SUPPLEMENTARY MATERIAL

Syntheses, characterizations, crystal structures and applications as sensitizers in solar cells of novel heteroleptic Cu(I) complexes containing nitrile-substituted 2,2´-bipyridyl ligands

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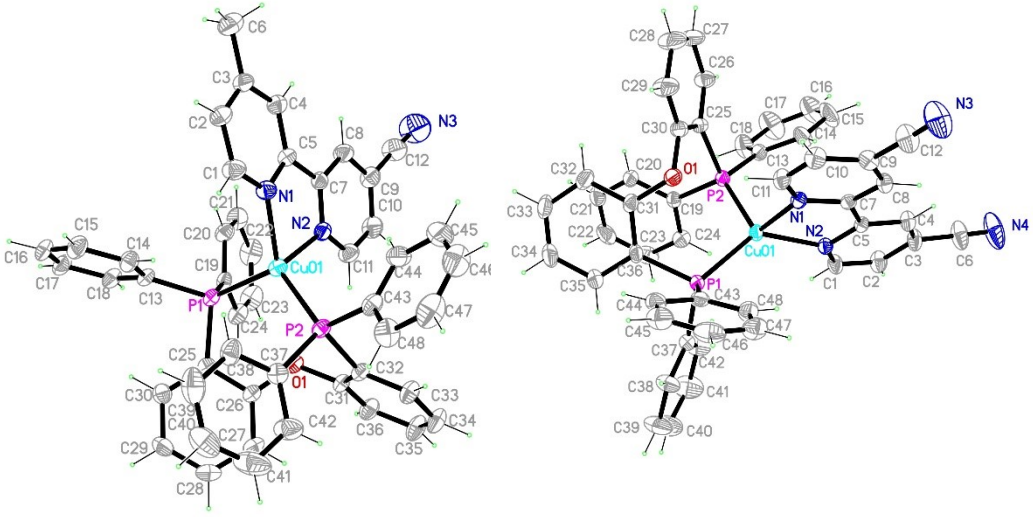

Figure S1. ORTEP representation of (**1**) (Left) and (**2**) (Right) showing the numbering scheme used and displacement ellipsoids drawn at the 50% probability level.

Table S1.- Crystal data and structure refinement at 298 K for (**1**) and (**2**).

Variable /Complex	**(1)**		**(2)**	
Empirical formula	$C_{52}H_{47}CuF_6N_3O_2P_3$		$C_{52}H_{44}CuF_6N_4O_2P_3$	
Formula weight	1016.37		1027.36	
Crystal system	Triclinic		Monoclinic	
Space group, Z	P-1, 2		P 21/c, 4	
Unit cell dimensions **a, b, c (Å)** **α, β, γ (°)**	a = 10.9709(4) b =12.4043(5) c = 19.8431(8)	α= 106.020(2) β= 96.377(2) γ = 105.536(2)	a = 20.2471(8) b = 12.9760(5) c = 18.7049(7)	α= 90° β= 92.1830(10) γ = 90°
Cell volume (Å^3)	2450.27(17)		4910.7(3)	
Density (calcd., mg/m^3)	1.378		1.390	
Absorption coef. (mm^{-1})	0.610		0.610	
F(000)	1048		2112	
Crystal size (mm^3)	0.400 x 0.100 x 0.050		0.700 x 0.300 x 0.080	
θ range for data collection (°)	1.780 to 26.405		1.864 to 26.377	
Reflections collected	126281		147602	
Independent reflections	10041 [R(int) = 0.1264]		10046 [R(int) = 0.1018]	
Refinement method	Full-matrix least-squares on F^2			

Data / restraints / parameters	10041 / 4 / 605	10046 / 4 / 613
Goodness-of-fit on F^2	1.154	1.177
Final R indices [I >2sigma(I)]	R1 = 0.0882, wR^2 = 0.2077	R1 = 0.0632, wR^2 = 0.1455
R indices (all data)	R1 = 0.1261, wR^2 = 0.2343	R1 = 0.0932, wR^2 = 0.1686
CCDC deposition number:	2287810	2287809

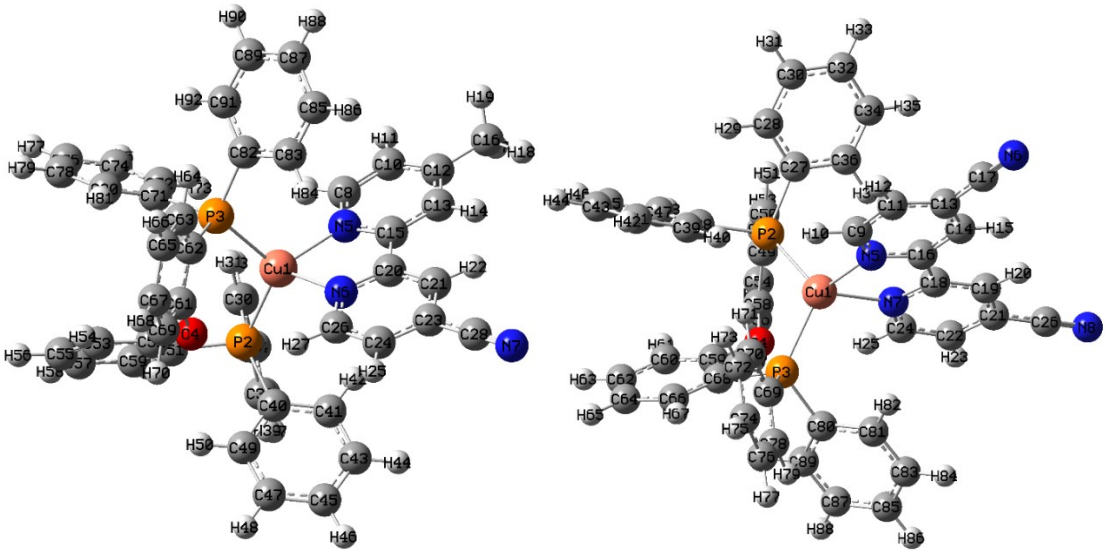

Figure S2.- Optimized structures and labels for (**1**, **left**) and (**2**, **right**) with B3LYP/6-311G(d,p) in CH_2Cl_2.

Table S2. Geometric description for hydrogen bond interactions for (**1**) and (**2**). [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Complex (1)				
C(52)-H(52C)...N(3)#1	0.96	2.49	3.42(2)	163.0
C(46)-H(46)….N(3)#2	0.93	2.75	3.432(15)	131.05
Complex (2)				
C(14)-H(14)….N(4)#3	0.93	2.75	3.467(15)	135.55
C(1)-H(1)...F(1)#4	0.93	2.60	3.506(6)	165.9
C(2)-H(2)...F(4)#4	0.93	2.52	3.207(6)	131.0
C(11)-H(11)...O(1)	0.93	2.45	3.175(5)	134.8
C(24)-H(24)...F(3)#4	0.93	2.64	3.366(6)	135.6
C(48)-H(48)...F(5)	0.93	2.39	3.075(6)	130.5

Symmetry transformations used to generate equivalent atoms:
#1 1–x, 2-y, 2-z
#2 x,1+y, z
#3 1-x,-1/2+y, 1/2 +z
#4 x,-y+1/2,z-1/2

Table S3. Torsion angles [°] for (**1**).

C(5)-N(1)-C(1)-C(2)	1.2(10)
Cu(01)-N(1)-C(1)-C(2)	-167.8(5)
N(1)-C(1)-C(2)-C(3)	-1.6(11)
C(1)-C(2)-C(3)-C(4)	0.7(10)
C(1)-C(2)-C(3)-C(6)	178.7(7)
C(2)-C(3)-C(4)-C(5)	0.6(9)
C(6)-C(3)-C(4)-C(5)	-177.5(6)
C(1)-N(1)-C(5)-C(4)	0.2(9)
Cu(01)-N(1)-C(5)-C(4)	170.7(4)
C(1)-N(1)-C(5)-C(7)	-179.0(5)
Cu(01)-N(1)-C(5)-C(7)	-8.5(6)
C(3)-C(4)-C(5)-N(1)	-1.1(9)
C(3)-C(4)-C(5)-C(7)	178.1(6)
C(11)-N(2)-C(7)-C(8)	-1.6(8)
Cu(01)-N(2)-C(7)-C(8)	-176.7(5)
C(11)-N(2)-C(7)-C(5)	177.3(5)
Cu(01)-N(2)-C(7)-C(5)	2.2(6)
N(1)-C(5)-C(7)-N(2)	4.2(7)
C(4)-C(5)-C(7)-N(2)	-175.0(5)
N(1)-C(5)-C(7)-C(8)	-176.9(6)
C(4)-C(5)-C(7)-C(8)	3.9(9)
N(2)-C(7)-C(8)-C(9)	-0.4(9)
C(5)-C(7)-C(8)-C(9)	-179.2(6)
C(7)-C(8)-C(9)-C(10)	1.7(10)
C(7)-C(8)-C(9)-C(12)	-177.9(7)
C(8)-C(9)-C(10)-C(11)	-1.0(11)
C(12)-C(9)-C(10)-C(11)	178.5(7)
C(7)-N(2)-C(11)-C(10)	2.3(9)
Cu(01)-N(2)-C(11)-C(10)	176.6(5)
C(9)-C(10)-C(11)-N(2)	-1.0(11)
C(25)-P(1)-C(13)-C(18)	-77.8(5)
C(19)-P(1)-C(13)-C(18)	32.4(6)
Cu(01)-P(1)-C(13)-C(18)	154.8(4)
C(25)-P(1)-C(13)-C(14)	99.7(5)
C(19)-P(1)-C(13)-C(14)	-150.1(5)
Cu(01)-P(1)-C(13)-C(14)	-27.8(5)
C(18)-C(13)-C(14)-C(15)	0.4(9)
P(1)-C(13)-C(14)-C(15)	-177.1(5)
C(13)-C(14)-C(15)-C(16)	0.8(10)
C(14)-C(15)-C(16)-C(17)	-1.4(11)
C(15)-C(16)-C(17)-C(18)	0.8(11)
C(14)-C(13)-C(18)-C(17)	-1.0(9)
P(1)-C(13)-C(18)-C(17)	176.5(5)
C(16)-C(17)-C(18)-C(13)	0.4(10)
C(25)-P(1)-C(19)-C(20)	174.1(4)
C(13)-P(1)-C(19)-C(20)	65.8(5)
Cu(01)-P(1)-C(19)-C(20)	-65.2(5)
C(25)-P(1)-C(19)-C(24)	-13.7(6)
C(13)-P(1)-C(19)-C(24)	-122.0(5)
Cu(01)-P(1)-C(19)-C(24)	107.0(5)
C(24)-C(19)-C(20)-C(21)	1.8(9)
P(1)-C(19)-C(20)-C(21)	174.4(5)

C(19)-C(20)-C(21)-C(22)	-2.6(10)
C(20)-C(21)-C(22)-C(23)	1.4(12)
C(21)-C(22)-C(23)-C(24)	0.5(12)
C(22)-C(23)-C(24)-C(19)	-1.3(11)
C(20)-C(19)-C(24)-C(23)	0.1(9)
P(1)-C(19)-C(24)-C(23)	-172.0(5)
C(13)-P(1)-C(25)-C(30)	-0.1(5)
C(19)-P(1)-C(25)-C(30)	-109.3(5)
Cu(01)-P(1)-C(25)-C(30)	133.0(4)
C(13)-P(1)-C(25)-C(26)	-172.7(4)
C(19)-P(1)-C(25)-C(26)	78.1(4)
Cu(01)-P(1)-C(25)-C(26)	-39.6(4)
C(31)-O(1)-C(26)-C(27)	-27.8(7)
C(31)-O(1)-C(26)-C(25)	153.2(5)
C(30)-C(25)-C(26)-C(27)	-1.5(8)
P(1)-C(25)-C(26)-C(27)	171.7(4)
C(30)-C(25)-C(26)-O(1)	177.4(5)
P(1)-C(25)-C(26)-O(1)	-9.4(6)
O(1)-C(26)-C(27)-C(28)	-177.6(5)
C(25)-C(26)-C(27)-C(28)	1.3(9)
C(26)-C(27)-C(28)-C(29)	-0.7(9)
C(27)-C(28)-C(29)-C(30)	0.5(10)
C(28)-C(29)-C(30)-C(25)	-0.8(10)
C(26)-C(25)-C(30)-C(29)	1.3(8)
P(1)-C(25)-C(30)-C(29)	-171.3(5)
C(26)-O(1)-C(31)-C(36)	95.4(6)
C(26)-O(1)-C(31)-C(32)	-88.0(6)
C(36)-C(31)-C(32)-C(33)	-3.4(9)
O(1)-C(31)-C(32)-C(33)	-179.9(5)
C(36)-C(31)-C(32)-P(2)	173.5(5)
O(1)-C(31)-C(32)-P(2)	-2.9(7)
C(37)-P(2)-C(32)-C(33)	-92.3(6)
C(43)-P(2)-C(32)-C(33)	16.2(6)
Cu(01)-P(2)-C(32)-C(33)	143.3(5)
C(37)-P(2)-C(32)-C(31)	91.0(5)
C(43)-P(2)-C(32)-C(31)	-160.5(5)
Cu(01)-P(2)-C(32)-C(31)	-33.4(5)
C(31)-C(32)-C(33)-C(34)	0.9(9)
P(2)-C(32)-C(33)-C(34)	-175.8(5)
C(32)-C(33)-C(34)-C(35)	1.7(11)
C(33)-C(34)-C(35)-C(36)	-2.0(12)
C(34)-C(35)-C(36)-C(31)	-0.4(11)
C(32)-C(31)-C(36)-C(35)	3.2(10)
O(1)-C(31)-C(36)-C(35)	179.7(6)
C(43)-P(2)-C(37)-C(38)	92.1(5)
C(32)-P(2)-C(37)-C(38)	-160.9(5)
Cu(01)-P(2)-C(37)-C(38)	-36.6(5)
C(43)-P(2)-C(37)-C(42)	-86.5(6)
C(32)-P(2)-C(37)-C(42)	20.5(7)
Cu(01)-P(2)-C(37)-C(42)	144.8(6)
C(42)-C(37)-C(38)-C(39)	-1.0(10)
P(2)-C(37)-C(38)-C(39)	-179.7(6)

C(37)-C(38)-C(39)-C(40)	-0.4(12)
C(38)-C(39)-C(40)-C(41)	1.9(14)
C(39)-C(40)-C(41)-C(42)	-1.9(16)
C(38)-C(37)-C(42)-C(41)	1.0(12)
P(2)-C(37)-C(42)-C(41)	179.6(7)
C(40)-C(41)-C(42)-C(37)	0.4(15)
C(37)-P(2)-C(43)-C(48)	23.0(6)
C(32)-P(2)-C(43)-C(48)	-85.8(6)
Cu(01)-P(2)-C(43)-C(48)	149.5(5)
C(37)-P(2)-C(43)-C(44)	-158.3(5)
C(32)-P(2)-C(43)-C(44)	92.9(5)
Cu(01)-P(2)-C(43)-C(44)	-31.8(6)
C(48)-C(43)-C(44)-C(45)	-0.6(11)
P(2)-C(43)-C(44)-C(45)	-179.4(6)
C(43)-C(44)-C(45)-C(46)	-0.2(12)
C(44)-C(45)-C(46)-C(47)	1.4(14)
C(45)-C(46)-C(47)-C(48)	-1.7(14)
C(44)-C(43)-C(48)-C(47)	0.2(11)
P(2)-C(43)-C(48)-C(47)	179.0(6)
C(46)-C(47)-C(48)-C(43)	0.9(12)
C(51)-O(2)-C(50)-C(49)	-177(4)
C(50)-O(2)-C(51)-C(52)	134(5)

Table S4. Torsion angles [°] for (**2**).

C(5)-N(2)-C(1)-C(2)	-1.2(6)
Cu(01)-N(2)-C(1)-C(2)	163.9(4)
N(2)-C(1)-C(2)-C(3)	0.2(7)
C(1)-C(2)-C(3)-C(4)	1.2(7)
C(1)-C(2)-C(3)-C(6)	-178.0(5)
C(2)-C(3)-C(4)-C(5)	-1.6(7)
C(6)-C(3)-C(4)-C(5)	177.7(5)
C(1)-N(2)-C(5)-C(4)	0.8(6)
Cu(01)-N(2)-C(5)-C(4)	-165.9(3)
C(1)-N(2)-C(5)-C(7)	178.5(3)
Cu(01)-N(2)-C(5)-C(7)	11.7(4)
C(3)-C(4)-C(5)-N(2)	0.5(6)
C(3)-C(4)-C(5)-C(7)	-177.0(4)
C(11)-N(1)-C(7)-C(8)	0.0(5)
Cu(01)-N(1)-C(7)-C(8)	-177.3(3)
C(11)-N(1)-C(7)-C(5)	179.8(3)
Cu(01)-N(1)-C(7)-C(5)	2.5(4)
N(2)-C(5)-C(7)-N(1)	-9.5(5)
C(4)-C(5)-C(7)-N(1)	168.2(4)
N(2)-C(5)-C(7)-C(8)	170.3(3)
C(4)-C(5)-C(7)-C(8)	-12.1(6)
N(1)-C(7)-C(8)-C(9)	-0.8(6)
C(5)-C(7)-C(8)-C(9)	179.4(3)

C(7)-C(8)-C(9)-C(10)	0.9(6)
C(7)-C(8)-C(9)-C(12)	179.3(4)
C(8)-C(9)-C(10)-C(11)	-0.1(6)
C(12)-C(9)-C(10)-C(11)	-178.6(4)
C(7)-N(1)-C(11)-C(10)	0.7(6)
Cu(01)-N(1)-C(11)-C(10)	177.7(3)
C(9)-C(10)-C(11)-N(1)	-0.7(7)
C(19)-P(2)-C(13)-C(18)	9.7(5)
C(25)-P(2)-C(13)-C(18)	-99.3(4)
Cu(01)-P(2)-C(13)-C(18)	138.8(4)
C(19)-P(2)-C(13)-C(14)	-172.8(4)
C(25)-P(2)-C(13)-C(14)	78.2(4)
Cu(01)-P(2)-C(13)-C(14)	-43.8(4)
C(18)-C(13)-C(14)-C(15)	1.6(8)
P(2)-C(13)-C(14)-C(15)	-176.0(4)
C(13)-C(14)-C(15)-C(16)	-0.9(10)
C(14)-C(15)-C(16)-C(17)	-0.7(12)
C(15)-C(16)-C(17)-C(18)	1.7(12)
C(14)-C(13)-C(18)-C(17)	-0.6(8)
P(2)-C(13)-C(18)-C(17)	176.8(5)
C(16)-C(17)-C(18)-C(13)	-1.0(11)
C(13)-P(2)-C(19)-C(20)	-103.9(4)
C(25)-P(2)-C(19)-C(20)	2.6(4)
Cu(01)-P(2)-C(19)-C(20)	125.2(3)
C(13)-P(2)-C(19)-C(24)	75.8(3)
C(25)-P(2)-C(19)-C(24)	-177.7(3)
Cu(01)-P(2)-C(19)-C(24)	-55.1(3)
C(24)-C(19)-C(20)-C(21)	-0.4(6)
P(2)-C(19)-C(20)-C(21)	179.3(3)
C(19)-C(20)-C(21)-C(22)	0.1(7)
C(20)-C(21)-C(22)-C(23)	0.3(8)
C(21)-C(22)-C(23)-C(24)	-0.3(8)
C(22)-C(23)-C(24)-C(19)	0.0(7)
C(20)-C(19)-C(24)-C(23)	0.4(6)
P(2)-C(19)-C(24)-C(23)	-179.4(3)
C(19)-P(2)-C(25)-C(30)	91.8(4)
C(13)-P(2)-C(25)-C(30)	-161.5(3)
Cu(01)-P(2)-C(25)-C(30)	-34.1(4)
C(19)-P(2)-C(25)-C(26)	-93.9(4)
C(13)-P(2)-C(25)-C(26)	12.8(4)
Cu(01)-P(2)-C(25)-C(26)	140.3(3)
C(30)-C(25)-C(26)-C(27)	1.9(7)
P(2)-C(25)-C(26)-C(27)	-172.6(4)
C(25)-C(26)-C(27)-C(28)	-0.3(8)
C(26)-C(27)-C(28)-C(29)	-0.8(10)
C(27)-C(28)-C(29)-C(30)	0.2(10)
C(28)-C(29)-C(30)-C(25)	1.6(8)
C(28)-C(29)-C(30)-O(1)	179.2(5)
C(26)-C(25)-C(30)-C(29)	-2.6(7)
P(2)-C(25)-C(30)-C(29)	172.1(4)
C(26)-C(25)-C(30)-O(1)	179.7(4)
P(2)-C(25)-C(30)-O(1)	-5.6(5)

C(31)-O(1)-C(30)-C(29)	99.5(5)
C(31)-O(1)-C(30)-C(25)	-82.8(4)
C(30)-O(1)-C(31)-C(32)	-40.8(5)
C(30)-O(1)-C(31)-C(36)	141.8(4)
C(36)-C(31)-C(32)-C(33)	-1.7(7)
O(1)-C(31)-C(32)-C(33)	-179.1(4)
C(31)-C(32)-C(33)-C(34)	-0.1(8)
C(32)-C(33)-C(34)-C(35)	0.8(9)
C(33)-C(34)-C(35)-C(36)	0.1(8)
C(34)-C(35)-C(36)-C(31)	-1.8(7)
C(34)-C(35)-C(36)-P(1)	179.7(4)
C(32)-C(31)-C(36)-C(35)	2.6(6)
O(1)-C(31)-C(36)-C(35)	-179.9(4)
C(32)-C(31)-C(36)-P(1)	-178.9(3)
O(1)-C(31)-C(36)-P(1)	-1.4(5)
C(43)-P(1)-C(36)-C(35)	-97.6(4)
C(37)-P(1)-C(36)-C(35)	8.3(4)
Cu(01)-P(1)-C(36)-C(35)	138.8(3)
C(43)-P(1)-C(36)-C(31)	84.0(3)
C(37)-P(1)-C(36)-C(31)	-170.1(3)
Cu(01)-P(1)-C(36)-C(31)	-39.6(4)
C(43)-P(1)-C(37)-C(38)	21.1(4)
C(36)-P(1)-C(37)-C(38)	-84.9(4)
Cu(01)-P(1)-C(37)-C(38)	150.9(3)
C(43)-P(1)-C(37)-C(42)	-160.0(4)
C(36)-P(1)-C(37)-C(42)	94.1(4)
Cu(01)-P(1)-C(37)-C(42)	-30.1(4)
C(42)-C(37)-C(38)-C(39)	-3.8(8)
P(1)-C(37)-C(38)-C(39)	175.2(4)
C(37)-C(38)-C(39)-C(40)	1.3(10)
C(38)-C(39)-C(40)-C(41)	1.4(11)
C(39)-C(40)-C(41)-C(42)	-1.5(11)
C(40)-C(41)-C(42)-C(37)	-1.1(10)
C(38)-C(37)-C(42)-C(41)	3.8(8)
P(1)-C(37)-C(42)-C(41)	-175.3(5)
C(37)-P(1)-C(43)-C(48)	89.4(3)
C(36)-P(1)-C(43)-C(48)	-164.7(3)
Cu(01)-P(1)-C(43)-C(48)	-43.8(3)
C(37)-P(1)-C(43)-C(44)	-87.5(4)
C(36)-P(1)-C(43)-C(44)	18.3(4)
Cu(01)-P(1)-C(43)-C(44)	139.2(3)
C(48)-C(43)-C(44)-C(45)	-0.1(6)
P(1)-C(43)-C(44)-C(45)	176.8(3)
C(43)-C(44)-C(45)-C(46)	-1.1(7)
C(44)-C(45)-C(46)-C(47)	1.5(8)
C(45)-C(46)-C(47)-C(48)	-0.7(8)
C(44)-C(43)-C(48)-C(47)	0.9(6)
P(1)-C(43)-C(48)-C(47)	-176.2(4)
C(46)-C(47)-C(48)-C(43)	-0.5(7)
C(51)-O(2)-C(50)-C(49)	162.3(13)
C(50)-O(2)-C(51)-C(52)	-173.7(12)

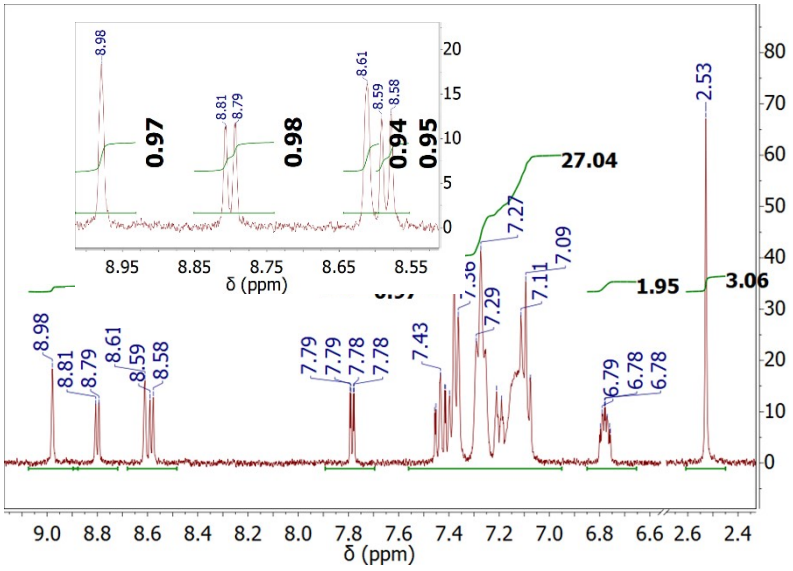

Figure S3.- ^{1}H-NMR spectrum for **1** in CD_3OCD_3 ν= 400 MHz. Inset: Expansion to the region between δ≈ 9.0 and 8.5 ppm.

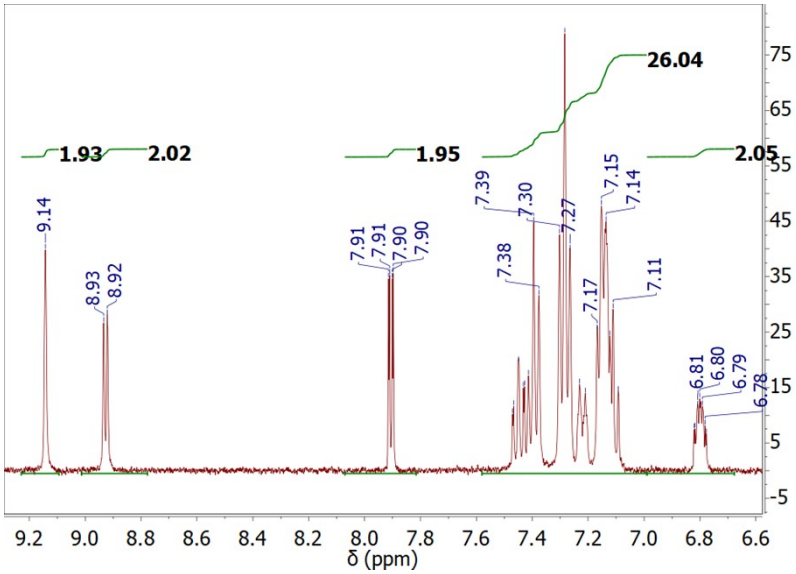

Figure S4.- ^{1}H-NMR spectrum for **2** in CD_3OCD_3 ν= 400 mHz.

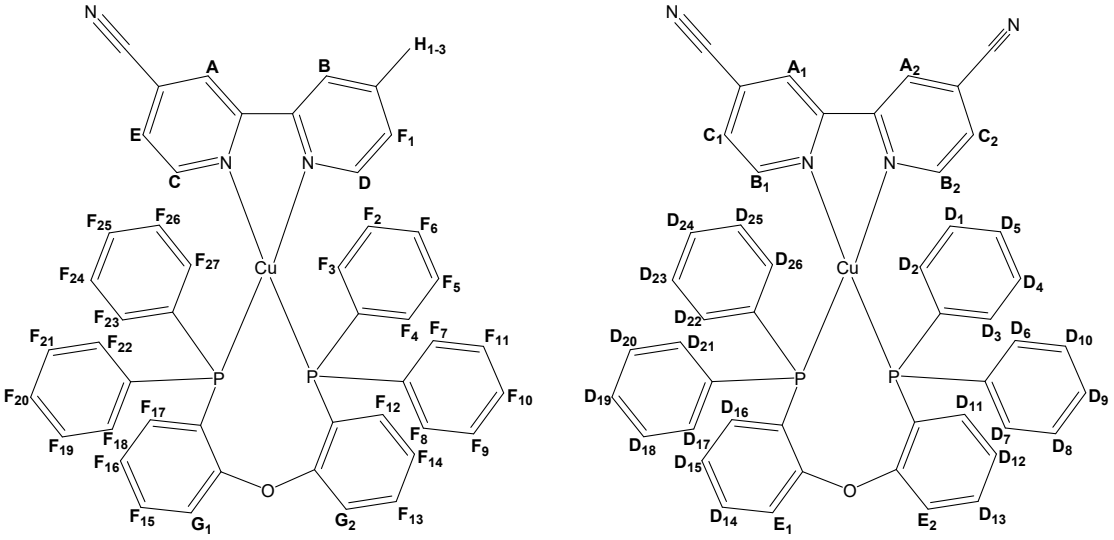

Figure S5.- Alphabetical assignment of the protons of (1, Left) and (2, Right). The bond distances and angle values are arbitrary.

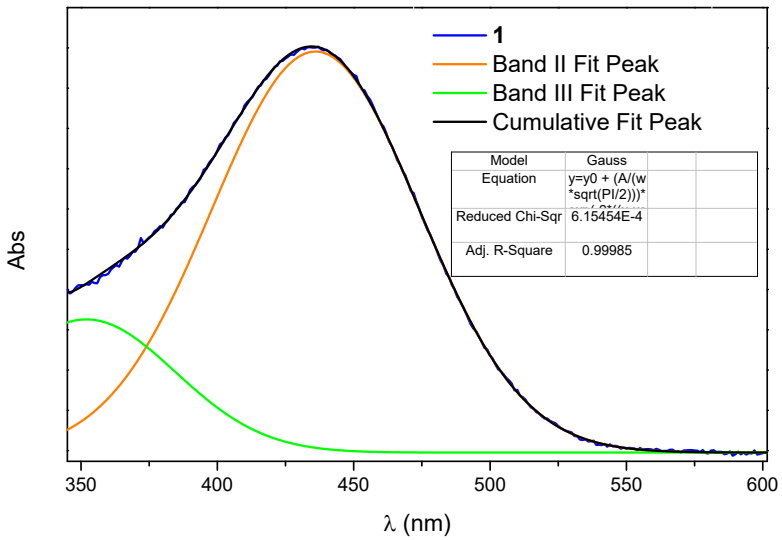

Figure S6.- MLCT Band II of (**1**) fitted with two Gaussian functions. The curves corresponding to the LC transitions are not shown, since their contribution is negligible in this region of the spectrum. **Inset table**: calculated fit parameters.

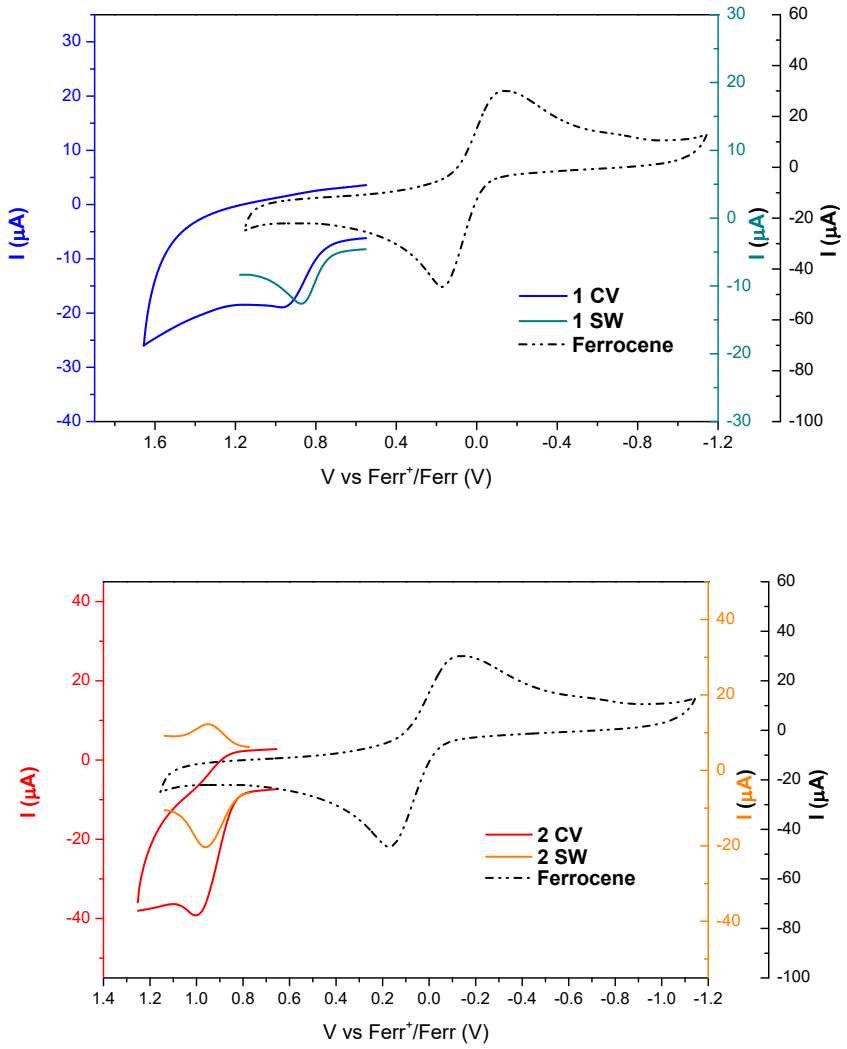

Figure S7.- Cyclic and square wave voltammograms for the first oxidation wave of (**1**) and (**2**) in CH_2Cl_2 0.1 M TBAH. WE: Glassy carbon, IRE: Ferrocene, CE: Pt wire, v= 100 mV s^{-1}. In **blue** and **red** are showing the cyclic voltammograms of (**1**) and (**2**), respectively, while in **dark cyan** and **orange** the square wave voltammograms of (**1**) and (**2**) are presented. The Cyclic voltammogram of ferrocene is showed in dashed-dot **black** line.

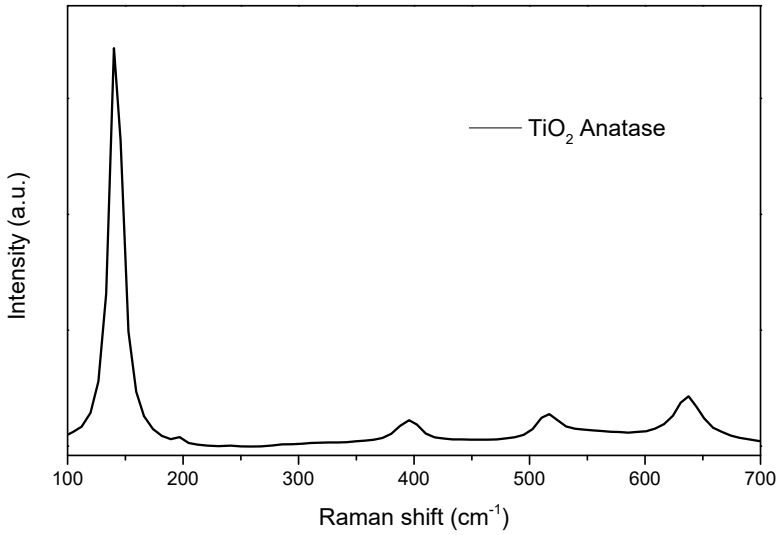

Figure S8.- Raman Spectrum of FTO/TiO_2. λ= 532 nm.