Electropolymerized highly photoconductive thin films of cyclopalladated and cycloplatinated complexes

Andreea Ionescu,[ab] Raffaella Lento,[c] Teresa F. Mastropietro,[d] Iolinda Aiello,[ab] Roberto Termine,[ae] Attilio Golemme,[ace] Mauro Ghedini,[abe] Nathalie Bellec,[f] Elena Pini,[g] Isabella Rimoldi,[g] and Nicolas Godbert*[ab]

[a]*Centro di Eccelenza CEMIF.CAL, LASCAMM CR-INSTM, Unità INSTM della Calabria, I-87036 Arcavacata di Rende, CS, Italy*

[b]*Dipartimento di Chimica e Tecnologie Chimiche – Università della Calabria, I-87036 Arcavacata di Rende, CS, Italy*

[c]*Dipartimento di Fisica – Università della Calabria, I-87036 Arcavacata di Rende, CS, Italy*

[d]*Dipartimento di Ingegneria per l'Ambiente e il Territorio e Ingegneria Chimica-Università della Calabria, I-87036 Arcavacata di Rende, CS, Italy*

[e]*UOS Licryl istituto IMIP del CNR c/o Dipartimento di Fisica, Università della Calabria, I-87036 Arcavacata di Rende, CS, Italy*

[f]*Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Campus de Beaulieu, Bât 10A, 35042 Rennes Cedex, France*

[g]*Dipartimento di Scienze Farmaceutiche – Sezione di Chimica Generale e Organica "A. Marchesini", Università di Milano, Via Venezian 21, 20133 Milano, Italy*

E-mail: nicolas.godbert@unical.it; Fax: +390984492066; Tel: +390984492881

Electronic Supplementary Information

Materials and methods

All commercially available starting materials were used as received without further purification. ^{1}H and ^{13}C NMR spectra were recorded either on a Bruker Avance AC-300 or on a Varian Mercury Plus 200 spectrometer in $CDCl_3$, using tetramethylsilane (TMS) as internal standard. Elemental analyses were performed with a Perkin Elmer 2400 microanalyzer by the Microanalytical Laboratory at the University of Calabria. Infrared spectra (KBr) in the range 4000-400 cm^{-1} were recorded on a Spectrum 100 FT-IR or on a Spectrum One Perkin Elmer spectrometer. The thermal stability was measured on a Perkin-Elmer Thermogravimetric Analyser Pyris 6 TGA, while phase transition temperatures were measured on a TA Instruments DSC Q 2000 Differential Scanning Calorimeter. Melting points were examined with a Leica DMLP polarising microscope equipped with a Leica DFC280 camera and a CalCTec (Italy) heating stage.

Electrochemical studies

All potentials were measured using an Epsilon electrochemical analyzer and an AUTOLAB potentiostat/galvanostat. Voltammetry experiments were performed in a 3 mL cell of dry, freshly distilled, and degassed (N_2) dichloromethane solution using tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte, a Pt disk working electrode, a Pt wire counter-electrode and an Ag wire as a pseudoreference electrode. Voltammograms were recorded at a 100 mV/s scan rate from a *ca.* 10^{-3} M complex solution. Redox potentials are given relative to a ferrocene/ferrocenium (Fc/Fc+) redox couple used as an internal reference. Estimation of HOMO energy values was performed taking into account -4.8 eV for Fc/Fc^{+}

Synthesis of the Schiff bases H(O^N)^n

The Schiff bases **H(O^N)^n** (Chart 1), with **n=1-3** were obtained by condensation of 5-methoxy-2-hydroxybenzaldehide with an opportunely substituted diphenylamino derivatives.

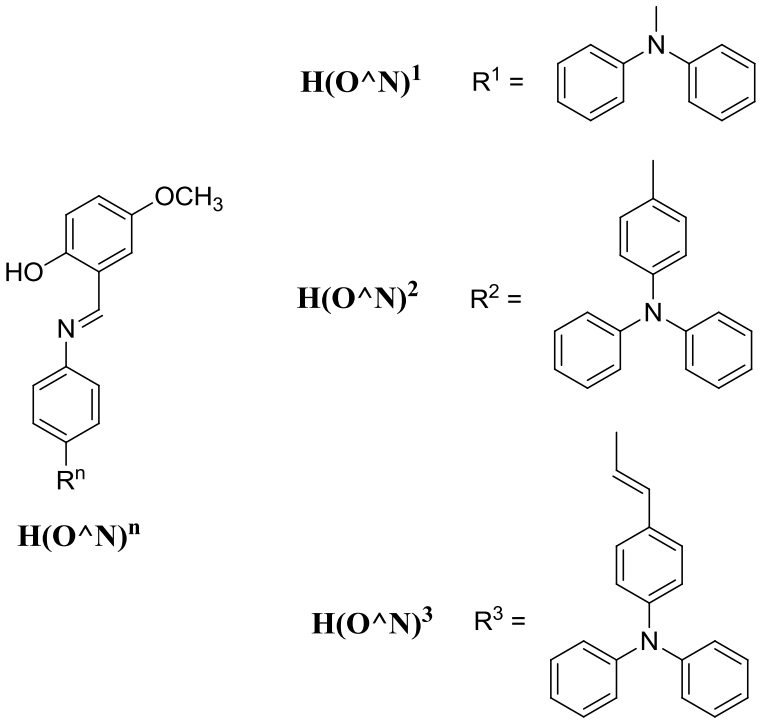
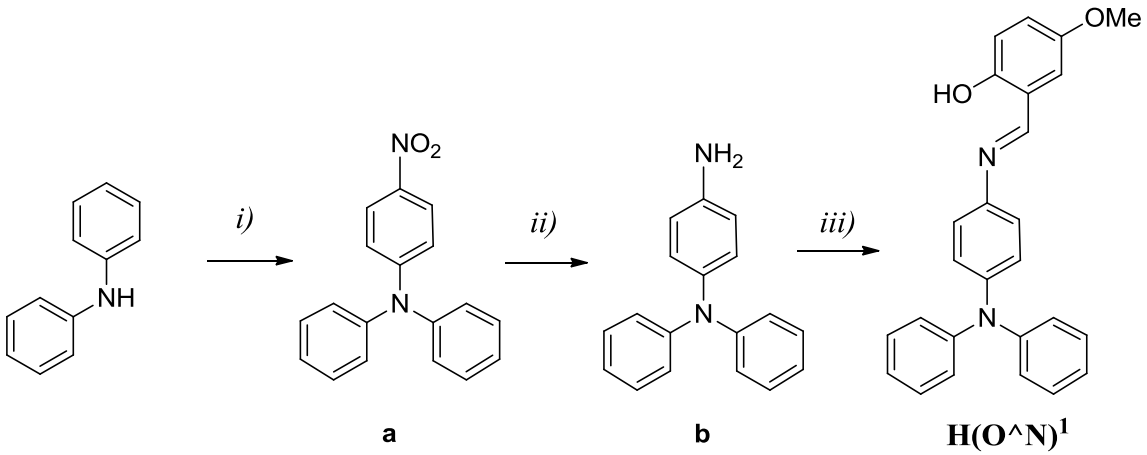


Chart S1. Chemical structures of the Schiff bases **H(O^N)^n, n=1-3**

Synthesis of H(O^N)^1



Reagents and conditions: *i)* NaH, *p*-chloronitrobenzene, dimethylformamide, reflux, 6 h, N_2, *ii)* H_2, 10% Pd/C, ethyl acetate, 18 h. iii) 5-methoxy-2-hydroxybenzaldehyde, ethanol, reflux, 3h.

Synthesis of intermediate **a**

Under a nitrogen atmosphere, to a stirred solution of N,N-diphenylaniline (1 g, 0.006 mol) in anhydrous DMF (6 mL) NaH (141.84 mg, 0.006 mol) in DMF (2 mL) was added at 0 °C. Then a solution of *p*-chloronitrobenzene in DMF was added dropwise; after stirring for 10 min at 0 °C, the mixture was heated at 110 °C for 6 h. After distillation of DMF in *vacuum*, the residue was dissolved in distilled water (15 mL) and the pH was corrected to 5 by addiction of HCl 10% and extracted with diethyl ether (3x30mL).The combined organic layers, dried over anhydrous Na_2SO_4, were evaporated in *vacuum* to give compound **a.**

Yellow solid; yield 40% (0.700 mg); m.p. 140-142 °C; ^{1}H NMR (200 MHz $CDCl_3$, 25°C) δ= 8.07 (d, J=9.10 Hz, 2H), 7.40-7.37 (m, 4H), 7.23-7.15 (m, 6H), 6.92 (d, J=9.10 Hz, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 153.7, 145.9,140.4, 130.2, 126.8, 125.9, 125.7, 118.3; FT-IR (KBr, cm^{-1}) 3435, 3059, 3036,1945,1913, 1654, 1581, 1489, 1324, 1296, 1110; elemental analysis calculated for $C_{18}H_{14}N_2O_2$ (290.312 g/mol): C 74.47 %, H 4.86%, N 9.65%, found: C 74.21%, H 5.19%, N 9.62%.

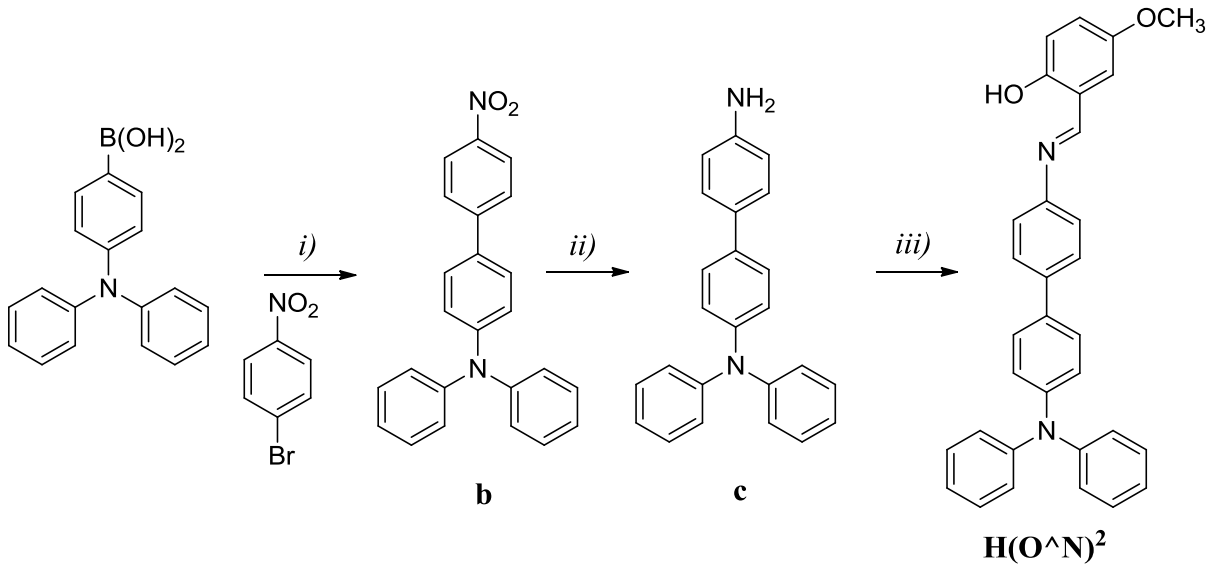
Synthesis of intermediate **b**

In a stainless steel autoclave connected with a hydrogen-supply vessel to N,N-diphenyl-p-nitroaniline **a** (3.3 g, 0.0114 mol) dissolved in ethylacetate (50mL), was added 10% Pd/C (60.65 mg, 0.0057 mol). The autoclave, equipped with temperature control and magnetic stirrer, was purged with hydrogen and pressurized. After 18 h the mixture was filtered through celite and the solvent evaporated in *vacuum*.

Purple solid; yield 88%; m.p. 147-148°C; ^{1}H NMR (200 MHz, $CDC1_3$, 25°C) δ 7.25 (d, J=9.5 Hz, 2H), 7.15-7.00 (m, 4H), 7.0-6.9 (m, 6H), 6.69 (d, J=9.5 Hz, 2H), 3.56 (s, 2H exch. D_2O); ^{13}C NMR (50.3 MHz $CDCl_3$) δ 148.5, 143.3,139.2, 129.3, 128.1, 122.8, 121.7, 116.4. FT-IR (KBr cm^{-1}) 3350, 3031, 1941,1860, 1730,1596, 1582, 1329, 1266, 1170, 1074,1026; elemental analysis calculated for $C_{18}H_{16}N_2$ (260.328 g/mol): C 83.04%, H 6.19%, N 10.76%, found: C 82.72%, H 6.56%, N 10.72%.

Synthesis of **H(O^N)[1]**

Synthesis of H(O^N)^2



Reagents and conditions: *i)* $Pd(PPh_3)_4$ cat., Na_2CO_3 (2M), ethanol/water/toluene, 36 h, N_2, *ii)* $NaBH_4$, $NiCl_2$, methanol/dichloromethane, overnight, *iii)* 5-methoxy-2-hydroxybenzaldehyde ethanol, reflux, 3 h.

Synthesis of intermediate **b**

N,*N*-diphenylphenyl boronic acid (2.01 g, 6.95 mmol) and *p*-nitrobromobenzene **5** (1.40 g, 6.93 mmol) are solubilized in 60 mL of a degassed solution of toluene/ethanol:5/1. 15 mL of a degassed 2 M aqueous solution of Na_2CO_3 and $Pd(PPh_3)_4$ (0.160 g, 0.14 mmol) are added. The reaction mixture is stirred at r.t. under N_2 for 24 h. The organic phase was extracted with dichloromethane, dried with $MgSO_4$, filtered and, eventually, the solvent evaporated. The crude product was purified by column chromatography (silica gel, petroleum ether /dichloromethane :3/2).

Orange solid; yield 93% (2.350 g); m.p. 158-160 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 8.27(d, J=9.91 Hz, 2H), 7.69 (d, J=9.06 Hz, 2H); 7.49 (d,J=8.79 Hz, 2H), 7.32-7.27 (m, 4H), 7.15-7.12 (m, 6H), 7.06 (t, J=1.23 Hz, 2H); FT-IR (KBr, cm^{-1}): 3060, 1587, 1484 (*stretching NO_2*), 1317; elemental analysis calculated for $C_{24}H_{18}N_2O_2$ (366.41 g/mol): C 78.67%, H 4.95%, N 7.65%, found: C 78.68%, H 4.91%, N 7.69%.

Synthesis of intermediate **c**

To 80 mL of a dichloromethane solution of intermediate **b** (2.2 g, 6.00 mmol), 80 mL of a methanol solution of $NiCl_2 \cdot 6H_2O$ (1 g, 13.2 mmol) is added. To the obtained solution, $NaBH_4$ (1.0 g, 26 mmol) is added slowly and under vigorous stirring. A black suspension is filtered off on a Celite column with ethyl acetate as an eluent. Part of the solvent is evaporated and a saturated aqueous solution of Na_2CO_3 is added. The organic phase is extracted with ethyl acetate and dried with $MgSO_4$. The crude product is purified by column chromatography (petroleum ether/dichloromethane:1/1).

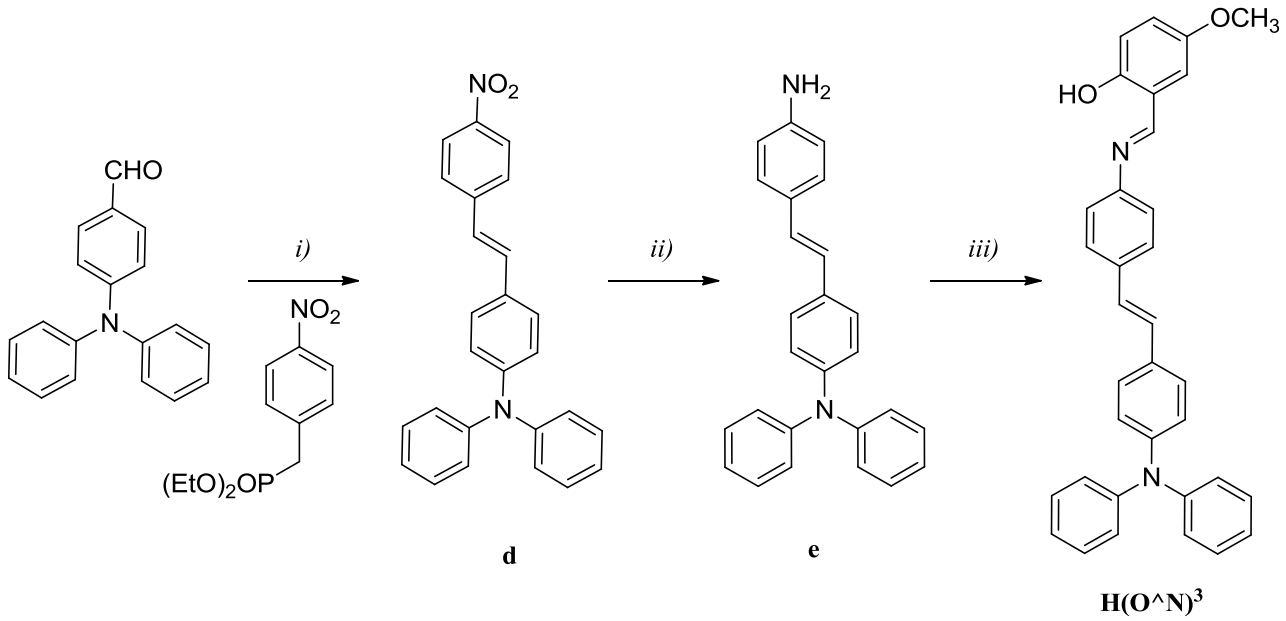
Brown-yellow solid; yield 82% (1.659 g) ; m.p. 180-181 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 7.44 (d, J=8.79 Hz, 2H), 7.31-7.24 (m, 8H); 7.02-6.95 (m, 8H) 6.59 (d,J=8.49 Hz, 2H), 5.17 (s, 2H); FT-IR (KBr, cm^{-1}): 3466, 1593, 1317; elemental analysis calculated for $C_{24}H_2ON_2$ (336.43 g/mol): C 85.68%, H 5.99%, N 8.33%, found: C 85.71%, H 6.09%, N 8.51%.

Synthesis of **H(O^N)^2**

To a ethanol solution of intermediate **c** (806 mg, 2.40 mmol), 5-methoxy-2-hydroxybenzaldehyde (372 mg, 2.40 mmol) is added and the reaction mixture is refluxed for 3 h. An orange solid precipitated after 12 h at -4 °C. The product was filtered off and washed with cold ethanol.

Orange solid; yield 94% (1.064 g) ; m.p. 165-166 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=12.86 (s, 1H), 8.65 (s, 1H), 7.63 (d, J=7.63 Hz, 1H), 7.49 (d, J=9.06 Hz, 1H), 7.35 (d, J=8.52 Hz, 2H), 7.30 (s, 1H), 7.28-7.26 (m, 5H), 7.16-7.12 (m, 6H), 7.04 (t, J=7.11 Hz, 3H), 6.99-6.95 (m, 3H), 6.91 (d, J=2.61 Hz, 2H), 3.82 (s, 3H); FT-IR (KBr, cm^{-1}): 3400 (*br*.), 3014 (*alkyl stretching*), 2950, 1323; elemental analysis calculated for $C_{32}H_{26}N_2O_2$ (470.56 g/mol): C 81.68%, H 5.57%, N 5.95%, found: C 81.72%, H 5.60%, N 6.17%.

Synthesis of H(O^N)^3



Reagents and conditions : *i)* NaOEt, dry DMF, 20h, RT, *ii)* $SnCl_2.2H_2O$, EtOH, reflux, 4h *iii)* 5-methoxy-2-hydroxybenzaldehyde, EtOH, reflux, 3h.

Synthesis of intermediate **d**

Freshly prepared ethanol solution of NaOEt (20 mmol, 20 mL of 1M solution) is added to a 20 mL dry DMF solution of phosphonate (2.73 g, 10 mmol). After 10 min at r.t., 4-(diphenylamino)benzaldehyde (2.73 g, 10 mmol) is added and stirring is continued for 20h at r.t. Solvents are evaporated and the organic phase is extracted with dichloromethane, washed with water and dried over $MgSO_4$. Compound **d** is purified by column chromatography (SiO_2, dichloromethane).

Orange solid ; yield 59% (2.31 g); ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS) : δ = 7.02 (d, 1H, J=16 Hz), 7.07-718 (m, 8H), 7.24 (d, 1H, J=16 Hz), 7.27-7.34 (m, 4H), 7.43 (d, 2H, J=6.5Hz), 7.60 (d, 2H, J=6.5Hz), 8.21 (d, 2H, J=6.5Hz); elemental analysis calculated for $C_{26}H_{20}N_2O_2$ (392.45 g/mol): C 79.57%, H 5.14%, N 7.14%, found: C 79.60%, H 5.19%, N 7.09%.

Synthesis of intermediate **e**

To 15 mL of an ethanol suspension of intermediate **d** (800 mg, 2.04 mmol) is added dihydrated $SnCl_2$ (2,26 g, 10 mmol). The reaction mixture is refluxed for 4 h under inert atmosphere (N_2) then poured in iced water and pH is allowed to reach 8 by addition of a NaOH solution. Compound **G** is extracted with ethyl acetate and dried with $MgSO_4$. The crude product is purified by column chromatography (SiO_2, dichloromethane).

Yellow solid ; yield 69% (510 mg) ; m.p.167-168 °C; ^{1}H-NMR (500 MHz, $CDCl_3$, 25°C, TMS) : δ = 3.65 (broad s, 2H), 6.70 (d, 2H, J=8.5 Hz), 6.92 (d, 1H, J=16.3 Hz), 6.98 (d, 1H, J=16.3 Hz), 7.06 (m, 2H), 7.09 (d, 2H, J=8.5 Hz), 7.16 (m, 4H), 7.30 (m, 4H), 7.36 (d, 2H, J=8.5Hz), 7.40 (d, 2H, J=8.5Hz); ^{13}C-NMR (75MHz, $CDCl_3$, 25°C, TMS) : δ = 115.4, 122.9, 124.4, 124.7, 127.1, 127.4, 127.7, 128.4, 129.4, 132.5, 145.9, 146.7, 147.8; FT-IR (KBr, cm^{-1}): 3390, 3020, 2338, 1586, 1515, 1488, 1277; HRMS calculated for $C_{26}H_{22}N_2$: 362.1783, found: 362.1789; elemental analysis calculated for $C_{26}H_{22}N_2$ (362.47 g/mol): C 86.15%, H 6.12%, N 7.73%, found: C 86.10%, H 6.19%, N 7.81%.

Synthesis of **H(O^N)^3**

To a hot ethanol solution of intermediate **e** (550 mg, 1.52 mmol), 5-methoxy-2-hydroxy-benzaldehyde (235 mg, 1.52 mmol) is added and the reaction mixture is refluxed for 3 h. An orange solid precipitated after cooling 12 h at -4 °C. The product was filtered off and washed with cold ethanol.

Orange solid ; yield 81% (610 mg) ; m.p. 157-158°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 25°C, TMS) : δ = 3.83 (s, 3H), 6.92 (d, 1H, J=1 Hz), 6.98-7.15 (m, 12H), 7.25-7.29 (m, 6H), 7.29-7.34 (m, 6H), 7.41 (d, 2H, J=8.1 Hz), 7.55 (d, 2H, J=8.1 Hz), 8.61 (s, 1H), 12.95 (s, 1H); ^{13}C-NMR (75MHz, $CDCl_3$, 25°C, TMS) : δ = 55.9, 115.2, 118.1, 118.9, 120.4, 121.7, 123.2, 123.5, 124.4, 126.1, 127.3, 127.5, 128.5, 129.4, 131.2, 136.6, 147.1, 147.5, 152.3, 155.5, 161.4; FT-IR (KBr, cm^{-1}): 3650, 2930, 2340, 1588, 1488, 1273; HRMS calculated for $C_{34}H_{28}N_2O_2$: 496.2151, found : 496.2134; elemental analysis calculated for $C_{34}H_{28}N_2O_2$ (496.60 g/mol): C 82.23%, H 5.68%, N 5.64%, found: C 82.26%, H 5.70%, N 5.60%.

Film electrochemistry

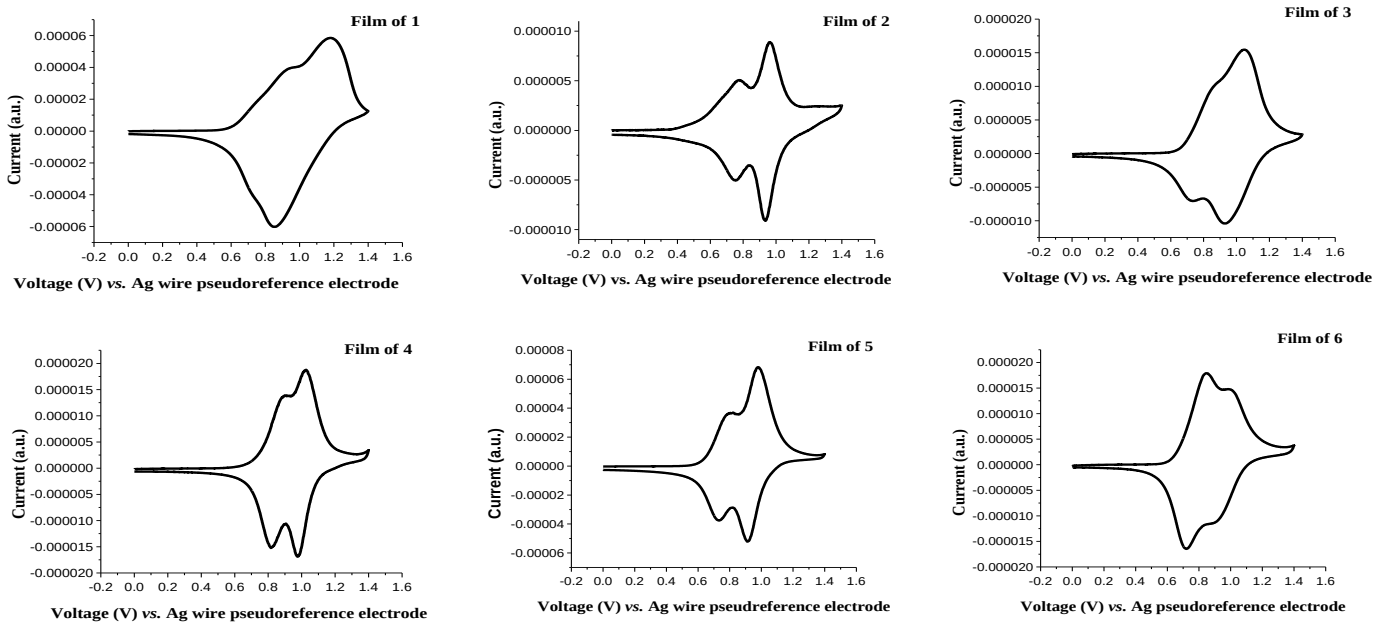


Figure S1. Cyclic voltammograms of the modified Pt disk working electrode covered with the electropolymerized films of **1-6** immersed in a fresh distilled dichloromethane 0.1 M electrolytic solution.

X-Ray diffraction studies

Table S1. Crystal data and structure refinement for **1-5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{37}H_{29}N_3O_2Pd$	$C_{43}H_{33}N_3O_2Pd$	$C_{45}H_{35}N_3O_2Pd$	$C_{37}H_{29}N_3O_2Pt$	$C_{86.50}H_{67}ClN_6O_4Pt_2$
Formula weight	654.03	730.12	756.16	742.72	1680.09
Temperature (K)	296(2)	273(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P2(1)/C	P -1	P-1	P2(1)/c	P2(1)/n
Unit cell dimensions	a = 28.390(2) Å	a = 10.0139(18) Å	a = 6.5511(19) Å	a = 28.230(13) Å	a = 21.956(3) Å
	b = 6.4428(5) Å	b = 10.033(2) Å	b = 9.456(3) Å	b = 6.498(3) Å	b = 10.0166(11) Å
	c = 16.4436(13) Å	c = 35.752(7) Å	c = 31.810(9) Å	c = 16.353(8) Å	c = 33.500(4) Å
	α= 90°	α= 91.858(9)°	α= 93.023(14)°	α= 90°	α= 90°
	β= 90.821(3)	β= 95.719(9)°	β= 92.432(14)°	β= 90.285(16)°	β= 103.785(5)°
	α= 90°	γ = 108.279(9)°	γ = 106.440(13)°	γ = 90°	γ = 90°
Volume ($Å^3$)	3007.5(4)	3386.2(11)	1884.0(9)	3000(2)	7155.2(14)
Z	4	4	2	4	4
Density (calculated) (Mg/m^3)	1.444	1.432	1.333	1.645	1.560
Absorption coefficient (mm^{-1})	0.655	0.590	0.533	4.716	4.001
F(000)	1336	1496	776	1464	3332
Crystal size (mm^3)	0.12 x 0.02 x 0.02	0.18 x 0.04 x 0.01	0.20 x 0.08 x 0.01	0.10 x 0.02 x 0.02	0.15 x 0.03 x 0.01
Theta range for data collection	0.72 to 26.79°	1.72 to 25.00°	0.64 to 25.50°	0.72 to 26.45°	1.01 to 25.00°
Index ranges	-36<=h<=36,	-11<=h<=11,	-7<=h<=7,	-35<=h<=35,	-26<=h<=26,
	-8<=k<=8,	-11<=k<=11,	-11<=k<=11,	-8<=k<=8,	-11<=k<=11,
	-20<=l<=20	-42<=l<=42	-38<=l<=38	-20<=l<=20	-39<=l<=39
Reflections collected	87288	45408	28985	49812	235853
Independent reflections	6354	11455	6977	6118	12604
	[R(int) = 0.0535]	[R(int) = 0.0673]	[R(int) = 0.0853]	[R(int) = 0.0818]	[R(int) = 0.1730]
Completeness to theta = 26.79°	98.8 %	96.4 %	99.8 %	99.0 %	100.0 %
Max. and min. transmission	0.9870 and 0.9255	0.9941 and 0.9012	0.9947 and 0.9008	0.9116 and 0.6499	0.9611 and 0.5852
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6354 / 0 / 389	11455 / 0 / 885	6977 / 0 / 548	6118 / 0 / 389	12604 / 0 / 910
Goodness-of-fit on F^2	1.079	1.026	1.103	1.137	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0939	R1 = 0.0499, wR2 = 0.1066	R1 = 0.1111, wR2 = 0.2813	R1 = 0.0278, wR2 = 0.0688	R1 = 0.0446, wR2 = 0.1065
R indices (all data)[a,b]	R1 = 0.0519, wR2 = 0.1135	R1 = 0.0872, wR2 = 0.1254	R1 = 0.1622, wR2 = 0.3191	R1 = 0.0482, wR2 = 0.1016	R1 = 0.0834, wR2 = 0.1347
Largest diff. peak and hole ($e.Å^{-3}$)	0.353 and 0.748	0.790 and -0.827	3.693 and -1.115	0.710 and -1.301	1.295 and -0.919

[a]$R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$ with $P = (F_o^2 + 2F_c^2)/3$, m = 0.0669 (**1**),0.0591 (**2**), 0.2000 (**3**), 0.0517(**4**) and 0.0666 (**5**), and n = 0.7915 (**1**), 0.6888 (**2**), 0.0000 (**3**), 0.0000 (**4**) and 16.0926 (**5**).

Table S2. Selected bond lengths [Å] and angles [°] for **1-5**. M = Pd(II) (**1**, **2** and **3**) or Pt(II) (**4** and **5**)

	1	**2**	**3**	**4**	**5**
M(1)-C(11)	2.011(3)	1.992(5)	2.037(11)	1.999(7)	2.013(8)
M(1)-N(1)	2.037(3)	2.017(4)	2.082(8)	2.027(5)	2.016(7)
M(1)-N(2)	2.059(2)	2.045(3)	2.104(8)	2.038(5)	2.039(7)
M(1)-O(1)	2.060(2)	2.056(3)	2.078(7)	2.064(5)	2.089(6)
C(11)-M(1)-N(1)	81.04(13)	81.11(17)	81.1(4)	80.9(3)	81.2(3)
C(11)-M(1)-N(2)	101.93(12)	101.80(15)	101.0(4)	102.3(2)	101.1(3)
N(1)-M(1)-N(2)	174.96(10)	173.61(14)	174.8(3)	175.25(18)	177.4(3)
C(11)-M(1)-O(1)	167.72(12)	168.62(14)	169.3(3)	167.3(2)	168.7(3)
N(1)-M(1)-O(1)	88.68(10)	88.04(15)	88.5(3)	88.5(2)	89.7(3)
N(2)-M(1)-O(1)	88.82(9)	89.34(13)	89.6(3)	88.86(18)	87.9(3)
M(2)-C(11B)		1.991(5)			2.016(9)
M(2)-N(1B)		2.026(4)			2.033(7)
M(2)-N(2B)		2.040(3)			2.036(7)
M(2)-O(1B)		2.048(3)			2.074(6)
C(11B)-M(2)-N(1B)		80.74(16)			80.3(3)
C(11B)-M(2)-N(2B)		101.67(15)			102.1(3)
N(1B)-M(2)-N(2B)		174.01(14)			175.1(3)
C(11B)-M(2)-O(1B)		167.61(15)			167.5(3)
N(1B)-M(2)-O(1B)		87.59(15)			87.9(3)
N(2B)-M(2)-O(1B)		90.34(13)			90.0(3)

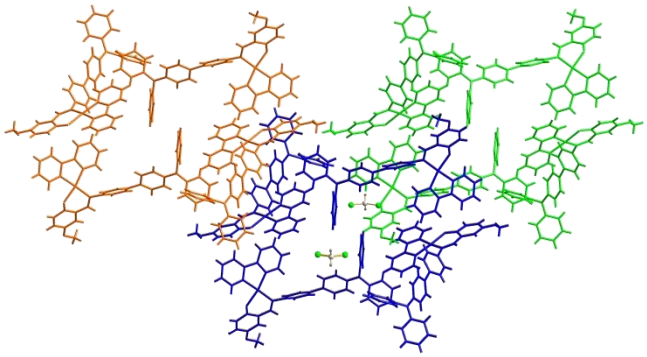


Figure S2. View of the crystal packing in **5**. Solvent molecules are shown for the blue tetranuclear motif, while they have been omitted for clarity for the red and green motifs.

Thermal behaviour

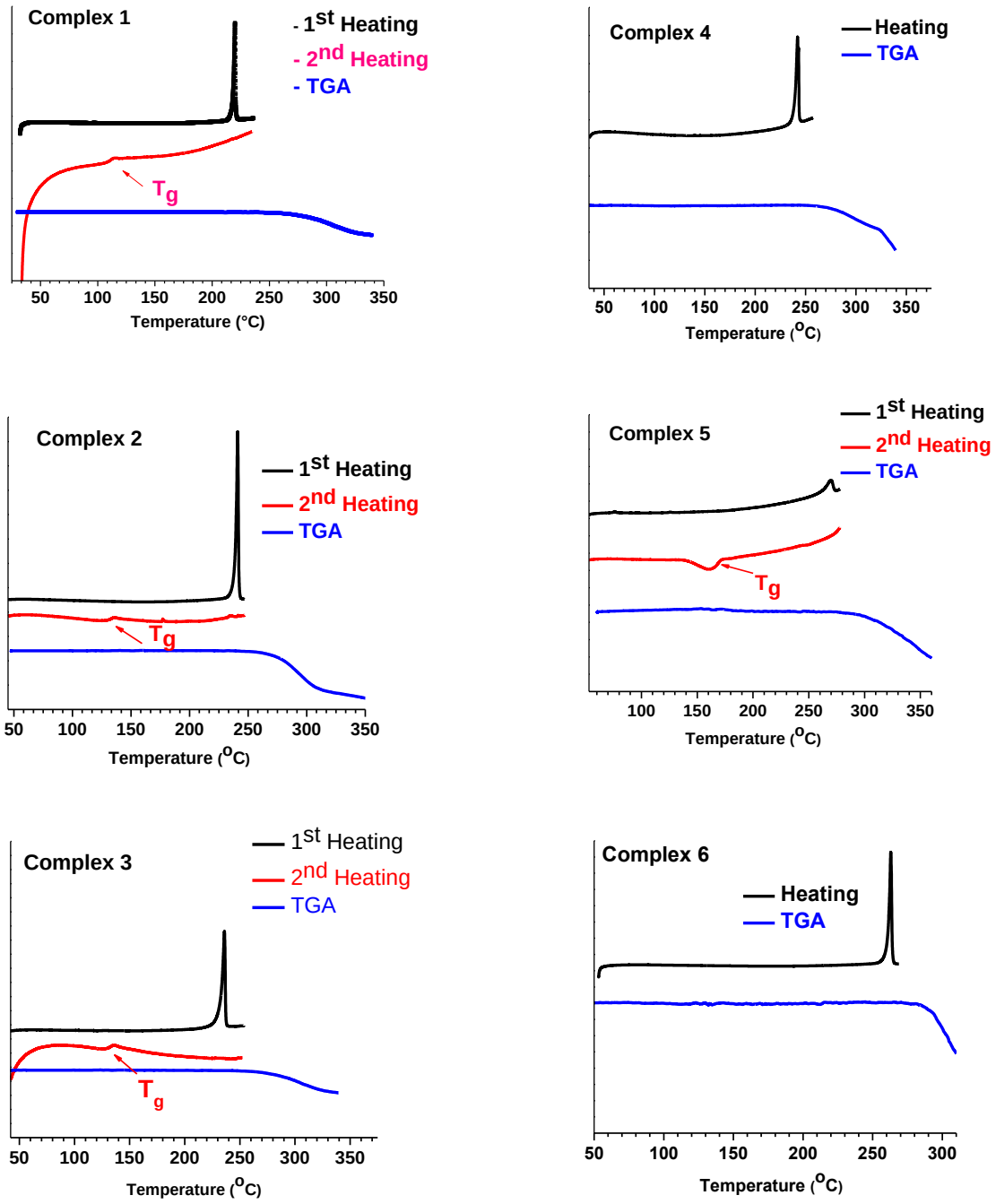
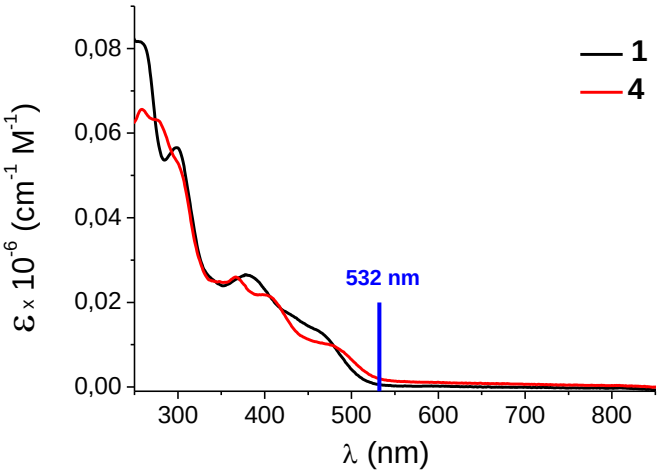
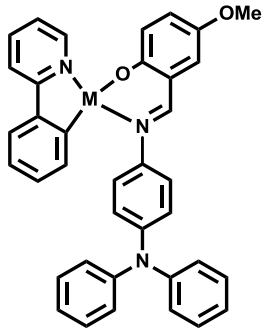


Figure S3. Differential scanning calorimetry (DSC) curves of complexes **1-6** and related thermal gravimetric (TGA) traces. For complexes **1**-**3** and **5**, the second heating scan allows the observation of the glass transition temperature of the obtained amorphous melt. For complexes **4** and **6**, decomposition occurs immediately after melting as shown by the TGA traces. All scans (DSC and TGA) were performed at 5°C/min.

Absorption properties

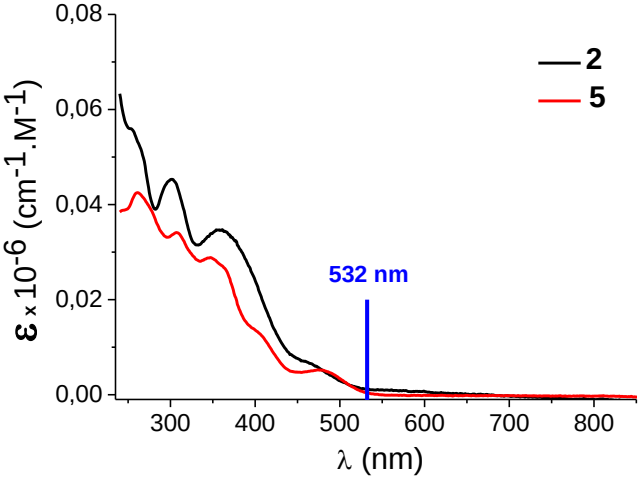
a)

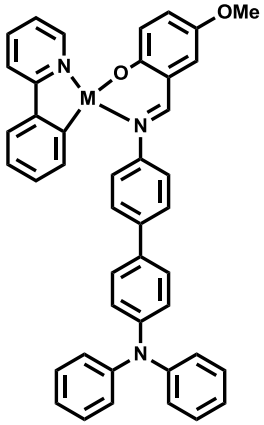




1: M = Pd
4: M = Pt

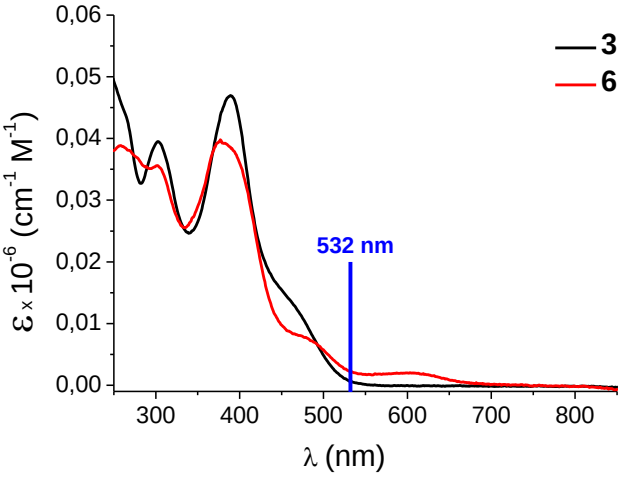
b)

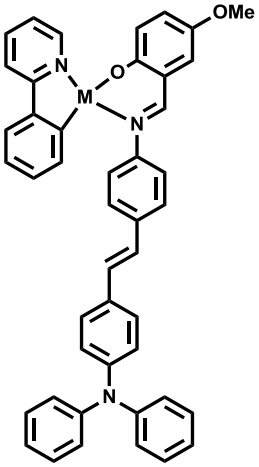




2: M = Pd
5: M = Pt

c)

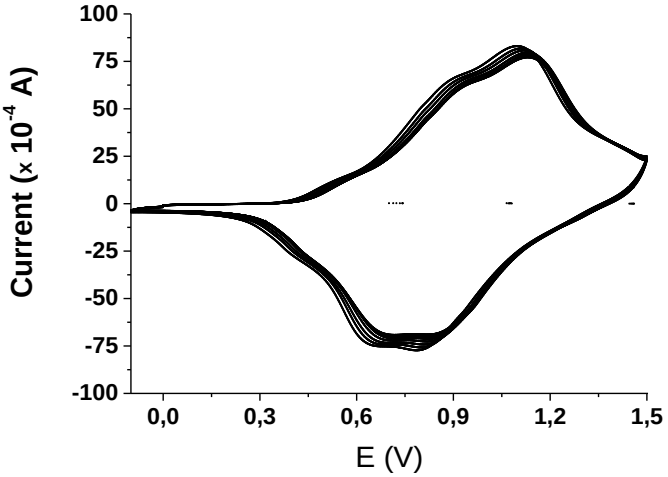




3: M = Pd
6: M = Pt

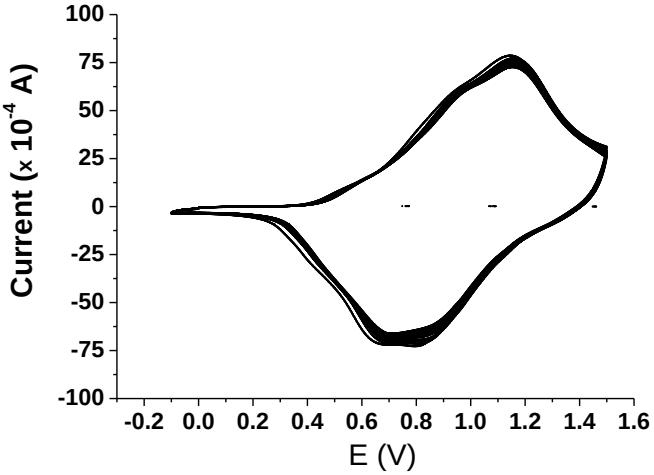
Figure S4. UV-Vis Absorption spectra of complexes **1-6** obtained in dichloromethane. The wavelength λ = 532 nm at which the photoconductivity measurements were performed is shown for clarity.

a)



Note that only 1 cycle over 10 is shown for clarity.

b)



Note that only 1 cycle over 10 is shown for clarity

c)

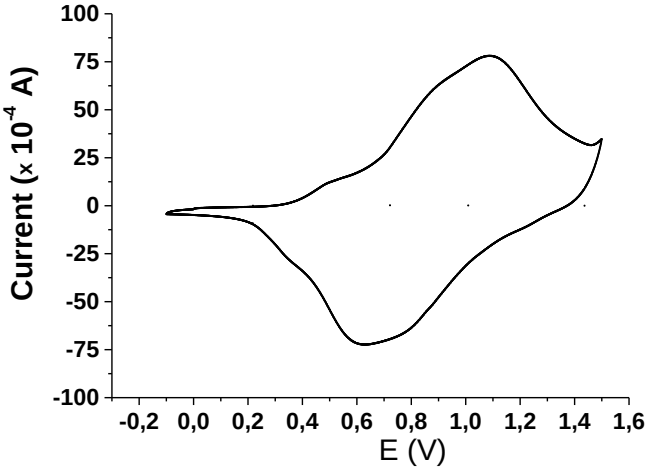


Figure S5: Stability of electrodeposited thin film of complex **2**. (a) 100 cycles on electrodeposited film (after washing with DCM), (b) 100 cycles on the film used in (a) after one full night exposure to air, (c) 1 cycle on the film used in (b) after having kept 1.5 V of applied voltage for 5 minutes.