dichlorobenzene (39 mL) was added, and the homogeneous reaction mixture was stirred at 80°C under nitrogen overnight. Then the mixture was refluxed for 24 h (180°C); after cooling to room temperature the solvent was evaporated at reduced pressure, and the residue was purified by column chromatography on silica gel with toluene/hexane 1/1 as eluent to give **1** as a pure product (yield 50%).

¹H-NMR (400 MHz, CDCl₃), δ: 7.23 (1H, s), 3.71 (3H, s), 2.94 (2H, *J* = 7.4 Hz, t), 2.79 (2H, *J* = 7.4 Hz, t), 2.59 (2H, *J* = 7.4 Hz, t), 2.29-2.25 (2H, m), 1.70 (2H, *J* = 7.1 Hz, t), 1.34-1.29 (6H, m), 0.90 (3H, *J* = 7.1 Hz, d), 0.30 (9H, s). ¹³C-NMR (100 MHz, CD₂Cl₂), δ:

173.10, 148.24, 147.97, 147.39, 145.71, 145.22, 145.16, 144.81, 144.74, 144.65, 144.59, 144.50, 144.20, 143.80, 143.01, 142.94, 142.15, 140.92, 140.73, 139.19, 138.28, 138.13, 133.40, 118.94, 96.99, 79.65, 51.50, 46.04, 33.72, 33.56, 31.63, 29.93, 29.56, 28.75, 22.72, 22.53, 13.98, 0.35. Anal. Calcd. (%) for $C_{81}H_{32}O_2SSi$: C 89.66, H 2.94. Found: C 89.10, H 3.08.

To a solution of **1** (282 mg, 0.26 mmol) in methanol/dichlorometane 1/1 (22 mL), anhydrous K_2CO_3 (142.7 mg, 1.03 mmol) was added under a nitrogen flow. The reaction mixture was left under stirring at room temperature overnight. The solvent was removed under reduced pressure and the residue was diluted with CH_2Cl_2 and washed with water; the organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography, using hexane/toluene 1/1 as eluent, to give the free alkyne **2** as a brown solid (180 mg; yield 64 %). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.25 (1H, s), 3.72 (3H, s), 3.55 (1H, s), 2.96 (2H, J = 7.7 Hz, t), 2.81 (2H, J = 7.7 Hz, t), 2.60 (2H, J = 7.2 Hz, t), 1.71 (2H, J = 7.2 Hz, t), 1.34-1.29 (6H, m), 0.89 (3H, s).

^{13}C-NMR (100 MHz, $CDCl_3$), δ: 173.78, 148.58, 148.39, 147.62, 146.01, 145.60, 145.43, 145.25, 145.04, 144.95, 144.64, 144.20, 143.45, 143.38, 142.58, 142.54, 141.40, 141.19, 139.90, 138.59, 84.53, 79.84, 34.16, 34.07, 32.05, 30.39, 29.97, 29.18, 23.10, 22.90, 14.55, 1.93. Anal. Calcd. (%) for $C_{78}H_{24}O_2$: C 94.38, H 2.44. Found: C 94.01, H 2.56.

Synthesis of Pt complexes 3-5

To a solution of the opportune platinumacetylide complex (**A**, **B** or **C**; 0.075 mmol; Scheme 1) in dry toluene (13.5 mL) CuI (0.07mmol) and TEA (2.5 mL) were added. The mixture was cooled to 0°C and a solution of the alkyne (0.075 mmol) in toluene dry (1mL) was added. The reaction mixture was left under stirring at room temperature for 24 h. After filtration, the solvent was removed under reduced pressure. The residue was diluted with CH_2Cl_2 and washed with a 5% solution of NH_4Cl and then with water. The organic layer was dried over Na_2SO_4 and the solvent evaporated at reduced pressure. The crude product was purified by flash chromatography on silica gel with CH_2Cl_2/hexane 1/1 as eluent to give the desired pure product.

Pt complex 3 was obtained in 60 % yield starting from **A** (43.5 mg), CuI (1.85 mg) and the alkyne (77 mg). ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.40 (2H, J = 8.2 Hz, d), 7.30-7.25 (2H, m), 7.22 (1H, s) 7.00 (1H, m), 3.55 (3H, s), 2.95 (2H, J = 9.5 Hz, t), 2.75 (2H, J = 7.4 Hz, t), 2.60 (2H, J = 7.4 Hz, t), 2.37-2.35 (2H, m), 2.25-2.20 (12H, m), 2.09-2.08 (18H, m) 1.70 (2H, J = 7.1 Hz, t), 1.34-1.29 (6H, m), 1.1-0.9 (3H, m). ^{13}C-NMR (100 MHz, CD_2Cl_2), δ: 148.24, 147.97, 147.39, 145.81, 145.22, 145.16, 144.81, 144.79, 144.62, 144.59, 144.50, 144.20, 143.80, 143.01, 142.94, 142.15, 141.28, 140.62, 139.19, 138.28, 138.19, 138.13, 133.40, 124.10, 123.70, 122.68, 51.50, 46.04, 33.72, 33.56, 31.63, 29.93, 29.56, 28.75, 22.72, 22.53, 14.60, 13.98, 7.84 Anal. Calcd. (%) for $C_{98}H_{58}O_2P_2PtS$: C 75.62, H 3.76. Found: C 76.23, H 3.98.

Pt complex 4 was obtained in 30 % yield starting from **B** (43.5mg), CuI (1.85 mg) and the alkyne (77 mg). ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.38 (2H, J = 8.2 Hz, d), 7.27-7.22 (2H, m), 7.18 (1H, s) 7.00 (1H, m), 3.55 (3H, s), 2.95 (2H, J = 9.5 Hz, t), 2.75 (2H, J = 7.4 Hz, t), 2.60 (2H, J = 7.4 Hz, t), 2.37-2.35 (2H, m), 2.20-2.18 (12H, m), 2.05-2.03 (18H, m) 1.70 (2H, J = 7.1 Hz, t), 1.34-1.29 (6H, m), 1.1-0.9 (3H, m). ^{13}C-NMR (100 MHz, CD_2Cl_2), δ: 148.24, 147.97, 147.39, 145.81, 145.22, 145.16, 144.81, 144.79, 144.62, 144.59, 144.50, 144.20, 143.80, 143.01, 142.94, 142.15, 141.28, 140.62, 139.19, 138.28, 138.19, 138.10, 138.13, 133.40, 124.10, 123.70, 122.68, 51.50, 46.04, 33.72, 33.56, 31.63, 29.93, 29.56, 28.75, 22.72, 22.53, 14.58, 13.71, 13.98, 8.25, 7.84. Anal. Calcd. (%) for $C_{98}H_{58}O_2P_2PtS$: C 75.62, H 3.76. Found: C 74.98, H 4.02.

Pt complex 5 was obtained in 50 % yield starting from **C** (56.4 mg), CuI (1.85 mg) and the alkyne (77 mg). ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.31-7.24 (8H, m), 7.15 (2H, J = 8.2 Hz, d), 7.12 (1H, s),

7.10-7.08 (2H, m), 6.93 (2H, J = 8.2 Hz, d) 3.55 (3H, s), 2.95 (2H, J = 7.4 Hz, t), 2.75 (2H, J = 7.4 Hz, t), 2.60 (2H, J = 7.1 Hz, t), 2.30-2.20 (12H, m), 2.05-2.00 (18H, m), 1.73 (2H, J = 7.1 Hz, t), 1.33-1.29 (6H, m), 1.1-0.9 (3H, m). ^{13}C-NMR (100 MHz, $CDCl_3$), δ: 148.74, 144.77, 145.81, 145.18, 145.17, 144.79, 144.62, 144.43, 144.13, 143.81, 143.48, 143.00, 142.61, 142.11, 141.28, 140.86, 140.62, 140.26, 138.19, 133.46, 129.15, 124.00, 122.62, 80.09, 51.42, 33.59, 31.86, 30.47, 29.68, 29.08, 22.76, 22.56, 14.56, 13.91, 8.23, 7.82.

Anal. Calcd. (%) for $C_{110}H_{67}NO_2P_2PtS$: C 76.64, H 3.92, N 0.81. Found: C 77.02, H 4.00, N 0.74.

Synthesis of 9 (Scheme 2)

The new methanofullerene **9** was prepared following the synthetic pathway of **1**. A mixture of p-tosylhydrazone derivative (63.8 mg, 0.11 mmol), sodium methoxide (6.0 mg, 0.11 mmol), and dry pyridine (1.1 mL) was stirred at room temperature for 30 min. Then a solution of C_{60}-fullerene (66 mg, 0.092 mmol) in o-dichlorobenzene (6.4 mL) was added, and the homogeneous reaction mixture was stirred at 80°C under nitrogen overnight. Then the mixture was refluxed for 24 h (180°C), after cooling to room temperature the solvent was evaporated at reduced pressure, and the residue was purified by column chromatography on silica gel with toluene/hexane 1/1 as eluent to give **5** as a pure product (yield 40%).

^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.43 (1H, J = 3.6 Hz d), 7.26 (1H, J = 3.6 Hz, d), 7.20-7.16 (3H, m), 7.06 (1H, J = 3.6 Hz, d), 3.71 (3H, s) 2.99 (2H, J = 7.7 Hz, t), 2.47 (2H, J = 7.7 Hz, t), 2.11 (2H, m), 0.26 (9H, s). ^{13}C-NMR (100 MHz, CD_2Cl_2), δ: 173.10, 148.24, 147.97, 147.39, 145.71, 145.22, 145.16, 144.81, 144.74, 144.65, 144.59, 144.52, 144.20, 143.80, 143.01, 142.94, 142.15, 140.92, 140.73, 139.19, 138.28, 138.13, 134.01, 133.40, 132.80, 118.98, 96.97, 79.65, 51.50, 46.04, 33.72, 33.56, 29.93, 29.56, 28.75, 0.35. Anal. Calcd. (%) for $C_{84}H_{24}O_2S_3Si$: C 84.83, H 2.03. Found: C 85.10, H 1.98.

Synthesis of Pt complex 7

The methanofullerene **9** (40 mg, 0.03 mmol) was dissolved in methanol/dichlorometane 1/1 (10 mL) and anhydrous K_2CO_3 was added under a flow of nitrogen (16 mg, 0.12 mmol). The reaction mixture was left under stirring at room temperature overnight. The solvent was removed under reduced pressure and the residue was diluted with CH_2Cl_2 and washed with water; the organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography, using hexane/toluene 1/1 as eluant, to give the free alkyne as a brown oil (25 mg; yield 71 %).

^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.45 (1H, J = 3.7 Hz d), 7.28 (1H, J = 3.7 Hz, d), 7.21-7.17 (3H, m), 7.06 (1H, J = 3.6 Hz, d), 3.71 (3H, s), 3.69 (1H, s), 2.99 (2H, J = 7.7 Hz, t), 2.47 (2H, J = 7.7 Hz, t), 2.11 (2H, m).

To a solution of complex **A** (9.6 mg, 0.017 mmol) in dry toluene (4.5 mL) CuI (2 mg, 0.01mmol) and TEA (0.5 mL) were added. The mixture was cooled to 0°C and a solution of the alkyne (20 mg 0.017 mmol) in dry toluene (1mL) was added. The reaction mixture was left under stirring at room temperature for 24 h, then the solvent was removed under reduced pressure. The residue was diluted with CH_2Cl_2 and washed with a 5% solution of NH_4Cl and then with water. The organic layer was dried over Na_2SO_4 and the solvent removed. The crude product was purified by flash chromatography on silica gel with CH_2Cl_2/hexane 2/3 as eluent to give the desired pure product **7** in 52% yield.

^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.42 (1H, J = 3.6 Hz d), 7.40 (2H, J = 8.2 Hz, d), 7.35 (3H, m), 7.24 (1H, J = 3.6 Hz, d), 7.20-7.16 (3H, m), 7.06 (1H, J = 3.6 Hz, d), 3.70 (3H, s), 2.95 (2H, J = 9.5 Hz, t), 2.75 (2H, J = 7.4 Hz, t), 2.60 (2H, J = 7.4 Hz, t), 2.25-2.20 (12H, m), 2.09-2.08 (18H, m). ^{13}C-NMR (100 MHz, CD_2Cl_2), δ: 148.24, 147.97, 147.39, 145.71, 145.22, 145.16, 144.81, 144.76, 144.65, 144.57, 144.50, 144.20, 143.80, 143.01, 142.94, 142.15, 140.92, 140.73, 139.19, 138.28,

138.13, 134.05, 133.40, 132.81, 51.50, 46.04, 33.72, 33.56, 29.93, 29.56, 28.75, 14.56, 7.84. Anal. Calcd. (%) for $C_{101}H_{50}O_2P_2PtS_3$: C 73.58, H 3.06. Found: C 74.66, H 2.96.

Preparation of thin films

Thin films of the complexes (**3** or **5**) dispersed in polymethyl-methacrylate (PMMA) or polystyrene were prepared by spin coating a few drops of a dichloromethane solution (complex/PMMA or polystyrene = 4-6 wt %, while PMMA or polystyrene = 10 wt % with respect to the solvent) on a glass substrate (thickness 1 mm) previously cleaned with water/acetone. Parameters of spinning (RPM = revolutions per minute): RPM 1 = 700; Ramp 1 = 1 s, Time 1 = 5 s; RPM 2 = 1000; Ramp 2 = 5 s, Time 2 = 10 s; RPM 3 = 1000; Ramp 3 = 1 s, Time 3 = 10 s.[15]

EFISH measurements

EFISH measurements were carried out in DMF solutions at a concentration of 10^{-4} M for , with a non-resonant incident wavelength of 1.907 μm, obtained by Raman-shifting the fundamental 1.064 μm wavelength produced by a Q-switched, mode-locked Nd^{3+}:YAG laser manufactured by Atalaser. The apparatus used for EFISH measurements is a prototype made by SOPRA (France). The μβ$_{EFISH}$ values reported are the mean values of 16 measurements performed on the same sample. The sign of μβ is determined by comparison with the solvent (DMF).

SHG measurements

Second Harmonic Generation (SHG) experiments were performed using a Q-switched Nd:YAG (Quanta System Giant G790-20) laser at 1.064 μm wavelength with a pulse of 7 ns and 20 Hz repetition rate. For poling measurements, the fundamental beam (0.55 mJ for pulse) was polarized in the plane of incidence (p-polarized) and focused with a lens (f = 600 mm) on the sample with an angle of about 55° in order to optimize the SHG signal. The sample was placed over the hot stage whose temperature was controlled by a GEFRAN 800, while the coronawire voltage was applied by a TREK610E high-voltage-supply. Rejection of the fundamental beam was performed by an interference filter and a glass cut-off filter, and the p-polarized SHG signal at 532 nm was detected with a UV-Vis Hamamatsu C3830 photomultiplier tube. The corona poling process was carried out at 9.5 kV while increasing the temperature at a rate of 2.3°C min−1 up to 65°C inside a specially built dry box, in N₂ atmosphere. The temperature was maintained at 65°C for 2 h and then decreased to room temperature. The setup for Maker fringe measurements was similar to the previous except that the fundamental beam was attenuated to 1 mJ for pulse and the sample was placed over a rotation stage.[25]

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