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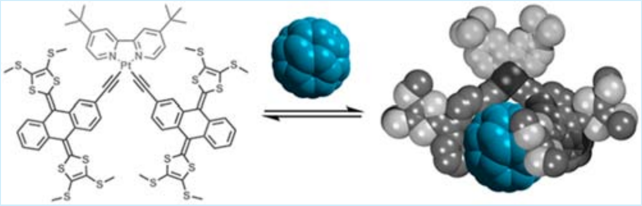
C$_{60}$ Recognition from Extended Tetrathiafulvalene *Bis*-acetylide Platinum(II) Complexes

Guillaume Bastien, Paul I. Dron, Manon Vincent, David Canevet, Magali Allain,
Sébastien Goeb,* and Marc Sallé*

Laboratoire MOLTECH-Anjou, Université d'Angers, CNRS UMR 6200, 2 bd Lavoisier, 49045 Angers Cedex, France

Supporting Information

ABSTRACT: The favorable spatial organization imposed by the square planar 4,4′-di(*tert*-butyl)-2,2′-bipyridine (dbbpy) platinum(II) complex associated with the electronic and shape complementarity of π-extended tetrathiafulvalene derivatives (exTTF) toward fullerenes is usefully exploited to construct molecular tweezers, which display good affinities for C$_{60}$.



Given the importance of fullerene derivatives for various types of applications, research related to their recognition through host−guest processes is very active.[1] In this context, different families of molecular receptors have been designed, be they covalent organic macrocycles,[2] self-assembled macrocycles[3] and cages,[4] or molecular tweezers.[5] Most often, such receptors involve two or more highly π-extended units, which are prone to interact with the fullerene surface. Recently, the π-extended tetrathiafulvalene (exTTF)[6] unit has known a strong interest in the designing of fullerene receptors, supported by a suitable combination of geometric and electronic specific features. In particular, the butterfly shape[6d] of exTTF allows for a favorable concave/convex interaction when its highly π-donating capability is complementary with the electron-poor nature of fullerene derivatives.[1c,7] Despite those electronic and geometric complementarities, to the best of our knowledge, the interaction between an isolated exTTF unit and fullerenes has never been detected in solution.[7] On the contrary, receptors bearing two suitably preorganized exTTF fragments do interact with theses guests, thanks to synergic effects.[7] On this basis, macrocyclic receptors incorporating two exTTF units were successfully designed.[2c,8] Nevertheless, related molecular tweezers, i.e., an open cavity formed by a central platform bearing two pendant units,[9] are still scarcely described,[10] despite the ability of such host compounds to be generally synthesized in a straightforward way.

We describe herein a simple procedure to produce exTTF-based molecular tweezers incorporating a metal complex as the central platform, by coupling two functionalized alkynes to a platinum diimine complex in a square planar *cis* configuration. The geometry that is imposed by the coordination to the metal center as well as the length of the acetylide spacer were selected to provide a suitable distance between both exTTF units in order to accommodate a fullerene C$_{60}$ acceptor.

The synthesis of target complexes **C1** and **C2** is depicted in Scheme 1. Monoacetylide exTTF **2** was quantitatively obtained upon deprotection of the silylated derivative **1** using potassium carbonate.[11] Bis-alkyne exTTF **4**[11] was synthesized from **3** according to a similar methodology and subsequently reacted with one equivalent of 4-iodopyridine through a Sonogashira cross-coupling. The target dissymmetrical ligand **6** was isolated with a 44% yield in addition to the symmetric compound **5** (40%). Finally, analogously to the preparation of *bis*-corannulene diphosphino platinum tweezers,[12] complexes **C1** and **C2** were respectively obtained via a CuI-catalyzed coupling reaction between alkynes **2** and **6** and the Pt(dbbpy)Cl$_2$ complex (dbbpy = 4,4′-di(*tert*-butyl)-2,2′-bipyridine) in the presence of diisopropylamine. Both target Pt(II) complexes were purified by silica gel chromatography and proved to be soluble in usual organic solvents. Thus, their structures could be confirmed by HR-MS spectrometry and NMR spectroscopy since both complexes exhibit well-defined NMR signals, and their purities confirmed through elemental analysis measurements.

Diimine platinum(II) acetylide complexes are known to exhibit remarkable luminescence properties at room temperature, characterized by bright emission in the visible range and long lifetimes decay, arising mainly from a ^{3}CT exited state.[13] Nevertheless, in some cases, the charge transfer transition can be used to sensitize acetylide-based ligand localized triplet states.[14] Even more, solvent-induced triplet state inversion could be observed in a bipyridine Pt (II) complex presenting energetically proximate ^{3}CT and ^{3}IL excited states.[15] However, tetrathiafulvalene and derivatives can act as efficient luminescence quencher by electron-donating effect.[16]

UV−vis absorption spectra of exTTF intermediates **1**−**6** and complexes **C1** and **C2** recorded in dichloromethane ($C = 2 \times 10^{-5}$ M) are shown in Figure 1. The corresponding maxima and extinction coefficients are given in Supporting Information (SI) (Table S1). The organic intermediates present four absorption bands attributed to $\pi-\pi^*$ transitions. Whereas no significant shift is observed upon deprotection of the TMS protecting groups, the increasing size of the π-system from the mono- (**1**, **2**) to the

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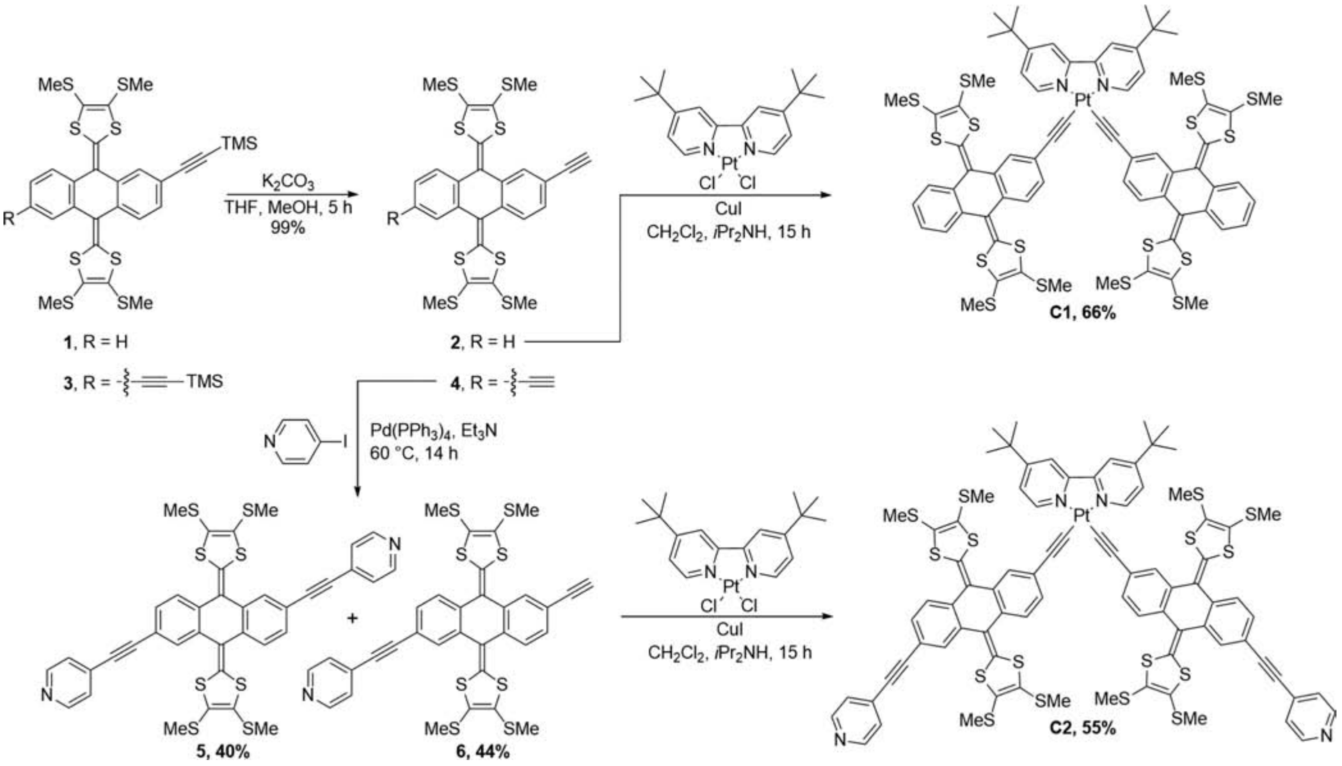
Scheme 1. Synthesis of Complexes C1 and C2



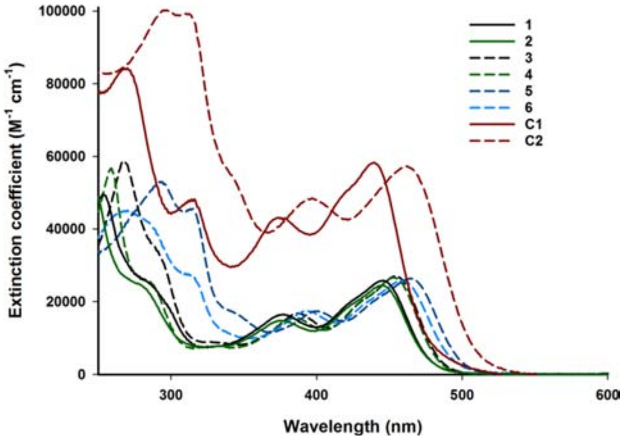


Figure 1. UV−vis absorption spectra of compounds **1**−**6** and complexes **C1** and **C2** recorded at room temperature in dichloromethane ($C = 2 \times 10^{-5}$ M).

corresponding bis-ethynyl derivatives (**3**, **4**) is accompanied by ca. 13 nm red-shifts. Grafting electron-withdrawing pyridine subunits in **5** and **6** leads to a similar effect for the lower energy bands with a redshift of ca. 12 nm compared to compounds **2** and **4**.[17] One should note that the presence of the peripheral ethynyl fragments leads to a red-shift of the lowest energy transition ranging from 9 nm (compound **1**) to 30 nm (compound **6**) when compared to the corresponding naked exTTF (435 nm, CH_2Cl_2).[18] This effect is not as important as for other linearly conjugated systems, most likely because of the nonplanar shape of the exTTF core in the neutral state.[19] As expected, the extinction coefficients are similar for all compounds. UV−vis absorption spectra of complexes **C1** and **C2** are close in terms of shape to those of **2** and **6**, respectively. The low energy transitions are not shifted after coordination to the platinum and their molar extinction coefficients correspond to the contributions of both exTTF donors **4** and **6** superimposed to slight CT contributions typical of acetylide diimine platinum complexes.[13a] Finally, the intense high energy transitions below 360 nm are attributed to the superimposition of intraligand $\pi-\pi^*$ localized on the tBu$_2$bpy and the ethynyl-exTTF fragments.

Upon excitation of complexes **C1** and **C2** in the CT region, no luminescence in the visible or near-IR region could be detected at room temperature under degassed conditions, although it is usually observed with platinum(II) diimine diethynyl complexes.[13a] This suggests that the lowest excited state could be exTTF centered, as previously reported with other classes of ligands,[14] or that a photoinduced electron transfer occurs from the exTTF moieties toward the CT excited state. Such a behavior has already been reported with similar platinum complexes bearing TTF[20] or phenothiazine donors.[21]

The electrochemical properties of precursors **1**−**6** and complexes **C1** and **C2** were studied by cyclic voltammetry (CV) in CH_2Cl_2/CH_3CN (3/1) mixtures (Figure 2). The resulting data are compiled in Table S1 (SI). Compounds **1**−**6** all exhibit the characteristic electrochemical exTTF behavior, with one pseudo-reversible two-electron process ranging from E^{ox} = +0.05 to +0.14 V vs Fc/Fc$^+$ depending on their substitution. Interestingly, mono- and bis-functionalized exTTF present the same oxidation potential, which therefore only depends on the nature of the substituent. In most cases, metal coordination leads to a loss of electron density on the anchored redox units and provokes an anodic shift of the oxidation wave.[22] In contrast, complexes **C1** and **C2** present exTTF-centered oxidation potentials shifted by ca. 50 mV toward lower potentials in comparison to alkyne derivatives **2** and **6**. Such a cathodic shift was already observed for acetylide TTF platinum(II) complexes[20] and reveals the electron-donating nature of the platinum acetylide complex. It is worth noting that both exTTF units of **C1** or **C2** do not seem to

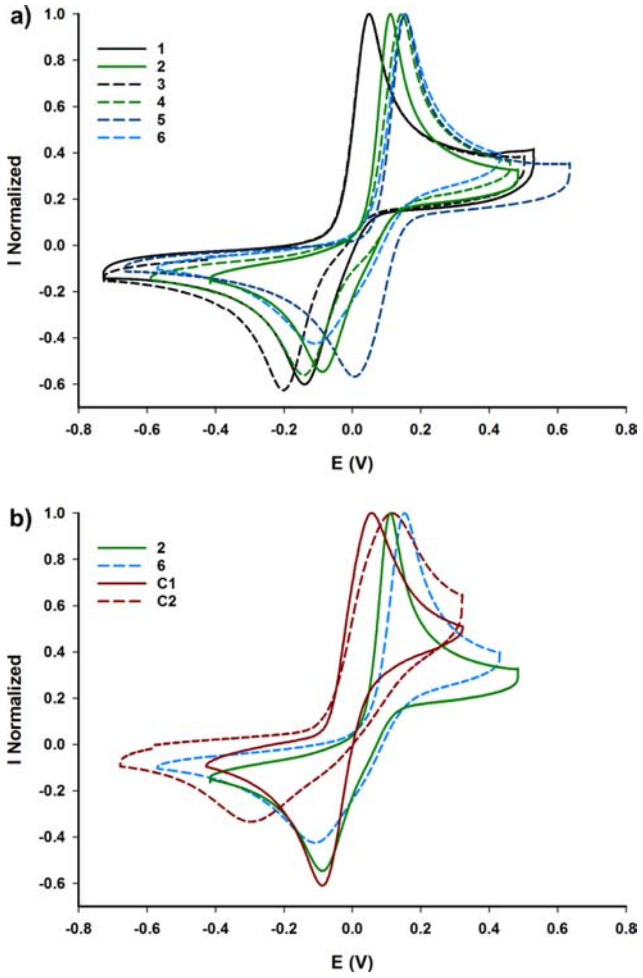


Figure 2. Normalized cyclic voltammogram of compounds **1**−**6** (a) and of complexes **C1** and **C2** (b); $C = 5 \times 10^{-4}$ M, CH_2Cl_2/CH_3CN (3/1), 0.1 M $n\mathrm{Bu_4NPF_6}$, 100 mV.s^{-1}, GC, V vs Fc/Fc$^+$.

interact from these CV studies, suggesting a four-electron process in each case.

Single crystals of complex **C1** were obtained by slow diffusion of MeOH in a CH_2Cl_2 solution, and the molecular structure was determined by X-ray diffraction analysis (Figure 3 and SI). In the solid state, the exTTF moieties exhibit the characteristic butterfly shape,[6d] with a slight distortion from planarity of the central anthraquinoidic platform. The bond lengths and the angles around the platinum atoms are similar to those usually observed for bis-acetylide Ptbpy complexes (Table S2, SI), within particular C−Pt−C angles close to 90°.[20] Importantly, the distance between the two exTTF fragments (measured between both quinoidic ring centers) is 12.2 Å, which suggests complex **C1** (and by extension **C2**) could host a fullerene guest.

The binding abilities of complexes **C1** and **C2** were evaluated for fullerene C_{60} by UV−vis titration. The spectral changes observed at $\lambda_{max} = 439$ nm (**C1**) and 462 nm (**C2**) ($C = 10^{-5}$ M in PhCl) were monitored upon addition of aliquots of C_{60} ($C = 5 \times 10^{-3}$ M in PhCl) and working at constant host concentration.[9] The corresponding Job plots (Figure 4) show the formation of 1:1 host−guest complexes. From these results, binding constants of $K_a = 250 \pm 42$ and 650 ± 60 were calculated for **C1** and **C2**, respectively (SI), illustrating the ability of these tweezers to bind the electron-deficient C_{60} in the competitive chlorobenzene solvent. It is worth noting that complex **C2**, which exhibits a

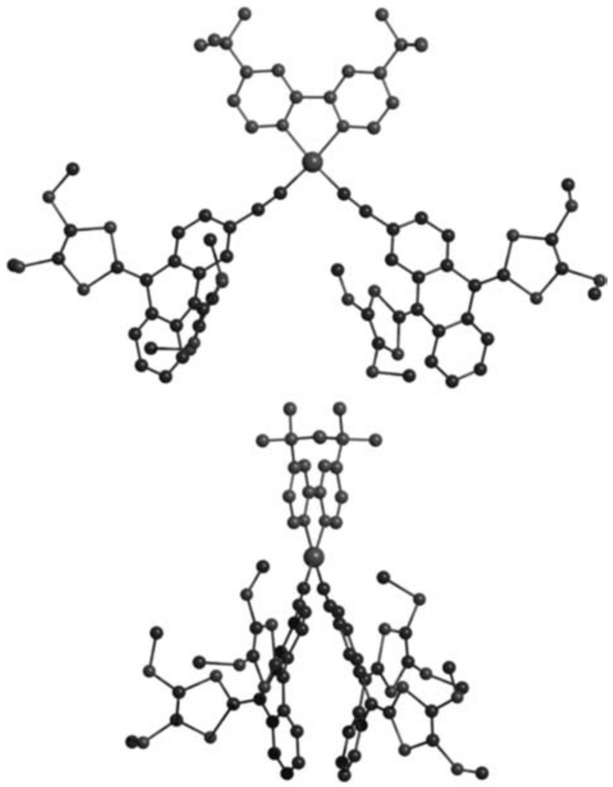


Figure 3. X-ray crystal structure of complex **C1**.

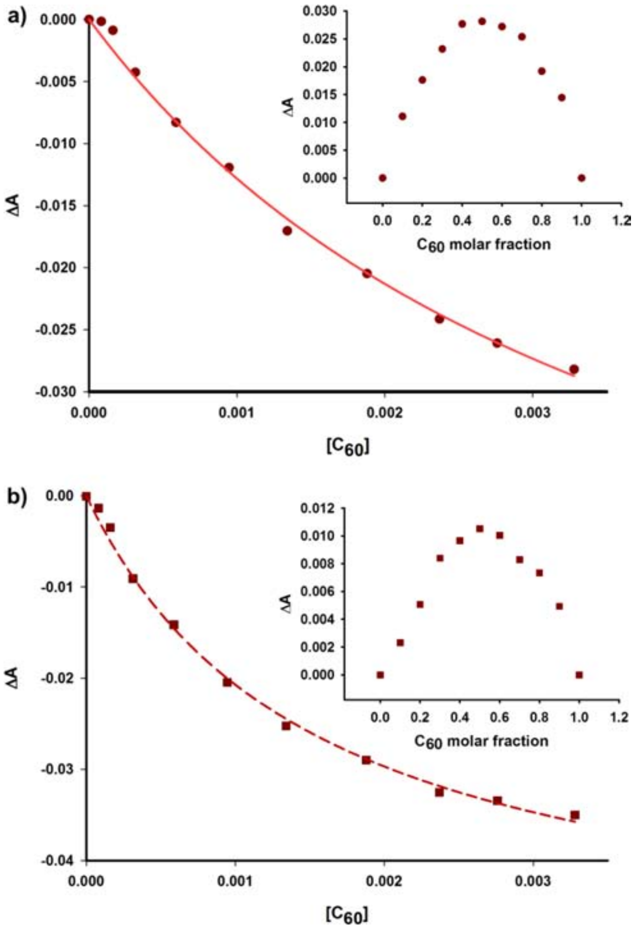


Figure 4. Plots of absorbance at 439 nm (**C1**) (a) and 462 nm (**C2**) (b); $C = 10^{-5}$ M in PhCl; addition of C_{60} ($C = 5 \times 10^{-3}$ M in PhCl). Inset: Job plot analyses at the same wavelength confirming the 1:1 stoichiometry.

lower electron-donating character as evaluated by CV measurements, presents a stronger interaction with the guest under consideration. This behavior is attributed to the larger interaction surface between both species in the case of **C2**, due to the presence of the 4-ethynylpyridine fragment. Importantly, this also confirms the prominent contribution of dispersive-type forces (which increase with size extension as in **C2** relatively to **C1**) over charge-transfer interactions.[1b]

In summary, two molecular tweezers **C1** and **C2**, which encompass two electron-rich extended tetrathiafulvalene (exTTF) units, were synthesized and fully characterized. They are prepared in a straightforward way by formation of *bis*-acetylide platinum(II) complexes. Their binding ability toward fullerene C_{60} is mainly governed by a suitable concave/convex shape complementarity.[1b] This host−guest interaction could be confirmed by UV−vis titrations, both tweezers being able to bind the complementary fullerene guest in a 1:1 stoichiometry (Job plots) with high binding constants in PhCl (K_a = 250 and 650, respectively). Given the simplicity and the efficiency of the metal-driven assembly approach, efforts are currently underway in our laboratory to extend the scope of this approach toward new families of molecular tweezers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02915.

> Detailed synthesis protocols, experimental methods, X-ray diffraction studies, and additional spectroscopic data for compounds **1−6** and complexes **C1** and **C2** (PDF)
> Complex **C1** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: marc.salle@univ-angers.fr.
*E-mail: sebastien.goeb@univ-angers.fr.

Notes

The authors declare no competing financial interest.

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