Influence of Spin Crossover Iron(III) Complex to the Detection of Analytes Phenylenediamines of Graphene-modified Screen Printed Electrodes

Basharat Ali,[a] Theerapoom Boonprab,[a] Warisa Thammasangwan,[b] Sittipong Kaewmorakot,[b] Chanpen Karuwan,[c] Adisorn Tuantranont,[d] Guillaume Chastanet,[e] David J. Harding[a]* and Phimphaka Harding[a]*

[a] School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand

[b] Functional Materials and Nanotechnology Centre of Excellence, Walailak University, Thasala, Nakhon Si Thammarat, 80160, Thailand

[c] National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani 12120, Thailand

[d] National Science and Technology Development Agency (NSTDA), Pathum Thani 12120, Thailand

[e] Université de Bordeaux, CNRS, Bordeuax INP, ICMCB, 87 avenue du Dr A. Schweitzer, Pessac, F-33608, France

E-mail: phimphaka@g.sut.ac.th or david@g.sut.ac.th

Experimental

General Experimental

All manipulations were performed in air with reagent-grade solvents. All other chemicals were purchased from Sigma-Aldrich or TCI Chemicals and used as received. Infrared spectra were collected as KBr discs on a Bruker Tensor 27 FT-IR spectrometer in the range of 400-4000 cm^{-1} using OPUS software for data collection. Electronic spectra were recorded in solution of **1** in CH_2Cl_2 (0.03125-0.25 mM) at room temperature on PG Instruments T80+ UV/Vis Spectrometer in the range of 200-900 nm. Elemental analyses were carried out by using a Eurovector EA3000 analyzer. ESI-MS were carried out on a Bruker AmaZon X LCMS Mass Spectrometer. Thermogravimetric analyses were performed on Mettler Toledo TGA/DSC1 in the range of 35-300°C.

Crystallographic data of [Fe(salEen-5-I)$_2$]NCS·0.3CH_2Cl_2·0.5H_2O was collected at 150 K on a Bruker Nonius Kappa CCD diffractometer using MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods within the SHELX suite of programs and refined on F^2 by the full-matrix least-squares method using the SHELXL program via the Olex^2. Powder X-ray diffraction data were measured on a Rigaku SuperNova diffractometer with a HyPix 3000 detector using CuKα radiation (λ = 1.54184 Å). The samples were ground and then suspended in Fomblim Y oil, and the data were collected between 2θ = 5−80°.

Magnetic susceptibility data were collected with a Quantum Design MPMS 5 SQUID magnetometer under an applied field of 1 T over the temperature range 220-430 K. The powdered or polycrystalline samples were placed in gel capsules and care was taken to allow long thermal equilibration times at each temperature.

Synthesis of [Fe(qsal-5-I)$_2$]NCS 1

A solution of 5-iodosalicyladehyde (0.496 g, 2 mmol) in ethanol (6 mL) was charged with N-ethylethylenediamine (0.210 mL, 2 mmol) and stirred at ambient condition for 2 h to produce HsalEen-5-I. Triethylamine (0.278 mL, 2 mmol) was then added and left for 15 minutes for deprotonation. To this mixture, a mixture of iron (III) chloride (0.170 g, 1.0 mmol) and potassium thiocyanate (0.296 g, 3.0 mmol) in ethanol (6 mL) was added through a celite® pad. The reaction was stirred at room temperature for 48 h. A blue tint characteristic of **1** gradually appeared. The solution was filtered and reduced to dryness *in vacuo* to give a black residue. The residue was dissolved in 20 mL CH_2Cl_2 and washed twice with water (20 mL). The resulting CH_2Cl_2 solution was dried with $MgSO_4$ and filtered. Hexane (10 mL) was added to the blue solution and volume slowly reduced under vacuum to give black microcrystals. The crystals were filtered, rinsed with cold Et_2O (5 mL) and dried in air. **1** was collected as a black microcrystalline solid (576 mg, 73%). Elemental analysis: cald (found) for $C_{23}H_{28}N_5O_2I_2SFe$: C, 36.92 (37.23); H, 3.77 (3.93); N, 9.36 (9.28).

FT-IR spectroscopy and UV-Vis Absorption

Table S1.1: Keys FT-IR signals and UV-Vis absorption band of [Fe(salEen-5-I)$_2$]NCS **1**.

	FT-IR				UV-Visible absorption (CH_2Cl_2)
	ν (N-H)	ν (C-H)	ν (NCS)	ν (C=N)	
[Fe(salEen-5-I)$_2$]NCS, **1**	3130	2945, 2939, 2872	2044	1629	240 nm (50976 $M^{-1}cm^{-1}$), 364 nm (8224 $M^{-1}cm^{-1}$), 403 nm (7328 $M^{-1}cm^{-1}$), 576 nm (2784 $M^{-1}cm^{-1}$), 660 nm (2316 $M^{-1}cm^{-1}$),

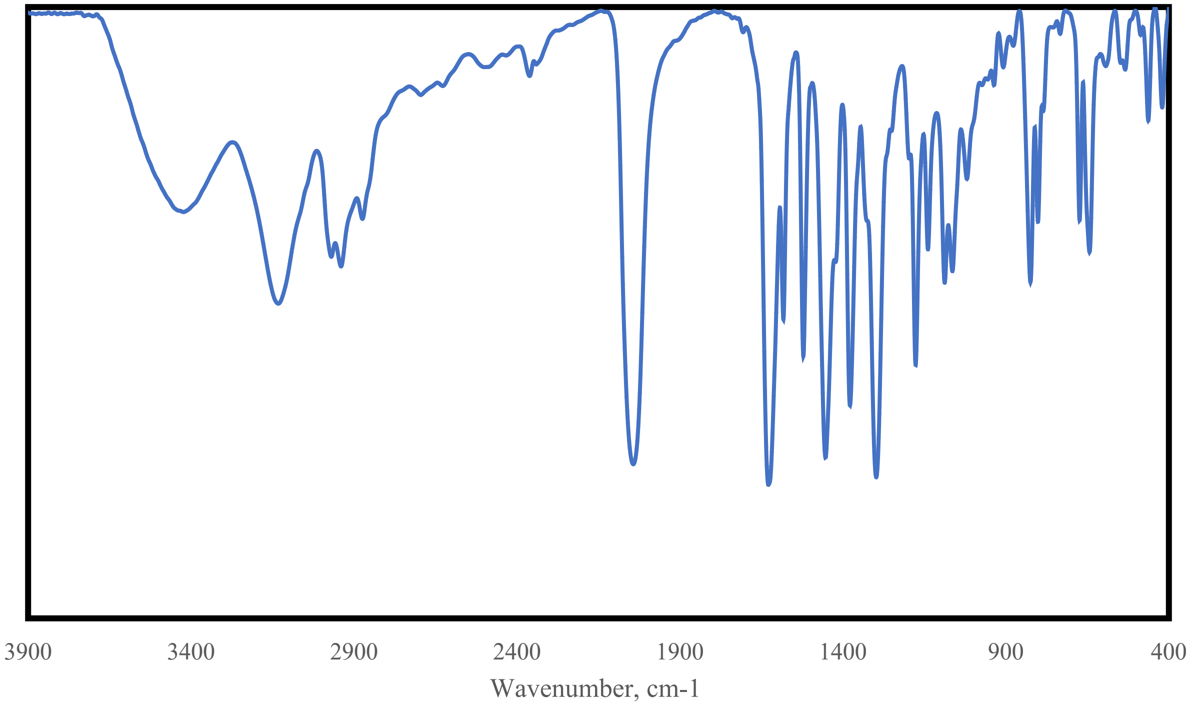

Figure S1. Infrared spectra of **1**

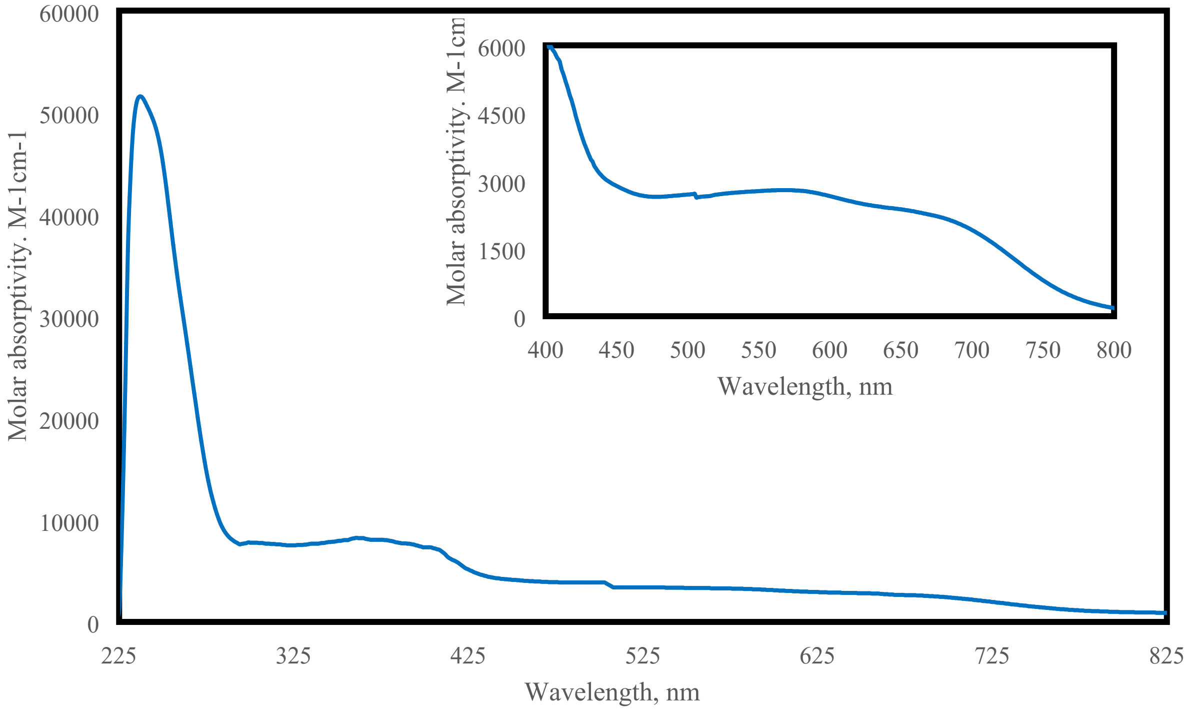

Figure S2. UV-Visible absorption spectra of **1** in CH_2Cl_2.

Mass Spectrometry

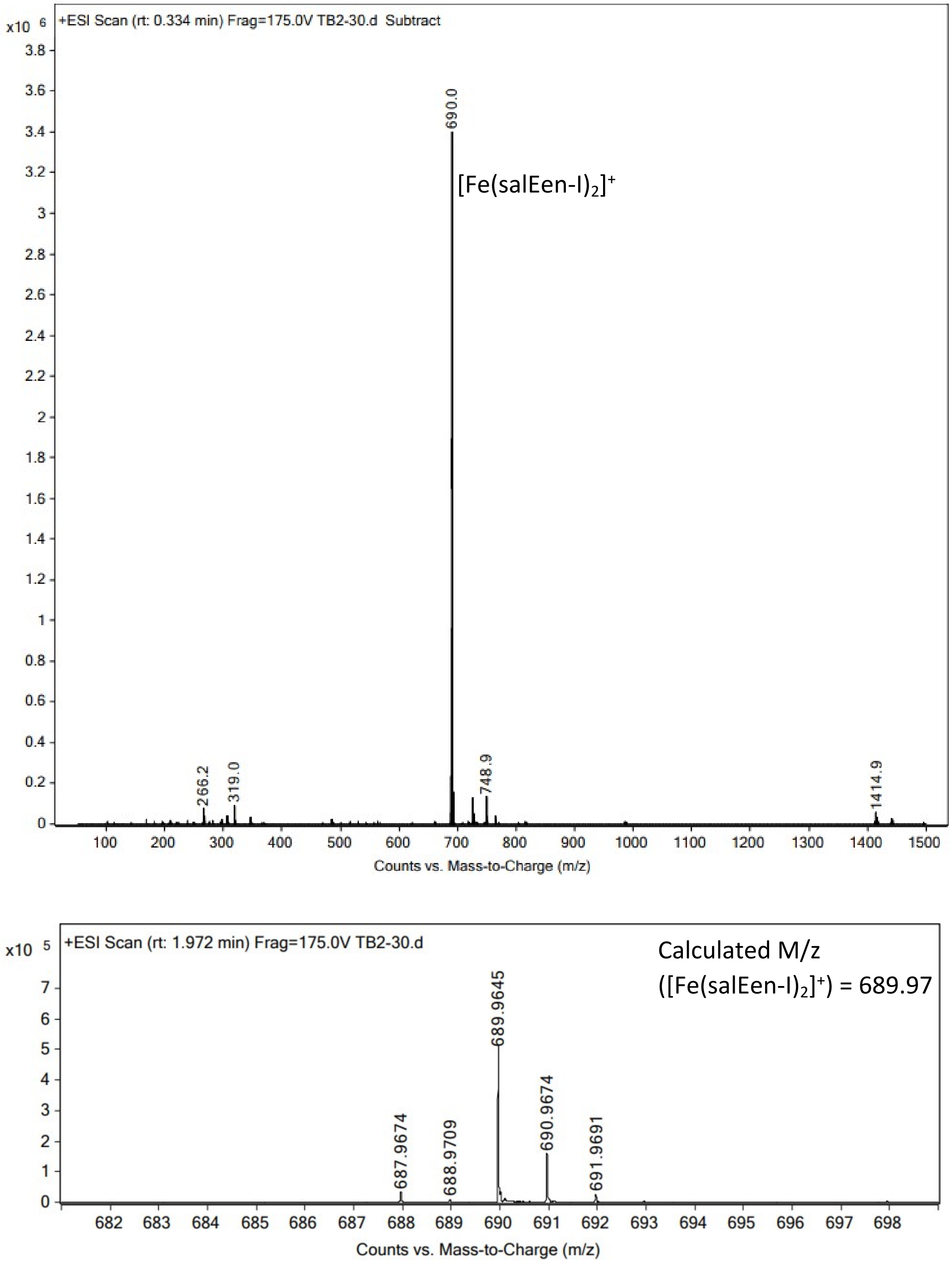

Figure S3. LC-MS (ESI+) of **1**.

Thermogravimetric analysis

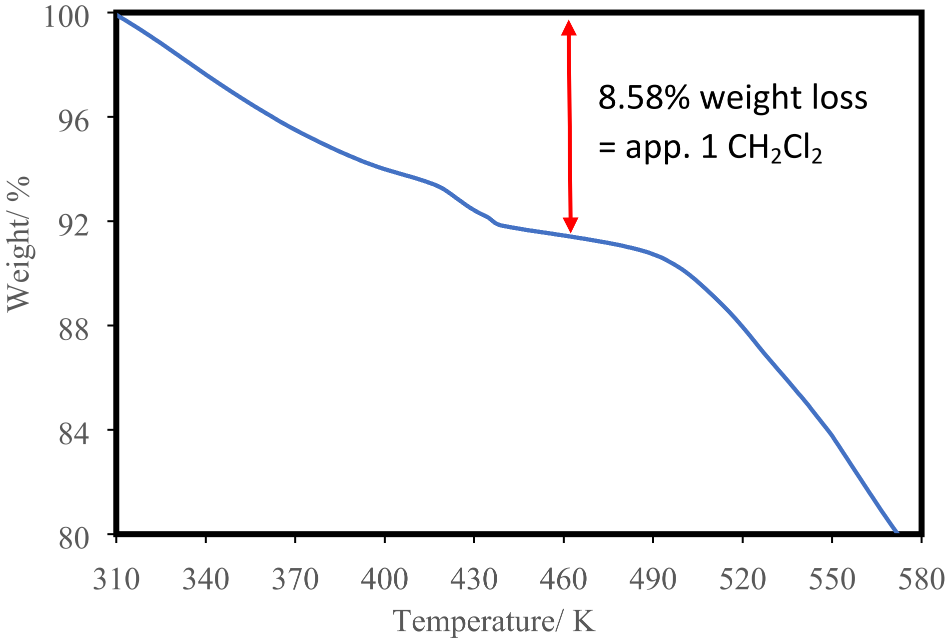

Figure S4. Thermogravimetric profile of **1** upon heating from 35-300°C in the rate of 5°C/min.

X-ray Crystallographic Studies

SCXRD structure

Table S2.1: Crystallographic data and refinement parameters for [Fe(salEen-5-I)$_2$]NCS·0.3CH$_2$Cl$_2$·0.5H$_2$O **1·0.3CH$_2$Cl$_2$·0.5H$_2$O**

	1·0.3CH$_2$Cl$_2$·0.5H$_2$O
Formula	$C_{23.3}H_{28.6}Cl_{0.6}FeI_2N_5O_{2.5}S$
T (K)	150
MW	781.69
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.9536(6)
b (Å)	28.9081(17)
c (Å)	10.6554(6)
α (°)	90
β (°)	109.240(3)
γ (°)	90
Cell volume (Å^3)	2894.7(3)
Z	4
μ (mm^{-1})	2.813
F(000)	1526.0
Crystal size/mm^3	0.1 × 0.05 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.934 to 51.358
Index ranges	$-12 \le h \le 11$, $-35 \le k \le 35$, $-12 \le l \le 12$
Reflections collected	19957
Independent reflections	5471 [R_{int} = 0.0778, R_{sigma} = 0.0789]
Data/restraints/parameters	5471/0/347
Goodness-of-fit on F^2	0.985
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.0853
Final R indexes [all data]	R_1 = 0.0940, wR_2 = 0.0987
Largest diff. peak/hole / e Å^{-3}	0.89/-0.83
CCDC no.	2417988

Table S2.2: Key intermolecular interactions for [Fe(salEen-5-I)$_2$]NCS·0.3CH$_2$Cl$_2$·0.5H$_2$O **1·0.3CH$_2$Cl$_2$·0.5H$_2$O**

	1
T (K)	150
Fe-O$_{ave}$ (Å)	1.880
Fe-N(imine)$_{ave}$ (Å)	1.929
Fe-N(amine)$_{ave}$ (Å)	2.044
Fe1-N/O$_{ave}$ (Å) (Å)	1.951
Σ (°)	46.1
Θ (°)	127
Spin state	LS

Table S2.3: Key intermolecular interactions [Fe(salEen-5-I)$_2$]NCS·0.3CH$_2$Cl$_2$·0.5H$_2$O **1·0.3CH$_2$Cl$_2$·0.5H$_2$O**

	1
T (K)	150
N3/4-H···NCS (Å)	2.004, 1.956 (N6) 2.124, 2.111 (N7)
S1···Cl2	3.679
***1*-D chain perpendicular to ac plane**	
C1-H···O1/2	3.286, 3.623
C15-H···I1	3.377
C19-H···I2	3.257
C32-H···I2	3.242
C16-H···S2	3.028
C22-H···S2	3.103
C32-H···S2	2.611
C16-H···S3	2.978
C22-H···S3	2.490
C11-H···S3	2.637
***2*-D plane perpendicular to ac plane compiling of inverted *1*-D chain**	
C19-H···I2	3.257
C32-H···I2	3.242
C15-H···S2	3.029
C16-H···S2	3.455
C12-H···N6	2.774
C15-H···N6	2.949
C12-H···N7	2.604
C15-H···N7	2.796
Stacking of *2*-D planes *via* translation	
C15-H···I1	3.377
C4-H···I2	3.085
C14-H···I2	3.302

C19-H···I2	3.257
C14-H···Cl1	3.063

PXRD pattern

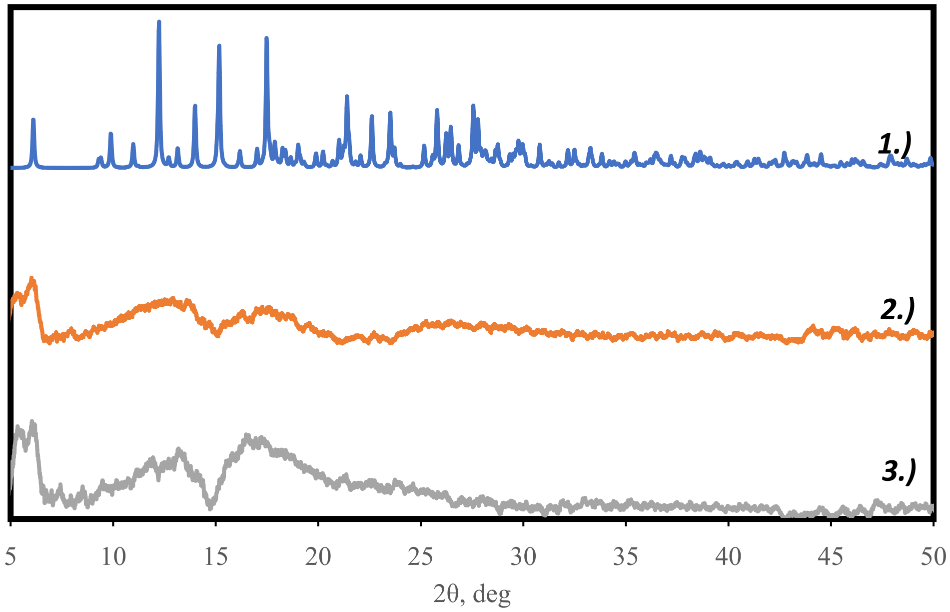

Figure S5. PXRD pattern of **1** displaying 1.) simulated PXRD pattern generated from SCXRD structure of **1**·CH_2Cl_2, 2.) PXRD of **1** after freshly filtered of the recrystallizing solution and 3.) PXRD of **1** after heating at 150°C for 30 minutes to eliminate solvate CH_2Cl_2.

Electrochemical Studies

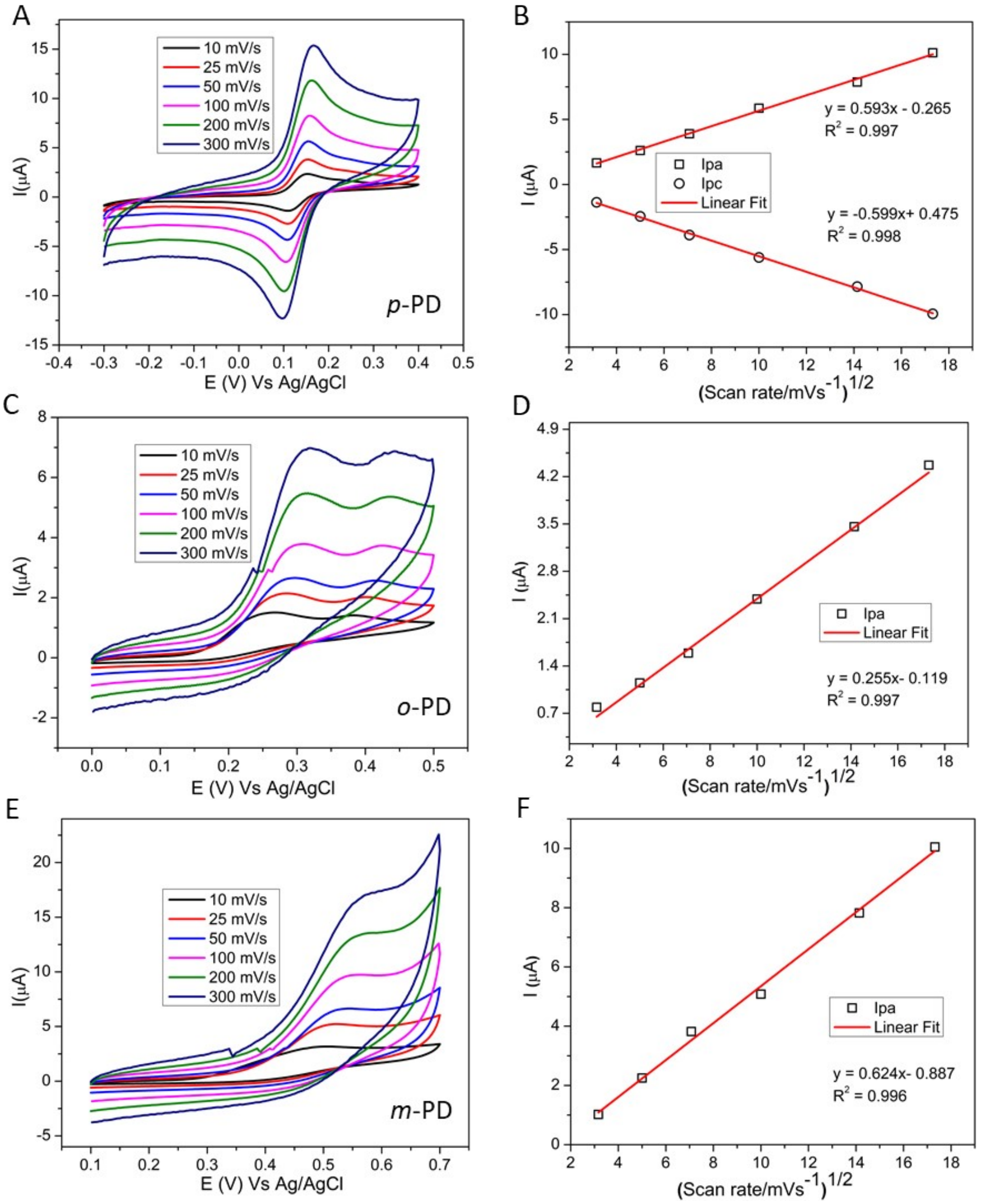

Figure S6. Different scan rate CV voltammograms and linear fitting using 100 μM concentration of indicated analyte in 0.1 M PBS buffer (pH-7) in aq. 0.1 M KCl.

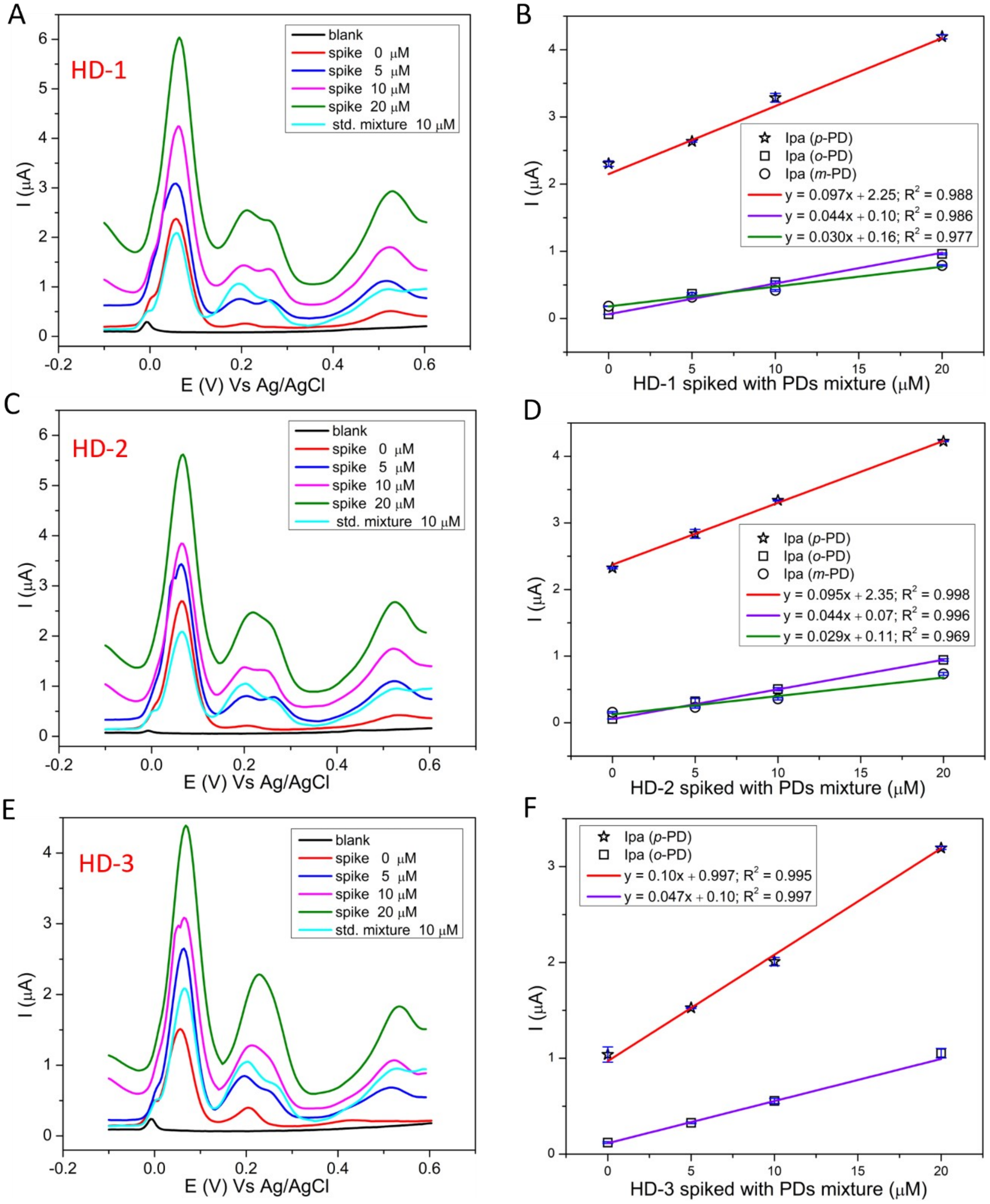

Figure S7. Real sample electrochemical analysis of **1**-SPGE for the quantitative determination of PDs in three different hair colors (HD-1, HD-2 and HD-3) employing spike method.

Table S3.1: comparative analysis of **1-SPGE** for phenylenediamine isomers detections with previously reported electrochemical methods

Electrode	**Method**	**Electrolyte**	**Analyte**	**Detection potential (V)**	**LOD (µM)**	**Linear range (µM)**	**Ref**
PANI/ZnO-starch-rGO/GCO	DPV	PBS, pH-7	*p*-PD	0.24	0.10	1-180	[1]
NG@GCE	LSV	KCl	*p*-PD	0.575	0.67	2-500	[2]
PSC82/GCE	CV	NaOH	*p*-PD	-0.2	0.17	0.5-10400	[3]
CPE	SWV	PBS, pH-7	*p*-PD	0.2	0.071	0.12-3	[4]
GCE	CV, SWV	PBS, pH-7	*p*-PD	0.2	1.2	2-200	[5]
CZE-AD/Pt	Amp	PBS, pH-5.8	*p*-PD	0.85	1.57	2-200	[6]
Laccase/Pt	CV	PBS, pH-6	*p*-PD	-	0.05	0.05-20	[7]
HRP/NPG/GCE	DPV	PBS, pH-7	*p*-PD	0.1	0.33	2-170	[8]
			o-PD	0.21	0.36	2-180	
IL-GO@Cu-Ag/GCE	DPV	PBS, pH-7	*p*-PD	0.21	0.0034	0.018-22	[9]
Fe_3O_4@*f*-MWCNTs/GCE	DPV	PBS, pH-7	*o*-PD	-	50	0.6-80	[10]
SCP/GCE	CV	NaOH	*p*-PD	-0.18	0.3	0.8-5000	[11]
1-SPGE	**DPV**	**PBS, pH-7**	***p*-PD**	**0.09**	**0.062**	**0.3-150**	**This Work**
			***O*-PD**	**0.24**	**0.2**	**0.5-100**	
			***m*-PD**	**0.48**	**0.41**	**0.5-50**	

Abbreviations: PDs – Phenylenediamines, GCE - glassy carbon electrode, PB - prussian blue, SAC – super activated carbon, PANI - polyaniline, rGO – reduced graphene oxide, NG – nitrogen doped graphene, PSC82 – Sr-doped $PrCoO_{3-\delta}$ perovskite oxides, CPE – carbon paste electrode, CZE-AD – capillary zone electrophoresis coupled with amperometric detection screen-printed porous gold, HRP – horseradish peroxidase, IL – Ionic liquid, GO – graphene oxide, Fe_3O_4@*f*-MWCNTs/GCE - Fe3O4 doped with functionalized multiwalled carbon nanotubes, SCP – P doped with perovskite oxide of $SrCoO_{3-\delta}$ (SC), **1-SPGE** – spin crossover Iron (III) complex-based graphene-modified screen printed electrode, *p*-PD - para-phenylenediamine, *o*-PD - ortho-phenylenediamine, *m*-PD - meta-phenylenediamine.

Notes and references

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