Supporting Information

A self-assembled bis(pyrrolo)TTF-based redox-active square

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1- Materials and methods

NMR spectra were recorded in deuterated solvents, at 500.13 MHz (^{1}H) and 125.75 MHz (^{13}C). Chemical shifts (δ are expressed in ppm and are related to the tetramethylsilane (TMS) signal.

Mass spectra (MALDI-TOF) were achieved on a Bruker Biflex-III TM spectrometer.

Concerning FT-ICR analyses, the experiments were performed on a hybrid Qh-FT/ICR (ApexQe, Bruker Daltonics, Billerica, MA, USA) equipped with an off-axisApollo II ESI source operated in the positive ion mode. The instrument is equipped with a 7 T actively shielded superconducting magnet. Sample solutions were infused directly into the mass spectrometer by a syringe pump at a flow rate of 2 µl/min suing acetone as solvent.

Cyclic voltammetry experiments were carried out on a potentiostat-galvanostat with solvents and electrolyte of electrochemical grades. CV experiments were carried out at 298K in a conventional three-electrode cell equipped with a Pt disk working electrode (diameter: 1mm), a Pt wire counter electrode, and a Ag, AgCl reference electrode.Unless otherwise noted, solvents and starting products were commercially available and used without further purification.
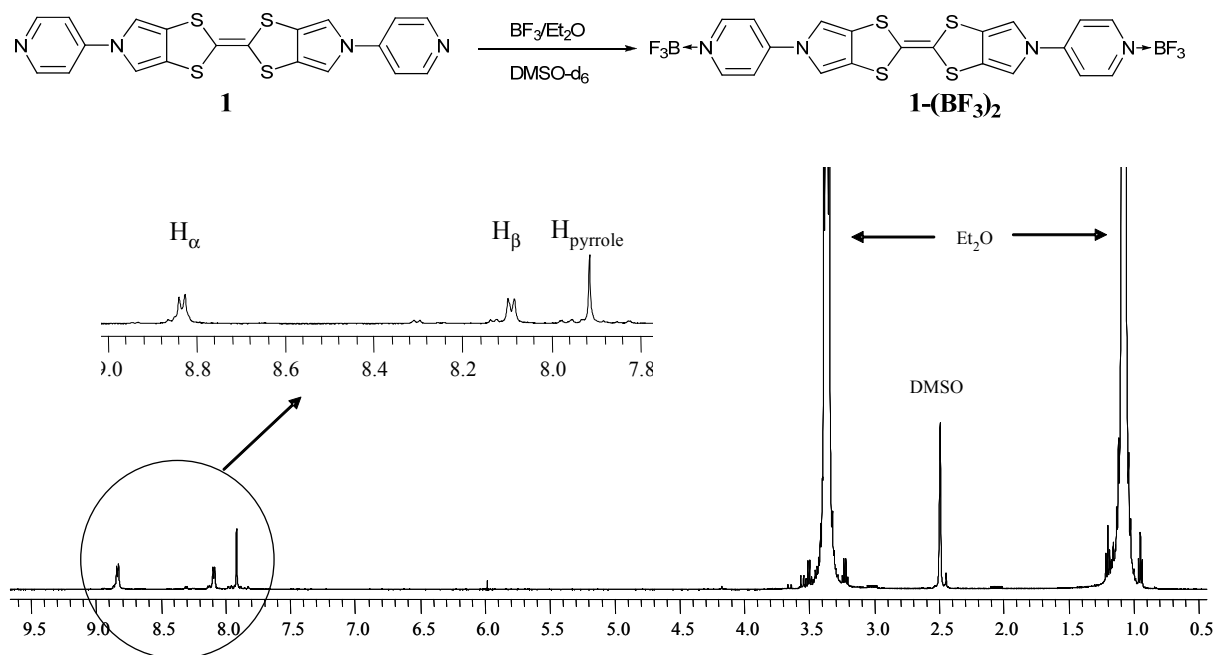
2- Figures

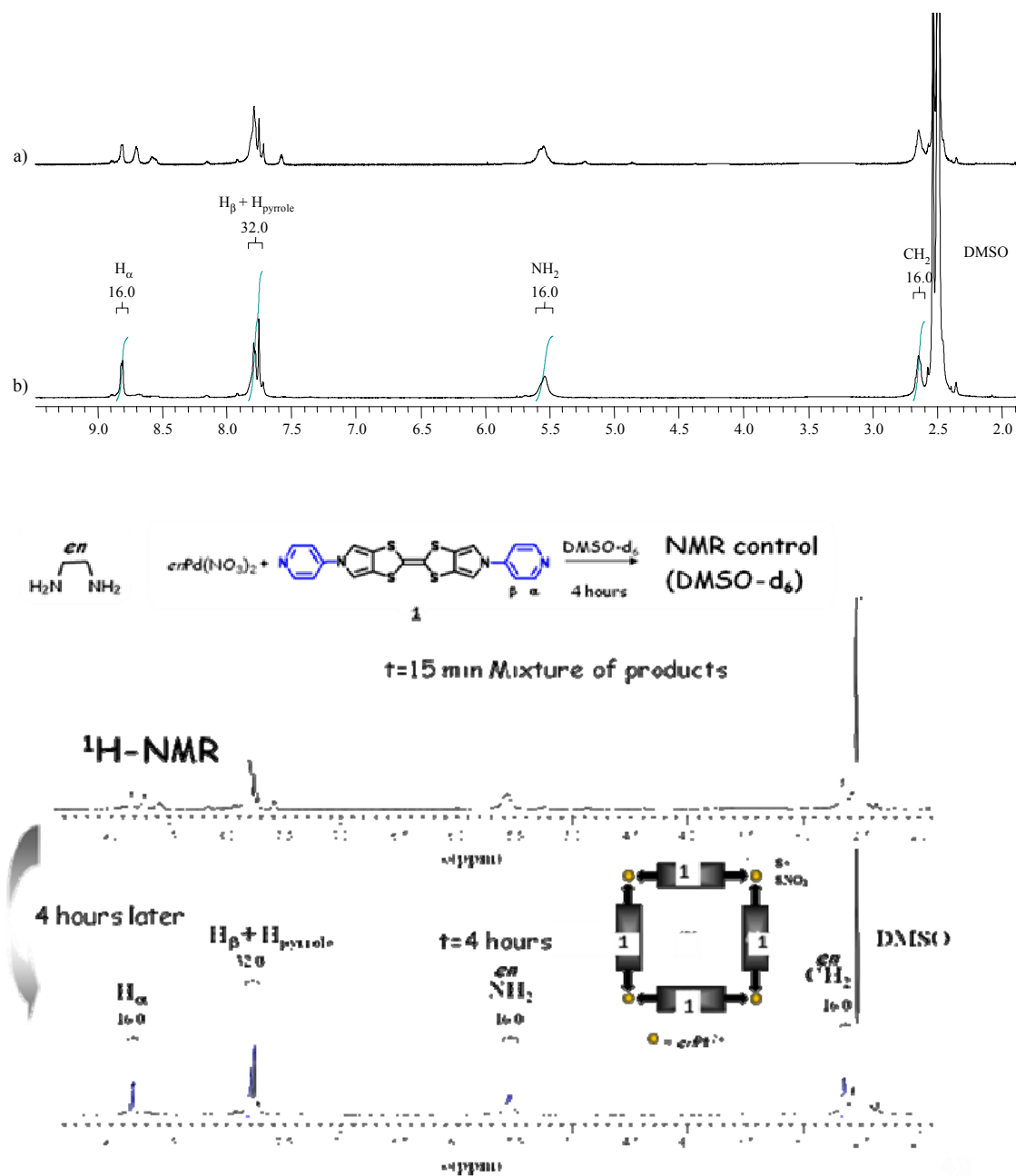**Figure S1** ^{1}H NMR spectrum of **1** in presence of BF$_3$/Et$_2$O (DMSO-d$_6$)

Figure S2 ^{1}H NMR of an equimolar mixture of **1** and *en*Pd(NO$_3$)$_2$ in DMSO-d$_6$: a) t = 15 min ; b) t = 4 hours.
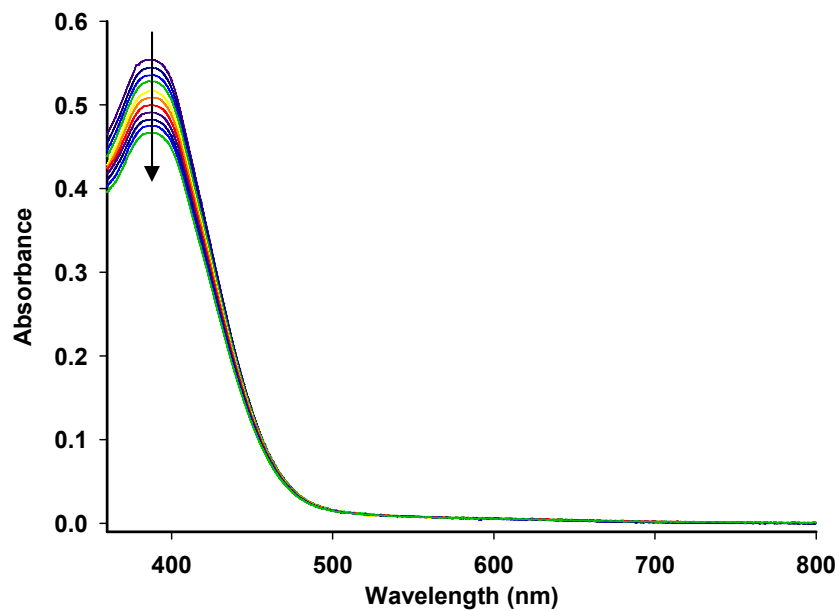
Fig. S3 Spectral changes in UV-vis titration experiment of **2** (8.0 x 10^{-6} M in CH_2Cl_2) *vs*. C_{60} (8.0 x 10^{-4} M in CS_2) (1-10 equiv) at room temperature. The absorption spectra of fullerene have been subtracted according ref 18d.
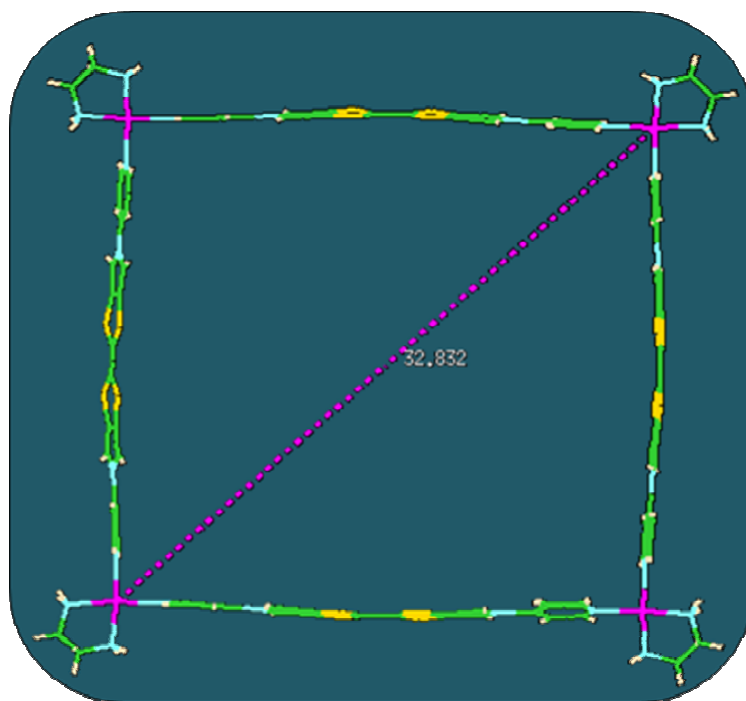
Figure S4 : Calculated structure of square obtained from mixing **1** and *en*Pd(NO$_3$)$_2$ (anions omitted).

A full optimization was carried out with Becke3Lyp Hybrid Functional using the package Gaussian03, leading to the correct geometry around the metal centers. The basis sets chosen for this optimization were LANL2DZ for the 8 metal centers of Pd, 6-31G* for S, C, O, N and 6-31G pour H.
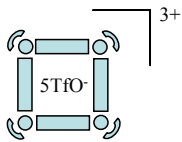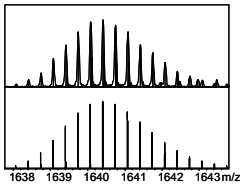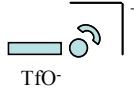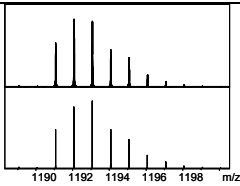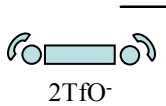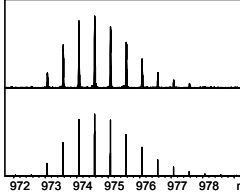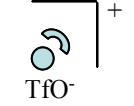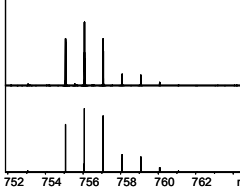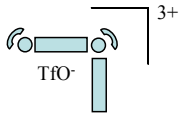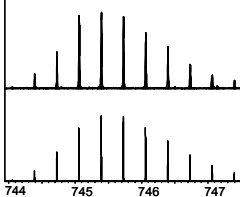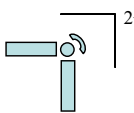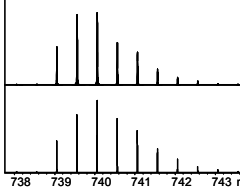
3- Tables

Table S1 NMR data for *dppp*Pt(OTf)$_2$ and **2** (acetone- d$_6$)

	H$_\alpha$ δ (ppm)	H$_\beta$ δ (ppm)	CH$_2$ δ (ppm)	CH$_2$P δ (ppm)	RMN-^{31}P δ (ppm)	RMN-^{19}F δ (ppm)
*dppp*Pt(OTf)$_2$	-	-	2.34	3.25	-11.4	-79.4
2	8.75	7.28	2.35	3.49	-13.4	-79.2

Table S2 : ESI-FT-ICR mass spectrum of **2** in acetone : isotope patterns

▭ (**1**), ⌇ (*dppp*), ○ (Pt)

Ion	*m/z*	$\left(\dfrac{\text{experimental}}{\text{théorique}}\right)$
$[(\mathbf{1}\text{-Pt}dppp)_4.5\text{OTf}]^{3+}$	1640	
$[\mathbf{1}\text{-Pt}dppp.\text{OTf}]^{+}$	1192	
$[(dppp\text{Pt})_2\mathbf{1}.2\text{OTf}]^{2+}$	974	
$[dppp\text{Pt}.\text{OTf}]^{+}$	756	
$[(\mathbf{1}\text{-Pt}dppp)_2.\text{OTf}]^{3+}$	745	
$[\mathbf{1}_2\text{Pt}dppp]^{2+}$	740	