Electronic Supplementary Information (ESI) †

Structural, Electrochemical and Spectroelectrochemical Study on the Geometric and Electronic Structures of [(corrolato)Au^{III}]^n (n = 0, +1, −1) Complexes

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Table S1 Crystallographic Data for **2**

molecular formula	C_{45} H_{27} Au N_6 O_2, C_6 H_6
Fw	958.83
Radiation	MoKα
crystal symmetry	Triclinic
space group	P-1
a(Å)	8.6926 (9)
b(Å)	15.5671 (16)
c(Å)	15.6537 (16)
a(deg)	106.257(3)
β(deg)	106.034(3)
γ(deg)	95.639(3)
V(Å^3)	1918.7(3)
Z	2
μ (mm^{-1})	3.887
T(K)	100 K
D_{calcd} (g cm^{-3})	1.660
2θ range (deg)	2.78 to 50.70
e data (R_{int})	6891 (0.0451)
R1 ($I>2\sigma(I)$)	0.0432
WR2	0.1195
GOF	0.995

Table S2 UV−vis. and electrochemical data

Compound	UV−vis. Data [a] λ_{max} / nm (ε / $M^{-1}cm^{-1}$)	Electrochemical data [a,b]	
		Oxidation E^0,V (ΔE_p, mV)	Reduction E^0,V (ΔE_p, mV)
1	422 (1,61,500) 494 (4,700) 530 (10,700) 574 (41,500)	0.39(70) 0.72(80)	-1.81(80) -2.17(80)
2	423 (1,42,200) 494 (3,700) 533 (9,300) 572 (37,000)	0.42(70) 0.79(80)	-1.78(80) -2.13(80)

[a]In dichloromethane / 0.1 M TBAP.

[b]Thepotentials are vs.Fc/Fc^+.

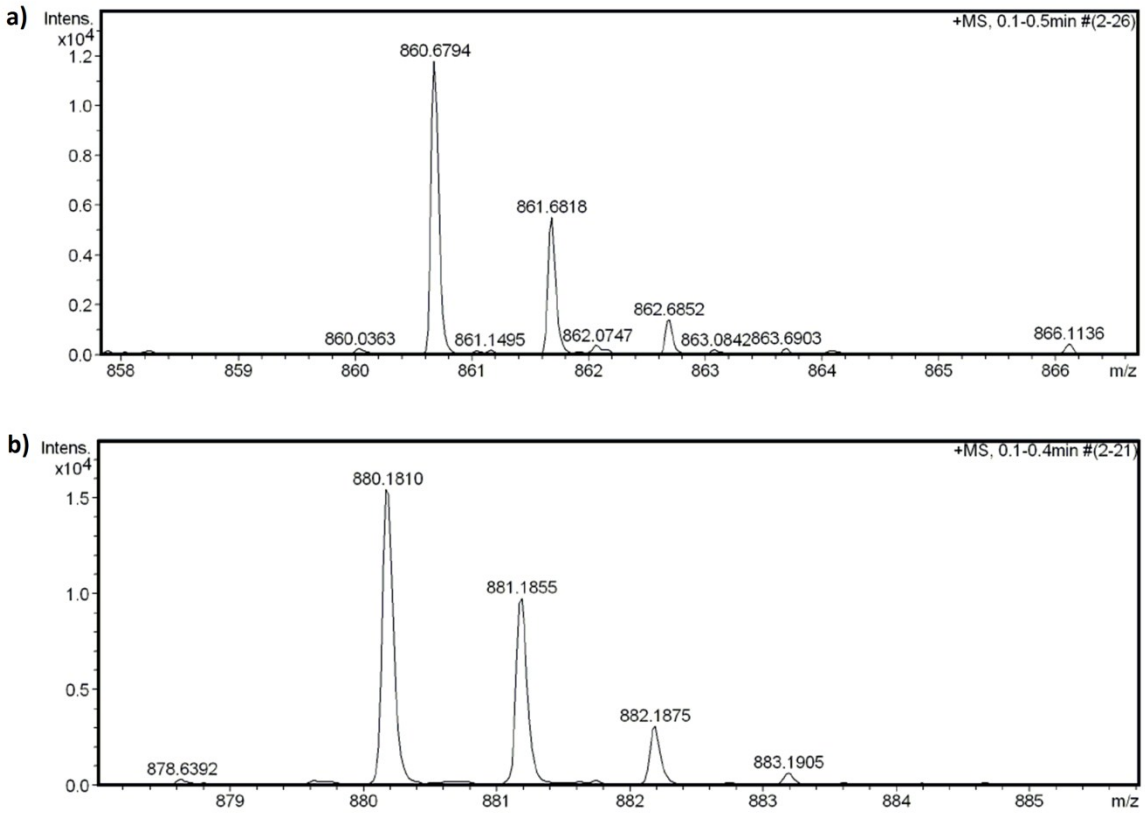

Fig. S1 ESI-MSspectrum of (a) 10-(2,4,5-trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-Au(III), **1**, and (b) 10-(4,7-dimethoxynaphthalen-1-yl)-5,15-bis(4-cyanophenyl) corrolato-Au(III), **2** inCH_3CN shows the measured spectrum with isotopic distribution pattern.

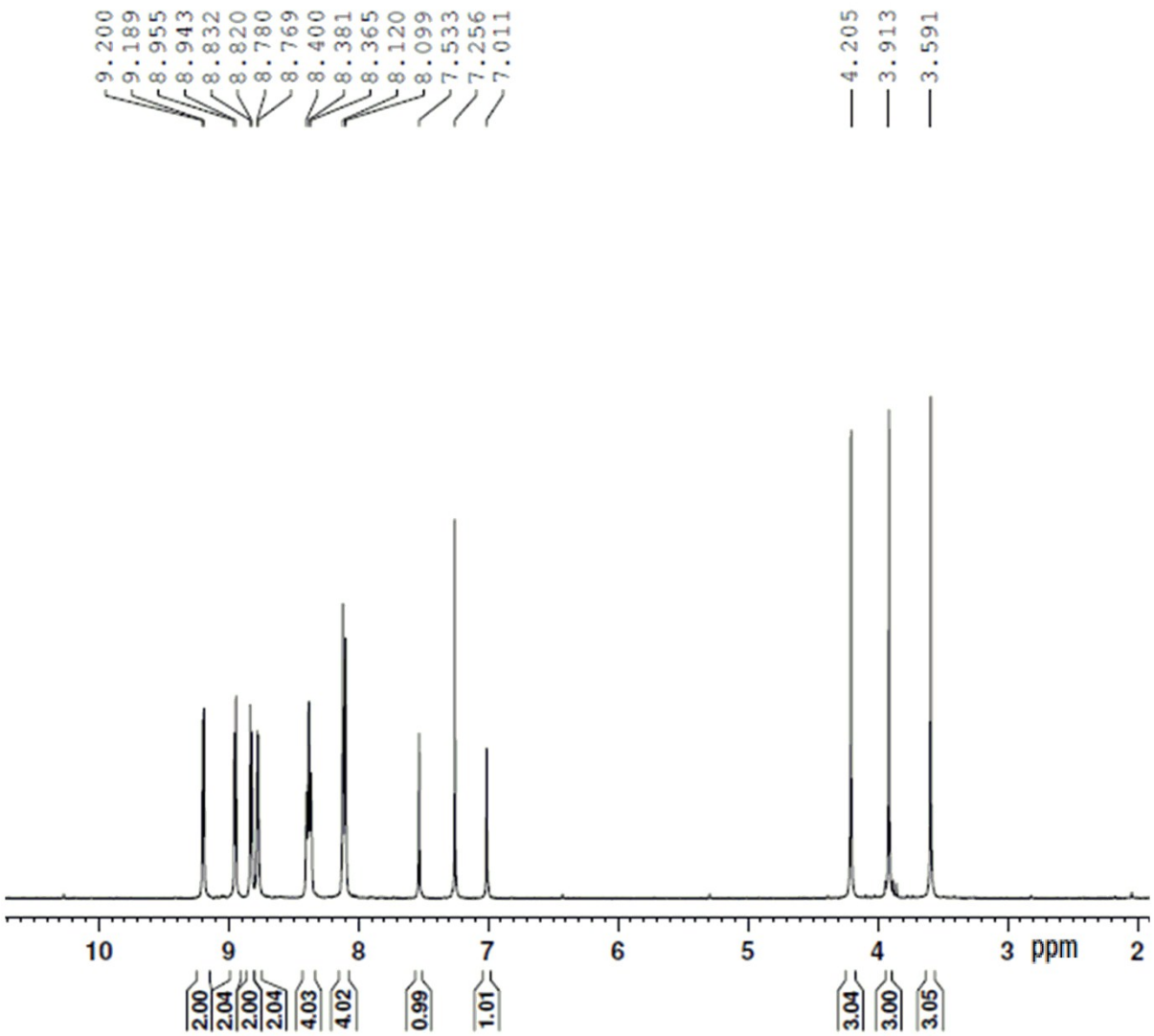

Fig. S2 ^{1}H NMR spectrum of 10-(2,4,5-Trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato- Au(III), **1** in$CDCl_3$.

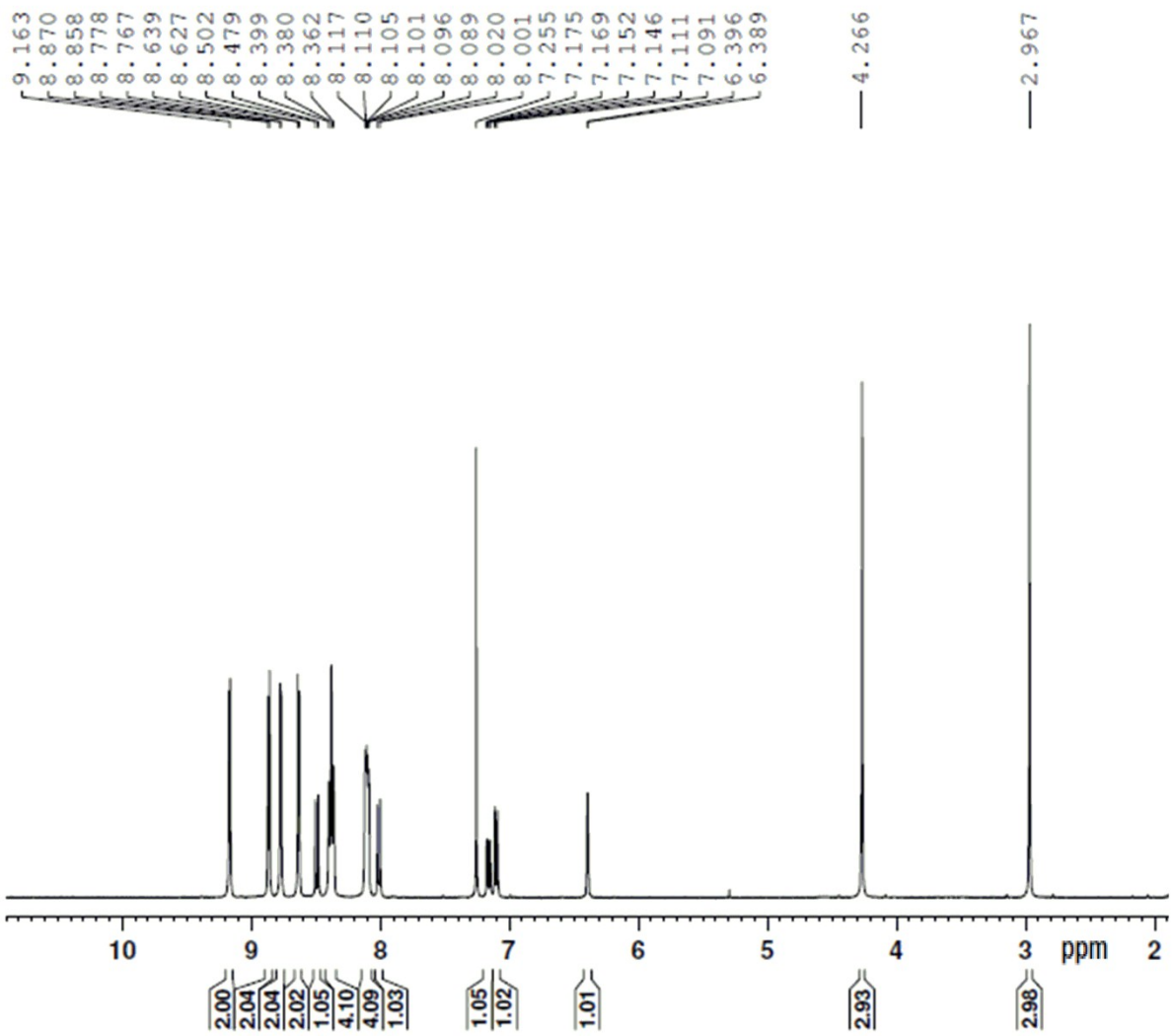

Fig. S3 ^{1}H NMR spectrum of 10-(4,7-dimethoxynaphthalen-1-yl)-5,15-bis(4-cyanophenyl) corrolato- Au(III), **2** in $CDCl_3$.

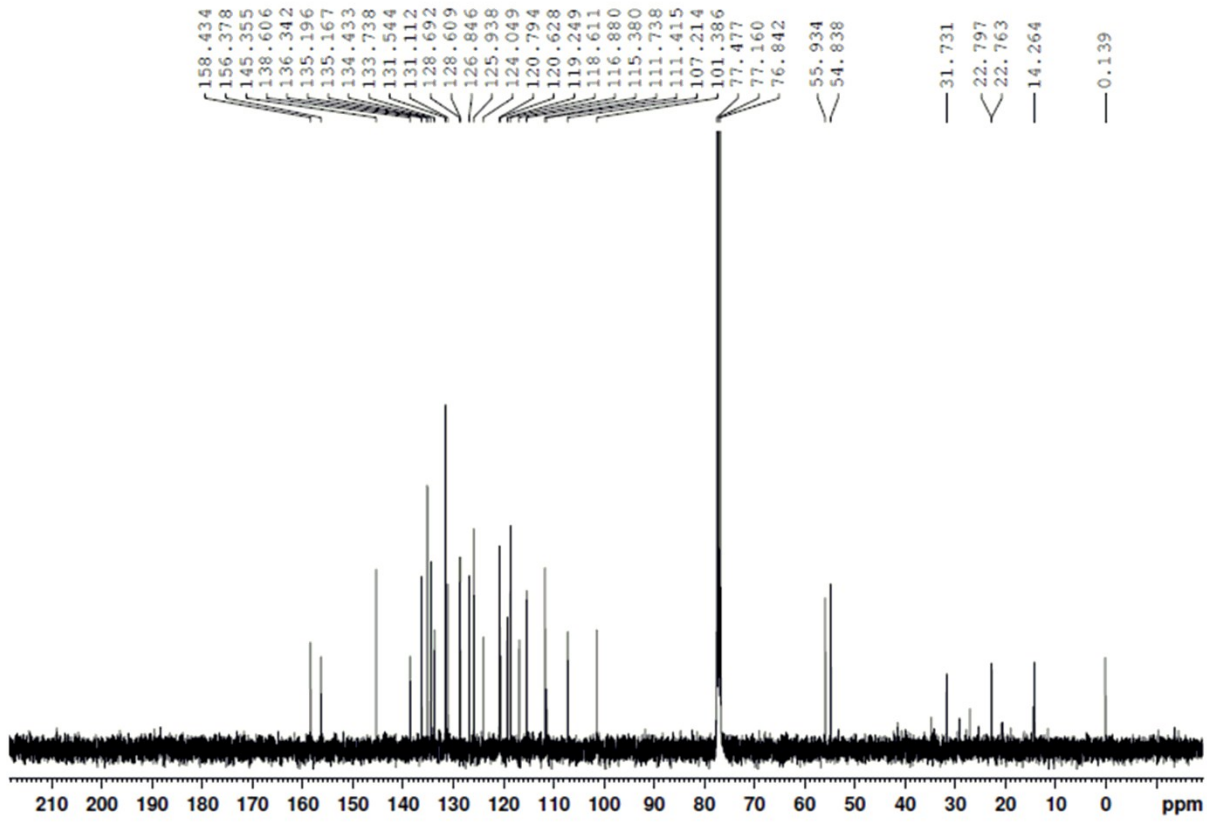

Fig. S4 ^{13}C NMR spectrum of 10-(4,7-dimethoxynaphthalen-1-yl)-5,15-bis(4-cyanophenyl)corrolato-Au(III), **2** in $CDCl_3$.

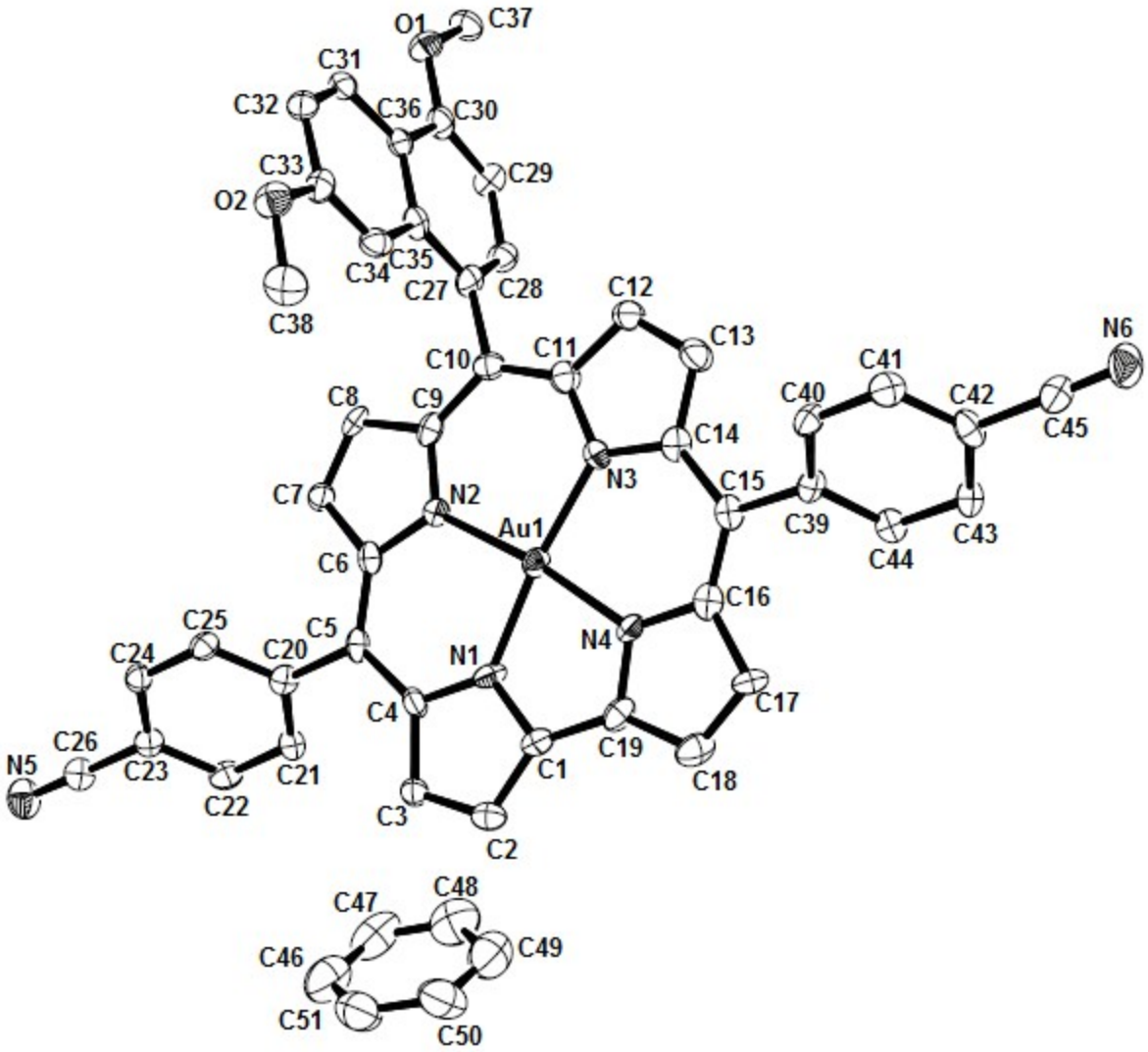

Fig. S5 ORTEP diagram of **2**. Ellipsoids are drawn at 50% probability.

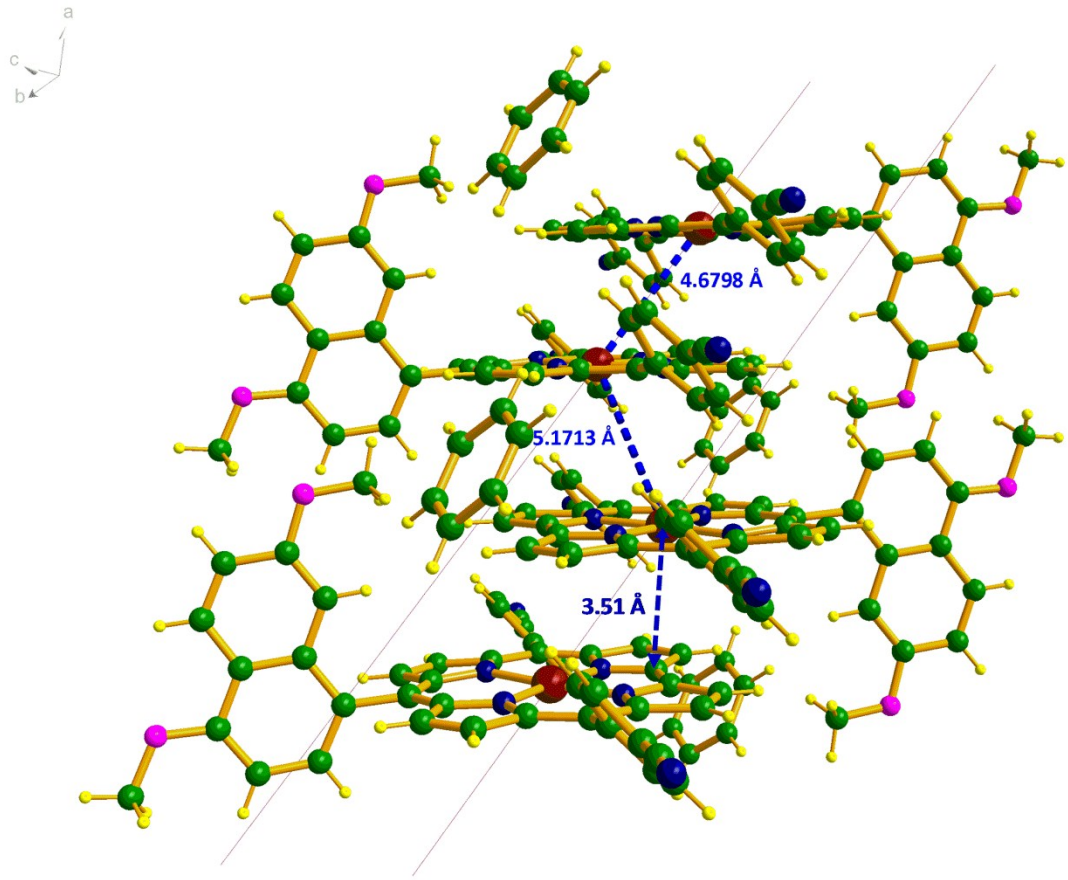

Fig. S6 Orientation of gold atoms in the single-crystal X-ray structure of **2**.

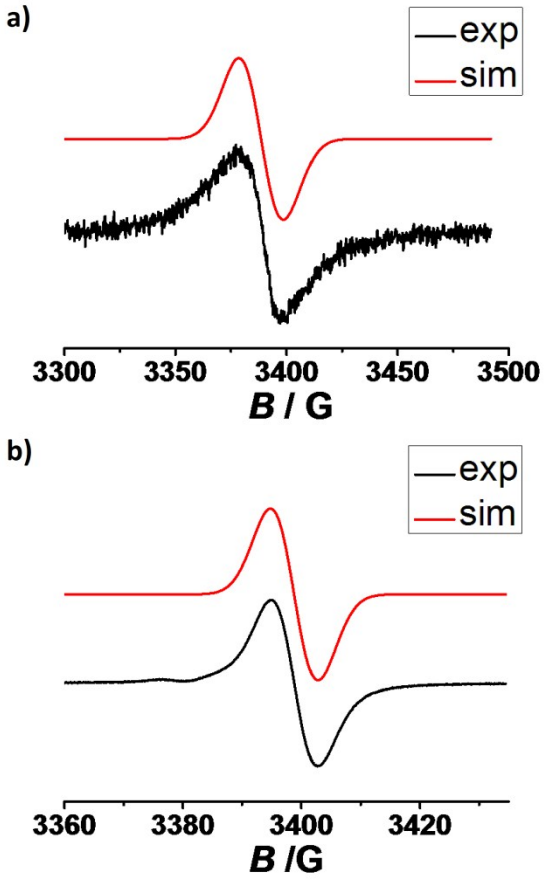

Fig. S7 X-band EPR spectrum of a) $(\mathbf{2})^{\bullet+}$ with simulation and b) $(\mathbf{2})^{\bullet-}$ generated by *in-situ* electrolysis at 295 K in CH_2Cl_2/0.1 M Bu_4NPF_6.

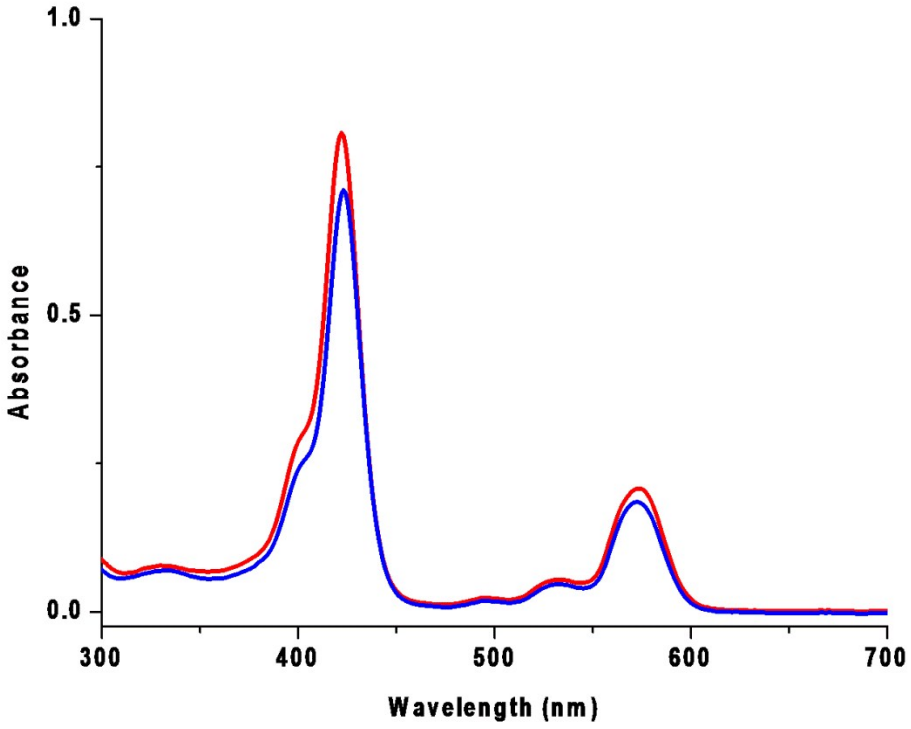

Fig. S8 Electronic absorption spectrum of 10-(2,4,5-trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-Au(III), **1**, (red line) and 10-(4,7-dimethoxynaphthalen-1-yl)-5,15-bis(4-cyanophenyl)corrolato-Au(III), **2**, (blue line)in CH_2Cl_2. (Color online.)

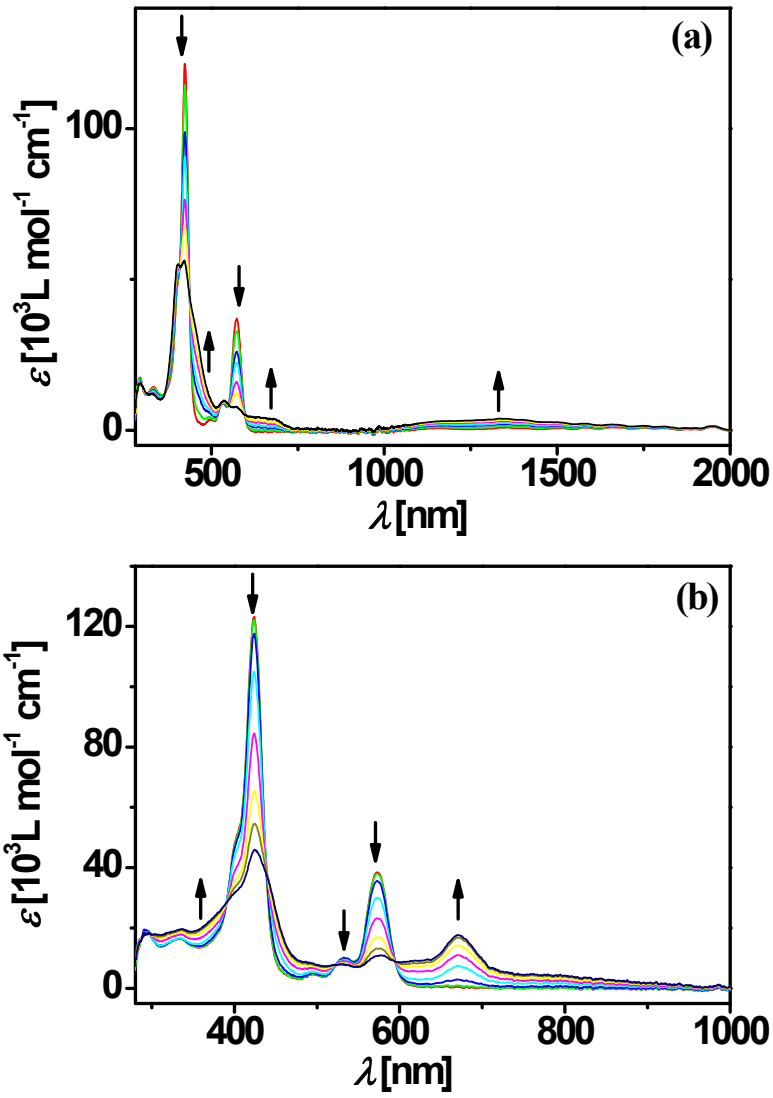

Fig. S9 Change in the UV-Vis spectrum of **2** during a) first oxidation and b) first reduction. Result from OTTLE spectroelectrochemistry in CH_2Cl_2 /0.1 M Bu_4NPF_6.

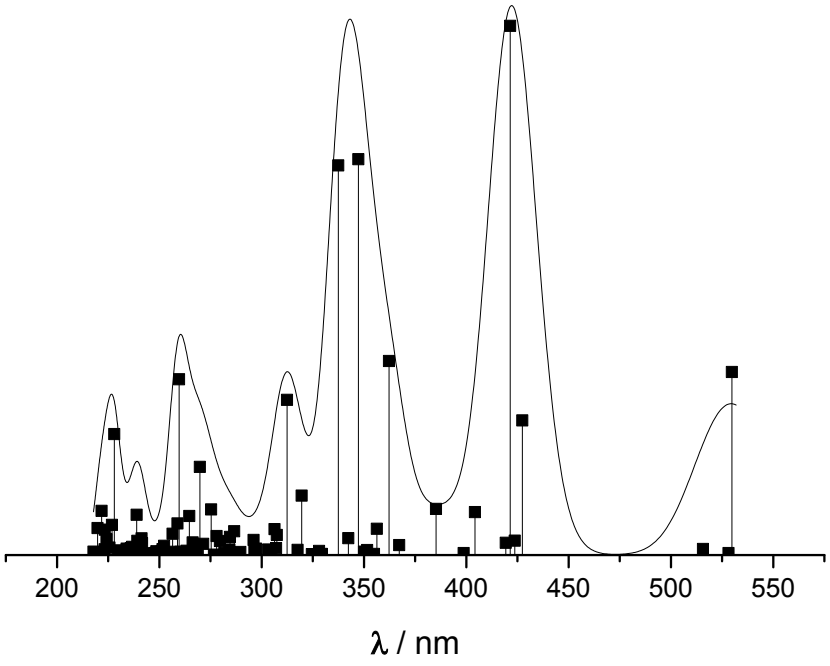

Fig. S10 The calculated absorption spectra for **1**, showing the TD-DFTcalculated electronic transitions.

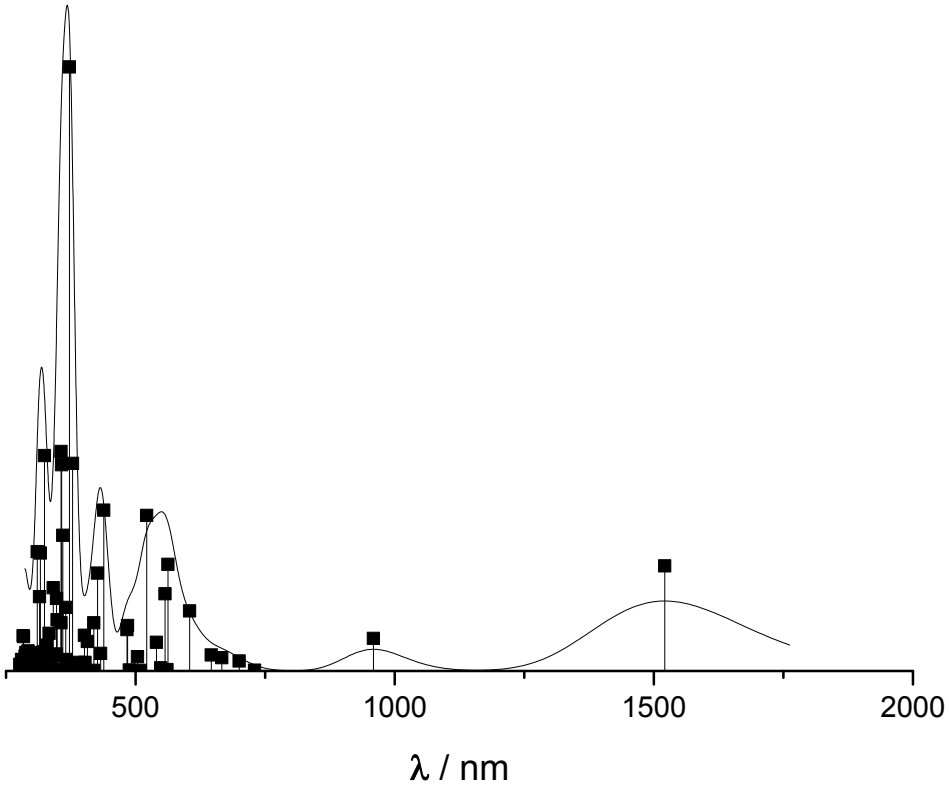

Fig. S11 The calculated absorption spectra for $\mathbf{1}^{+}$, showing the TD-DFTcalculated electronic transitions.

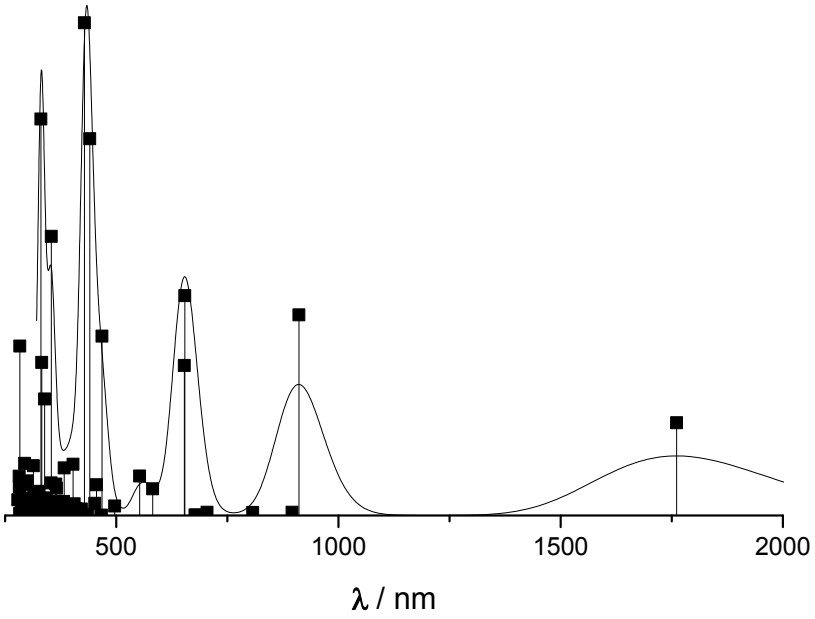

Fig. S12 The calculated absorption spectra for **1**$^{-}$, showing the TD-DFTcalculated electronic transitions.

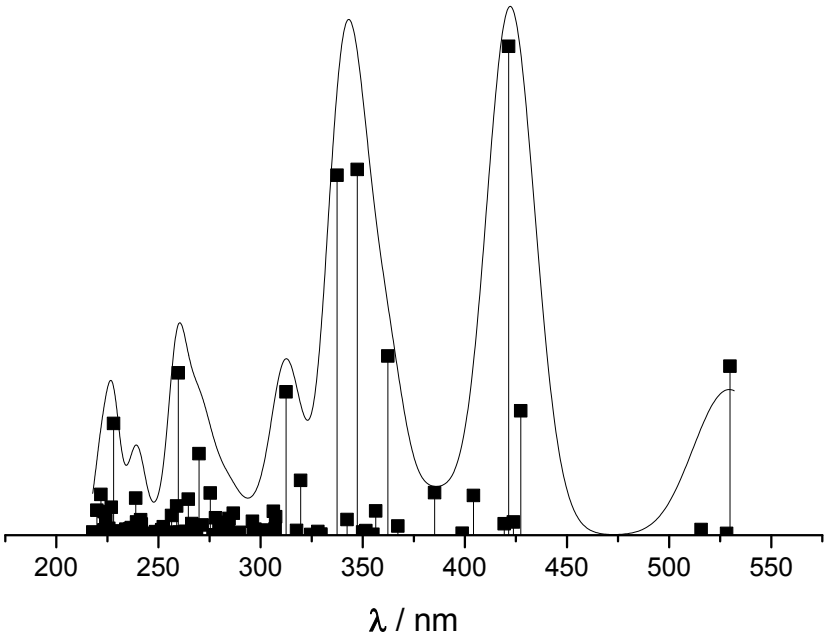

Fig. S13 The calculated absorption spectra for **2**, showing the TD-DFTcalculated electronic transitions.

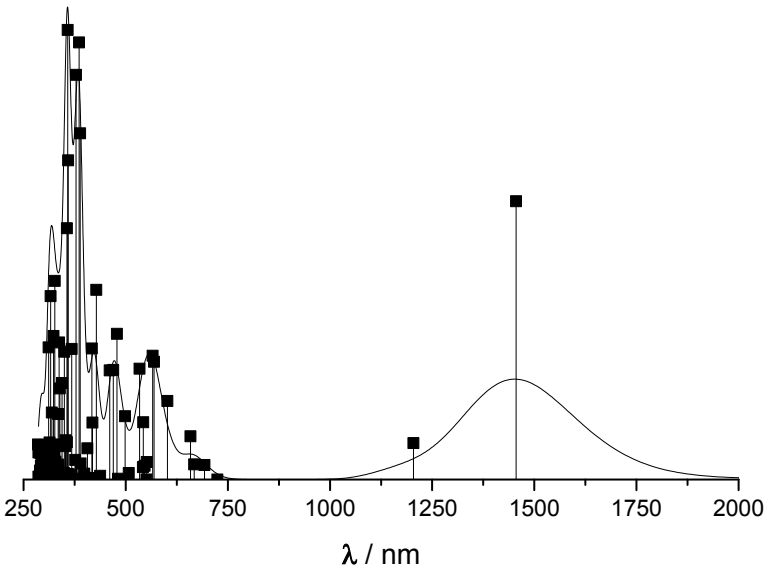

Fig. S14 The calculated absorption spectra for $\mathbf{2}^{+}$, showing the TD-DFTcalculated electronic transitions.

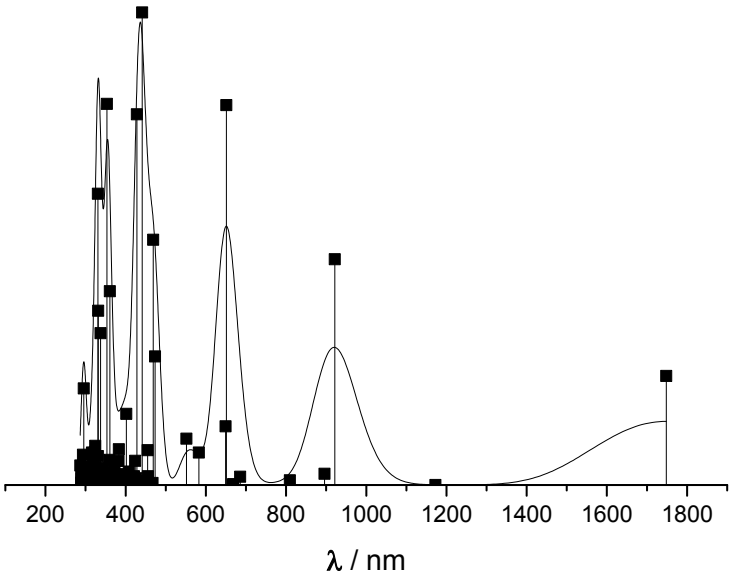

Fig. S15 The calculated absorption spectra for $\mathbf{2}^{-}$, showing the TD-DFTcalculated electronic transitions.