Para-substituted Anilines as Potential Precursors for Molecular Electronics: Theoretical and Experimental Investigation

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Introduction

Aniline based compounds play a very important role in designing organic materials for molecular electronics. Thus, for instance, nitroaniline shows an intense negative differential resistance effect and also, its use as possible molecular memory unit has been suggested [1]. This finding leads to an increased interest for substituted aromatic amines as potential units or precursors for molecular electronics, especially when metal-molecule junctions are envisaged.

The nature of metal-molecule contacts and the electronic structure of the molecular backbone represent Critical factors that determine conductivity in a MMM junction.

Both theoretically and experimentally, in order to connect molecules to the metal electrodes S-gold junctions are usually formed. However, in a very recent study [2] it was shown that the variability of the measured conductance for diamine molecule-gold junctions is much less than the variability for dithiol-gold junctions. In view of recent interest in this field, we initiated a structural and electronic structure investigation of a series of substituted aromatic amines and here we will present a joint experimental (FT-IR, Raman, SERS, NMR) and theoretical study on a series of para-substituted anilines: A-NO2, A-CN, and A-CH3 (where A = p-C6H4-NH2).
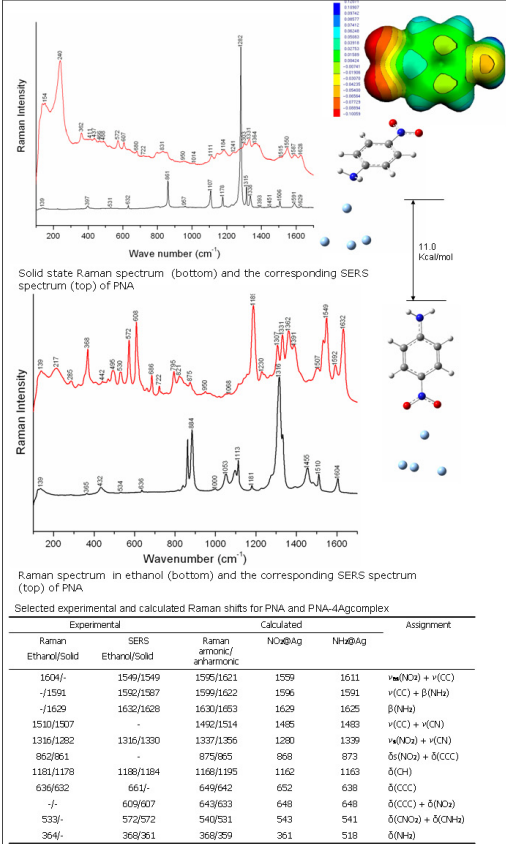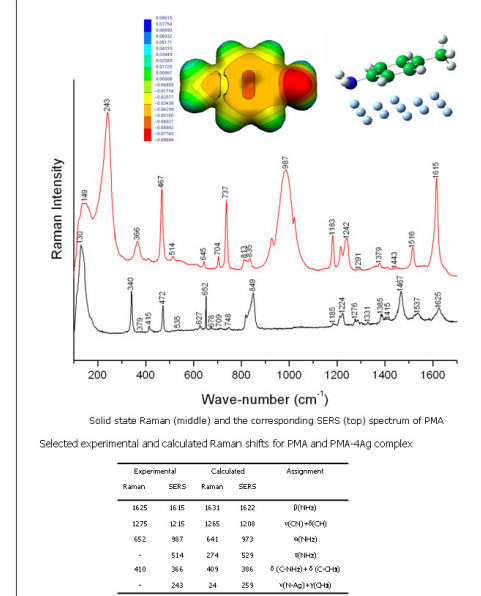
Experimental

The silver colloidal SERS substrate, was prepared according to the method proposed by Leopold and Lendl [3]. Briefly, 0.017 g silver nitrate were solved in 90 ml distilled water. In a separate recipient, 0.017 g of hydroxylamine hydrochloride were solved in 10 ml water, followed by the addition of 0.15 ml sodium hydroxide solution, 2 mol/l (v). The hydroxylamine/sodium hydroxide solution was then added rapidly to the silver nitrate solution under vigorous stirring. After a few seconds a grey brown colloidal solution resulted, with pH value 7.5, and was further stirred for 10 minutes.

Raman spectra were recorded with a Raman Microspectrometer LabRam HR800 (Jobin Yvon) equipped with a coupled charge detector (CCD) and a HeNe laser emitting at 632.8 nm with power set to 14.5 mW. All Raman spectra were recorded with a spectral resolution of 4 cm⁻¹. The SERS spectra were obtained by dissolving a few micrograms of analyte in silver colloid, in a 2.5 ml quartz cuvette. The pH of the silver colloid was 7.5, ensuring the unprotonation of the amino group. The SERS spectra were recorded by averaging 2 scans, each of 60 s. To avoid photodegradation the Raman spectrum of anilin-p-CH3 was recorded by 2 scans, each of 10 minutes and employing a filter to attenuate the laser intensity.
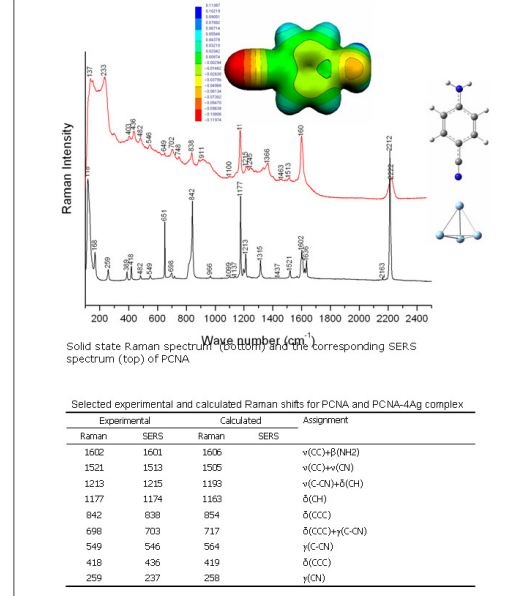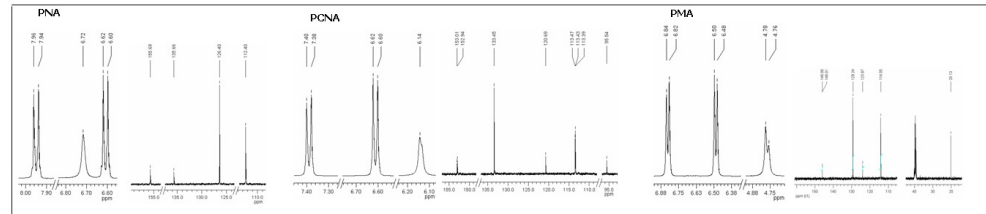
Computational details

DFT approach
Systems: neutral molecules, anions, cations and M-4Ag complexes, where M=PNA, PMA and PCNA
Exchange-correlation functionals: B3LYP, B1LYP, PBEPBE
Basis sets: 6-31G(d), 6-31+G(d,p), 6-311++G(2df,p), cc-pVDZ, LanI2DZ
Properties: geometries, IR, Raman and NMR spectra, frontier MO, MEP, excitation energies (TDDFT//B3LYP/6-31G(d))

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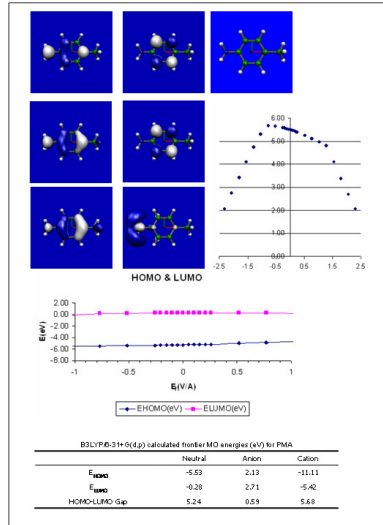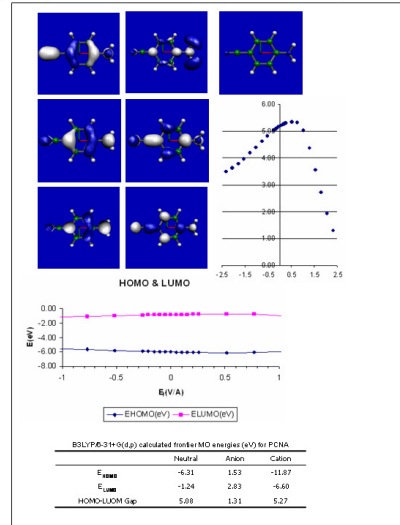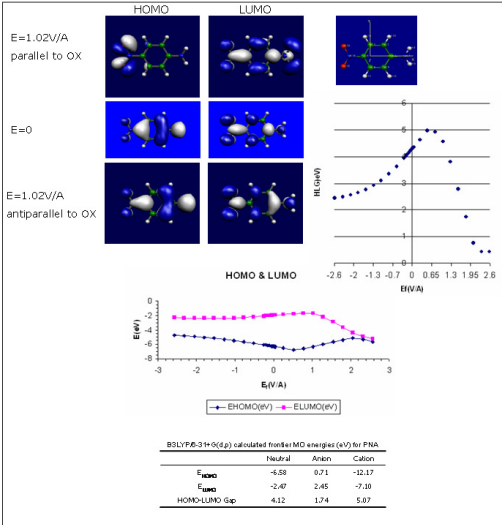
Raman and SERS spectra

Solid state Raman spectrum (bottom) and the corresponding SERS spectrum (top) of PNA

11.0 Kcal/mol

Raman spectrum in ethanol (bottom) and the corresponding SERS spectrum (top) of PNA

Selected experimental and calculated Raman shifts for PNA and PNA-4Agcomplex

Experimental		Calculated		Assignment
Raman Ethanol/Solid	SERS Ethanol/Solid	Raman armonic/anharmonic	NO2@Ag	NH2@Ag	
1604/-	1549/1549	1595/1621	1559	1611	νas(NO2) + ν(CC)
-/1591	1592/1987	1599/1622	1596	1591	ν(CC) + β(NH2)
-/1629	1632/1628	1630/1653	1629	1625	β(NH2)
1510/1507	-	1492/1514	1485	1483	ν(CC) + ν(CN)
1316/1282	1316/1330	1337/1356	1280	1339	νs(NO2) + ν(CN)
862/861	-	875/865	868	873	δs(NO2) + δ(CCC)
1181/1178	1188/1184	1168/1195	1162	1163	δ(CH)
636/632	661/-	649/642	652	638	δ(CCC)
-/-	609/607	643/633	648	648	δ(CCC) + δ(NO2)
533/-	572/572	540/531	543	541	δ(NO2) + δ(CNH2)
364/-	368/361	368/359	361	518	δ(NH2)

Solid state Raman spectrum (bottom) and the corresponding SERS spectrum (top) of PCNA

Selected experimental and calculated Raman shifts for PCNA and PCNA-4Ag complex

Experimental		Calculated		Assignment
Raman	SERS	Raman	SERS	
1602	1601	1606		ν(CC)+β(NH2)
1521	1513	1505		ν(CC)+ν(CN)
1213	1215	1193		ν(C-CN)+δ(CH)
1177	1174	1163		δ(CH)
842	838	854		δ(CCC)
698	703	717		δ(CCC)+γ(C-CN)
549	546	564		γ(C-CN)
418	436	419		δ(CN)
259	237	258		γ(CN)

Solid state Raman (middle) and the corresponding SERS (top) spectrum of PMA

Selected experimental and calculated Raman shifts for PMA and PMA-4Ag complex

Experimental		Calculated		Assignment
Raman	SERS	Raman	SERS	
1625	1615	1631	1622	β(NH2)
1275	1215	1265	1208	ν(CN)+β(NH2)
652	987	641	973	ω(NH2)
-	514	274	529	τ(NH2)
410	366	409	386	δ (C-NH2) + δ (C-CH3)
-	243	24	259	ν(C-Ag)+β(C-CH3)

NMR spectra

PNA

PCNA

PMA

Frontier molecular orbitals

Calculated HOMO-LUMO gap of PNA, PCNA and PMA in an electric field. Negative values means E antiparallel to OX axis

HOMO   LUMO

E=1.02V/A parallel to OX

E=0

E=1.02V/A antiparallel to OX

HOMO & LUMO

HOMO & LUMO

HOMO & LUMO

B3LYP/6-31+G(d,p) calculated frontier MO energies (eV) for PNA

	Neutral	Anion	Cation
E_HOMO	-6.58	0.71	-12.17
E_LUMO	-2.47	2.45	-7.10
HOMO-LUMO Gap	4.12	1.74	5.07

B3LYP/6-31+G(d,p) calculated frontier MO energies (eV) for PCNA

	Neutral	Anion	Cation
E_HOMO	-6.31	1.53	-11.87
E_LUMO	-0.28	2.71	-6.60
HOMO-LUOM Gap	5.08	1.31	5.27

B3LYP/6-31+G(d,p) calculated frontier MO energies (eV) for PMA

	Neutral	Anion	Cation
E_HOMO	-5.53	2.13	-11.11
E_LUMO	-0.28	2.71	-5.42
HOMO-LUMO Gap	5.24	0.59	5.68

PNA ¹H NMR

Protons	Experimental	Calculated
H_amine	6.72	3.00
H10,H13	6.61	6.15
H11,H12	7.95	7.96

PCNA ¹H NMR

Protons	Experimental	Calculated
H_amine	6.14	2.81
H10,H13	6.61	6.19
H11,H12	7.39	7.18

PMA ¹H NMR

Protons	Experimental	Calculated
H_amine	4.77	2.36
H10,H13	6.49	6.18
H11,H12	6.83	6.80
H_methyl	2.13	2.04

PNA ¹³C NMR

Carbons	Experimental	Calculated
C1	155.7	142.2
C2,C6	112.4	106.0
C3,C5	126.4	121.0
C4	135.7	133.5

PCNA ¹³C NMR

Carbons	Experimental	Calculated
C1	153.0	140.4
C2,C6	113.5	106.7
C3,C5	133.5	128.1
C4	95.5	97.7
C14	113.5	107.8

PMA ¹³C NMR

Carbons	Experimental	Calculated
C1	146.0	136.3
C2,C6	114.1	107.0
C3,C5	129.2	123.2
C4	124.0	119.7
C14	20.1	21.3

- Preponderant perpendicular orientation to the silver surface.
- Adsorption through nitro group is energetically more favored than through NH2 group.
- Tilted orientations can not be excluded
- Strong intermolecular interactions between PNA and DMSO molecules through NH2 group
- HOMO-LUMO gap increases in the order: PNA, PCNA, PMA for neutral molecules and cations
- HOMO-LUMO gap decreases in the order: PNA, PCNA, PMA for anions due to increasing of the HOMOs energies

- Preponderant perpendicular orientation to the silver surface.
- Adsorption through nitro and CN groups are both possible
- Strong intermolecular interactions between PCNA and DMSO molecules through NH2 group

- Preponderant flat orientation to the silver surface.
- Amino group adopts a orientation according to which the stretching vibrations occur parallel to the silver surface.
- sp³ hybridized C atom vibrations, suggest that the methyl group lies in the close vicinity of the silver surface.
- Weaker intermolecular interactions between PMA and DMSO molecules through NH2 group than for PNA and PCNA