Supporting Information

Evolution of Self-Organized Microcapsules with Variable Conductivities from Self-Assembled Nanoparticles at Interfaces

Voichita Mihali, † Andrei Honciuc*†

†Institute of Chemistry and Biotechnology, Zurich University of Applied Sciences, Einsiedlerstrasse 31, 8820 Waedenswil, Switzerland

*andrei.honciuc@zhaw.ch

This PDF file includes:

Materials
Synthesis of Nanoparticles
Microcapsules Obtained by Pickering Emulsion Polymerization
Electrical and Optical Properties of Microcapsules
Figures and Table
References
MATERIALS

Styrene (Sty) (> 99%), divinylbenzene (DVB) (80%), sodium 4-vinylbenzenesulfonate (NaVBS) (> 90%), ammonium peroxydisulfate (APS) (> 98%), 2,2′-azobis(2-methylpropionitrile) (AIBN) (> 98%), ammonium hydroxide solution (NH₄·OH) (28%), basic alumina (Al₂O₃) (≥ 98%), 3,4-ethylenedioxythiophene (EDOT), 3-(triethoxysilyl)propyl-methacrylate (TSPM) (> 99%), aniline were purchased from Sigma-Aldrich. Sty and DVB were passed through basic alumina to remove the stabilizer before usage. AIBN was purified by re-crystallization twice from methanol and stored at -20 °C before usage. Other reagents were used as received. Ultrapure water (UPW; conductivity c=0.055 µS/cm and resistivity, ρ=18.2 MΩ cm at 298 K) was obtained from an Arium 611 VF water purification system (Startorius stedim biotech, Aubagne, France).

SYNTHESIS OF NANOPARTICLES

Surfactant-Free Seed PS Nanoparticles (PS-HNPs). The NaVBS (100 mg) and APS (135 mg) were dissolved in 200 mL mixture of H₂O and methanol (v/v = 9/1) at room temperature. Then 27 mL mixture of Sty and DVB (810 µL) was added into the solution. The polymerization was carried out under Ar atmosphere at 70 °C for 16 h. The PS seed NP were purified by centrifugation and rinsed with UPW and ethanol; the rinsing procedure was repeated three times. Their diameter was 300±10 nm with a zeta potential of -42.1 mV and the SEM image of seed PS nanoparticles are given in Figure 1a in the main text.

Surfactant-Free Snowman Janus Nanoparticles with Varying Lobe Sizes. 1 g seed PS NPs were dispersed in 30 mL UPW and this solution was deoxygenated by bubbling Ar for 30 minutes at r.t. Separately 10 mg AIBN were dissolved in 1 mL or 2 mL TSPM monomer and then dispersed in 15
mL UPW to prepare JNPs-1 and JNPs-2 respectively. This mixture was emulsified by ultrasonication (with a Branson 450, with a ½ inch processing horn at 50% intensity amplitude) for 1 minutes with ice-cooling. This emulsified solution was added dropwise into the PS solution at r.t for 20 minutes. Then the pH value of reaction was adjusted to 9.0 with NH₄OH and the polymerization was carried out under Ar atmosphere at 70 °C for 24 h with 400 rpm. The JNPs were purified by centrifugation and rinsed with UPW and ethanol; the rinsing procedure was repeated twice. The SEM image of Janus nanoparticles are given in Figure 1b,c in the main text and show that relative size ration between the PTSPM lobe (appearing brighter) vs. PS lobe is larger for the JNPs-2 and oppositely for JNPs-1. The zeta potential of JNPs was -41.7 mV for JNPs-1 and -42.5 mV for JNPs-2.

**Mechanism of Asymmetric Modification of JNPs with PANI.** The mechanism of asymmetric modification of JNPs with PANI appears to be in agreement with the previously reported observations on the selective modification of JNPs with PPy. In acidic conditions, pH < 2, the anilinium salt (aniline pKa ~ 4.63) can migrate by electrostatic attraction to the PS Janus lobe carrying negatively charged sulfonic –SO₃⁻ groups.

**Nanoparticle Characterization.** The NPs, JNPs and PEDOT microcapsules were characterized with the scanning electron microscopy (SEM) (FEI Quanta FEG 250, operating at 5–30 kV accelerating voltage in the secondary electron (SE) mode, in high vacuum mode (3 × 10⁻⁶ – 1.8 × 10⁻⁵ mbar). The PANI-HNPs, selectively modified PANI-JNPs and PEDOT microcapsules were Au sputtered, when specified, with a sputter-coater (Q15OR-S Sputter Coater, Quorum) with operating parameter at 20 mA for 30 sec, under Ar atmosphere (sputter vacuum: 5 × 10⁻² mbar). UV-vis-NIR absorption spectra were measured on the solid-state using UV-vis-NIR spectrophotometer (Metrohm AG, NIRS XDS MasterLab Analyzer).

**MICROCAPSULES OBTAINED BY PICKERING EMULSION POLYMERIZATION**
The Pickering emulsion of molten paraffin wax/water mixtures was obtained from 70 mg PANI-JNPs-2, 0.5 mL paraffin wax and 7 mL UPW, in the same condition used for a synthesis of PEDOT microcapsule, but the working temperature was 85°C, above the melting point of the paraffin wax \( (C_nH_{2n+2}, \text{m.p. } 53-57 \, ^\circ\text{C}, \text{CAS: } 8002-74-2, \text{Sigma-Aldrich}) \). The obtained emulsion was rapidly cooled with ice down to room temperature and the molten wax solidified into colloidosomes that were analyzed with SEM, Figure S1.

![Figure S1. Armor of self-assembled monolayer of JNPs formed during emulsification at the paraffin wax-water interface. SEM images of the self-assembled of PANI-JNPs-2 monolayers at the paraffin wax-water interface obtained with 70 mg of PANI-JNPs-2. (a, c) SEM image of the paraffin wax colloidosome resulting from cooling and solidification of the paraffin wax/water Pickering emulsion stabilized by the PANI-JNPs-2. (b, d) Magnified SEM image showing the monolayer of JNPs at the surface of the paraffin wax colloidosome, where a large fraction of JNPs appear to have a preferred orientation: the more hydrophilic PANI lobe (the lobe with rough surface) is oriented toward water and the more hydrophobic PTSPM lobe (the lobe with smooth surface) toward paraffin wax.](image)
The PANI-HNPs and the asymmetric modified PANI-JNPs in different concentration with a good dispersity in the water are used for Pickering emulsion of PEDOT. From the fluorescent microscopy we can observe that the size of the droplet (oil phase) decrease by increasing the amount of PANI-HNPs, PANI-JNPs-1 or PANI-JNPs-2, see Table S1. The PEDOT droplets stabilized from NPs form stable oil in water emulsion which is still stable for more than 6 month, see Figure S2. We have attempted to synthesize microcapsules by using 50 mg of HNPs, JNPs-1 and JNPs-2 but no Pickering emulsion could be obtained, which suggests that the PANI nanoparticles play a key role in the Pickering emulsion formation, in re-enforcing and preserving the structural integrity of the microcapsule.

Table S1. The droplets size obtained from fluorescent microscopy of EDOT stabilized with different amount of nanoparticles: PANI-HNPs (10 mg, 25 mg, 50 mg, 70 mg; Entry 1-4); PANI-JNPs-1 (10 mg, 25 mg, 50 mg, 70 mg; Entry 5-8) and PANI-JNPs-2 (10 mg, 25 mg, 50 mg, 70 mg; Entry 9-12).

| Entry | Particle type   | Weight NPs (mg) | Diameter of droplets (µm) |
|-------|-----------------|-----------------|---------------------------|
| 1     | PANI-HNPs       | 10              | 87 ± 6                    |
| 2     | PANI-HNPs       | 25              | 77 ± 5                    |
| 3     | PANI-HNPs       | 50              | 25 ± 1                    |
| 4     | PANI-HNPs       | 70              | 18 ± 0.7                  |
| 5     | PANI-JNPs-1     | 10              | 79 ± 1                    |
| 6     | PANI-JNPs-1     | 25              | 61 ± 3                    |
| 7     | PANI-JNPs-1     | 50              | 23 ± 1                    |
| 8     | PANI-JNPs-1     | 70              | 16 ± 0.7                  |
| 9     | PANI-JNPs-2     | 10              | 63 ± 3                    |
| 10    | PANI-JNPs-2     | 25              | 59 ± 3                    |
| 11    | PANI-JNPs-2     | 50              | 20 ± 2                    |
| 12    | PANI-JNPs-2     | 70              | 12 ± 1                    |

The presence of electrolyte may also affect the stability of the Pickering emulsion obtained, in this case the APS oxidant initiator; therefore we have tested the emulsion stability in the presence of a neutral electrolyte, namely 4.67 mmol (NH₄)₂SO₄ in an emulsion of 0.5 mL EDOT (4.67 mmol) and 50 mg PANI-JNPs as emulsion stabilizer in 7 mL UPW. We have monitored the o/w emulsion by fluorescence microscopy and the emulsion was still stable after 6 month (Figure S2).
Figure S2. Fluorescent microscopy image of EDOT/water (v/v = 0.5/7) emulsion formed in the presence of 4.67 mmol of \((\text{NH}_4\text{)}_2\text{SO}_4\) in 7.5 mL emulsion volume.

Figure S3. Mechanism of polymerization of an EDOT droplet stabilized by JNPs. In the initial stage the JNPs monolayer build a protective armor around the oil droplet. During polymerization the EDOT monomer at the interface polymerizes. As the PEDOT layer grows thicker more monomer must diffuse through the formed PEDOT layer to meet the APS initiator. In the final stage a PEDOT layer builds around and in between the JNPs.
Figure S4. Polymerization of a macroscopic droplet of EDOT in water (in the absence of stabilizing nanoparticles) after ultrasonication initiated by APS. EDOT undergoes an interfacial polymerization mechanism. The PEDOT is smooth in the interior and at the exterior volcano-like protuberances bulging out toward the water phase indicate that membrane rupturing, and healing took place to enable the ejection of the EDOT monomer through the growing PEDOT layer at the interface.

The microcapsules obtained by interfacial polymerization of Pickering emulsions have on the interior side of the wall (inner) a honeycomb-like morphology with one nanoparticle occupying one cell, as seen in the SEM images Figure S5 and Figure S6.
Figure S5. Self-organization in microcapsule walls. SEM images of the self-organized PEDOT PANI-HNPs microcapsule walls obtained with variable amount of PANI-HNPs: (a) 10 mg, (b) 25 mg, (c) 50 mg, (d) 70 mg. The first row of images show the structure of the outer wall, and second row of images shows the inner structure of the wall with PANI-HNPs occupying each cell.

Figure S6. Self-organization in microcapsule walls. SEM images of the self-organized PEDOT PANI-JNPs-1 microcapsule walls obtained with variable amount of PANI-JNPs-1: (a) 10 mg, (b) 25 mg, (c) 50 mg, (d) 70 mg. The first row of images show the structure of the outer wall, and second row of images shows the inner structure of the wall with PANI-JNPs-1 occupying each cell.

Table S2. Evolution of the wall parameters of the hierarchical microcapsule function of the nanoparticle and APS concentration: thickness of PEDOT layer ($T_1$), distance between particles
outside ($D_1$), distance between particles inside ($D_2$) and the interparticle thickness ($T_2$) from the SEM images measurement of microcapsule of PEDOT and effective number density of nanoparticles ($\rho_A$) per surface area of microcapsule calculated with the formula: $\rho_A = \frac{N_{\text{nanoparticles}}}{A_{\text{microcapsule}}}$.

| Entry | Particle type  | Amount of Nanoparticles (mg) | Molar ratio (APS/EDOT) | $T_1$ (nm) | $D_2$ (nm) | $D_1$ (nm) | $T_2$ (nm) | $\rho_A$ ($\mu$m$^{-2}$) |
|-------|----------------|------------------------------|------------------------|------------|------------|------------|------------|-------------------|
| 1     | PANI-HNPs      | 10                           | 0.25                   | 164 ± 3    | 415 ± 2    | 654 ± 8    | 195 ± 4    | 5.8               |
| 2     | PANI-HNPs      | 25                           | 0.25                   | 105 ± 2    | 335 ± 10   | 452 ± 7    | 101 ± 3    | 7.6               |
| 3     | PANI-HNPs      | 50                           | 0.25                   | 90 ± 3     | 362 ± 5    | 403 ± 8    | 79 ± 4     | 8.9               |
| 4     | PANI-HNPs      | 70                           | 0.25                   | 92 ± 4     | 328 ± 3    | 383 ± 9    | 51 ± 6     | 9.3               |
| 5     | PANI-HNPs      | 50                           | 0.5                    | 92 ± 1     | 395 ± 1    | 498 ± 4    | 99 ± 7     | 6.4               |
| 6     | PANI-JNPs-1    | 10                           | 0.25                   | 173 ± 3    | 607 ± 6    | 803 ± 3    | 217 ± 8    | 1.7               |
| 7     | PANI-JNPs-1    | 25                           | 0.25                   | 141 ± 4    | 532 ± 5    | 646 ± 4    | 203 ± 3    | 3.5               |
| 8     | PANI-JNPs-1    | 50                           | 0.25                   | 108 ± 3    | 508 ± 3    | 521 ± 6    | 151 ± 6    | 3.8               |
| 9     | PANI-JNPs-1    | 70                           | 0.25                   | 95 ± 2     | 506 ± 2    | 560 ± 6    | 115 ± 7    | 3.9               |
| 10    | PANI-JNPs-1    | 50                           | 0.5                    | 236 ± 3    | 687 ± 4    | 805 ± 3    | 190 ± 4    | 2.1               |
| 11    | PANI-JNPs-2    | 10                           | 0.25                   | 250 ± 7    | 750 ± 12   | 820 ± 14   | 254 ± 9    | 1.7               |
| 12    | PANI-JNPs-2    | 25                           | 0.25                   | 203 ± 3    | 660 ± 13   | 773 ± 16   | 207 ± 8    | 2.3               |
| 13    | PANI-JNPs-2    | 50                           | 0.25                   | 130 ± 4    | 537 ± 2    | 652 ± 6    | 192 ± 4    | 3.4               |
| 14    | PANI-JNPs-2    | 70                           | 0.25                   | 106 ± 4    | 539 ± 8    | 564 ± 6    | 132 ± 5    | 3.5               |
| 15    | PANI-JNPs-2    | 50                           | 0.5                    | 281 ± 2    | 672 ± 2    | 806 ± 4    | 223 ± 4    | 2.2               |
| 16    | PANI-JNPs-2    | 50                           | 1                      | 310 ± 3    | 798 ± 5    | 834 ± 5    | 242 ± 6    | 1.6               |
| 17    | PANI-JNPs-2    | 25                           | 1                      | 293 ± 4    | 820 ± 5    | 923 ± 5    | 283 ± 5    | 1.5               |
| 18    | PANI-JNPs-2    | 70                           | 1                      | 178 ± 5    | 655 ± 4    | 756 ± 4    | 165 ± 6    | 2.3               |
ELECTRICAL PROPERTIES OF MICROCAPSULES

Electrical resistance of the nanoparticles and microcapsules was measured using a standard two-point probe technique at room temperature. For this purpose, 80 mg of powder consisting of hierarchical PEDOT microcapsules were pressed with a 10 ton hydraulic press into pellets (0.035 cm thick, 1.30 cm diameter) for 4 minutes under vacuum. Current-voltage (I-V) sweeps of the samples were acquired using a computer controlled Keithley 2182A as voltage source and a Fluke 8846A 6.5 digit precision multimeter for the current measurement. The resistance was calculated from the slope of the I-V curves and converted into resistivity (Ω·cm) and electrical conductivity (S/cm). The resistivity was calculated from the resistance $R$ with the formula: $\rho = \frac{A \cdot R}{l}$, where $A$ – was calculated as the cross section area of the pellet with a radius 0.65 cm and $l$ - the current path length was the same as the thickness of the pellet ($l=0.035$ cm).

The conductivity of the PANI-HNPs, selective modified PANI-JNPs and the microcapsule obtained by using different amount of PANI-JNPs as a stabilizer and different amount of APS was determined from the current vs. voltage (I-V) curves presented in Figure S7, Figure S8 and Figure S9. From the slope of the I-V curved in Figure S7, S8 and S9 it can be clearly seen that the largest resistance corresponds to the PANI-JNPs-2, followed by PANI-JNPs-1 and PANI-HNPs while the smallest resistance to the microcapsule obtained with PANI-HNPs, APS/EDOT molar ratio 0.5 and these data are presented in Table S3.
Figure S7. Current- voltage (I-V) sweeps of PANI-HNPs and microcapsule. (a) I-V data of PANI-HNPs. I-V curves of microcapsules obtained with constant APS/EDOT molar ratio 0.25 and different amounts of PANI-HNPs: (b) 10 mg, (c) 25 mg (d) 50 mg and (e) 70 mg. (f) I-V sweeps of microcapsules obtained with 50 mg PANI-HNPs and molar ratio APS/EDOT 0.5. The I-V data were acquired at room temperature on 0.05 cm thick pellets made in the same conditions for all the samples. The I–V sweeps were performed on three different samples and the average data are presented here; the error bars represent the standard deviation of the measurement.
Figure S8. Current-voltage (I-V) sweeps of PANI-JNPs-1 and microcapsule. (a) I-V data of PANI-JNPs-1. I-V curves of microcapsules obtained with constant APS/EDOT molar ratio 0.25 and different amounts of PANI-JNPs-1: (b) 10 mg, (c) 25 mg (d) 50 mg and (e) 70 mg. (f) I-V sweeps of microcapsules obtained with 50 mg PANI-JNPs-1 and molar ratio APS/EDOT 0.5. The I-V data were acquired at room temperature on 0.05 cm thick pellets made in the same conditions for all the samples. The I–V sweeps were performed on three different samples and the average data are presented here; the error bars represent the standard deviation of the measurement.
Figure S9. Current-voltage (I-V) sweeps of PANI-JNPs-2 and microcapsule. (a) I-V data of PANI-JNPs-2. I-V curves of microcapsules obtained with constant APS/EDOT molar ratio 0.25 and different amounts of PANI-JNPs-2: (b) 10 mg, (c) 25 mg (d) 50 mg and (e) 70 mg. I-V sweeps of microcapsules obtained with 50 mg PANI-JNPs-2 and different APS/EDOT molar ratio: (f) 0.5 and (g) 1. The I-V data were acquired at room temperature on 0.05 cm thick pellets made in the same conditions for all the samples. The I–V sweeps were performed on three different samples and the average data are presented here; the error bars represent the standard deviation of the measurement.
Table S3. The resistance, resistivity and conductivity of the PANI-HNPs, PANI asymmetric modify JNPs and microcapsule.

| Entry | Structure type | Particle type | Amount of Nanoparticles (mg) | Molar ratio (APS/EDOT) | Resistance* ($R$) (Ω) | Resistivity** ($\rho$) (Ω cm) | Conductivity*** ($c$) mS cm$^{-1}$ |
|-------|----------------|---------------|-------------------------------|------------------------|------------------------|-------------------------------|----------------------------------|
| 1     | Microcapsule   | PANI-HNPs     | 340.90 ± 0.01                 | 12921.91               | 7.73 x 10$^{-2}$ ± 0.01|
| 2     | Microcapsule   | PANI-HNPs     | 14.00 ± 0.01                  | 530.38                 | 1.89 ± 0.01             |
| 3     | Microcapsule   | PANI-HNPs     | 12.80 ± 0.01                  | 485.12                 | 2.06 ± 0.01             |
| 4     | Microcapsule   | PANI-HNPs     | 10.67 ± 0.01                  | 404.09                 | 2.47 ± 0.01             |
| 5     | Microcapsule   | PANI-HNPs     | 5.70 ± 0.01                   | 216.14                 | 4.62 ± 0.01             |
| 6     | Microcapsule   | PANI-HNPs     | 4.33 ± 0.02                   | 164.42                 | 6.08 ± 0.02             |
| 7     | Microcapsule   | PANI-JNPs-1   | 50.00 ± 0.01                  | 18952.14               | 5.27 x 10$^{-2}$ ± 0.01|
| 8     | Microcapsule   | PANI-JNPs-1   | 20.28 ± 0.01                  | 768.85                 | 1.30 ± 0.01             |
| 9     | Microcapsule   | PANI-JNPs-1   | 19.16 ± 0.01                  | 726.60                 | 1.38 ± 0.01             |
| 10    | Microcapsule   | PANI-JNPs-1   | 11.53 ± 0.02                  | 437.02                 | 2.29 ± 0.02             |
| 11    | Microcapsule   | PANI-JNPs-1   | 7.50 ± 0.02                   | 284.42                 | 3.51 ± 0.02             |
| 12    | Microcapsule   | PANI-JNPs-1   | 7.16 ± 0.01                   | 271.52                 | 3.68 ± 0.01             |
| 13    | Microcapsule   | PANI-JNPs-2   | 250.00 ± 0.01                 | 952.37                 | 1.05 ± 0.01             |
| 14    | Microcapsule   | PANI-JNPs-2   | 25.12 ± 0.01                  | 952.37                 | 1.05 ± 0.01             |
| 15    | Microcapsule   | PANI-JNPs-2   | 21.25 ± 0.01                  | 805.33                 | 1.24 ± 0.01             |
| 16    | Microcapsule   | PANI-JNPs-2   | 13.88 ± 0.01                  | 526.20                 | 1.90 ± 0.02             |
| 17    | Microcapsule   | PANI-JNPs-2   | 8.23 ± 0.02                   | 312.14                 | 3.20 ± 0.02             |
| 18    | Microcapsule   | PANI-JNPs-2   | 7.36 ± 0.01                   | 279.25                 | 3.58 ± 0.01             |
| 19    | Microcapsule   | PANI-JNPs-2   | 10.61 ± 0.01                  | 402.38                 | 2.48 ± 0.01             |
| 20    | Microcapsule   | PANI-JNPs-2   | 13.89 ± 0.01                  | 526.44                 | 1.89 ± 0.02             |
| 21    | PEDOT polymer   | no particles  | 66.08 ± 0.01                  | 2504.68                | 3.99 x 10$^{-4}$        |

*Data calculated from the slope of the I-V curves in Figure S7, Figure S8 and Figure S9. **Data calculated from the resistance values, the thickness of the pellet ($l = 0.035$ cm) and cross-section area with the formula: $\rho = (A \cdot R)/l$, where the current length is the same of thickness of the pellet and the cross section area was the area of the pellet with a radius 0.65 cm. ***Data calculated from the resistivity values with the formula $c = 1/\rho$ and the respective errors propagated from resistance.
Figure S10. UV-Vis-NIR absorption spectra: (a) Microcapsule with different concentration of PANI-HNPs (I) 10 mg, (II) 25 mg (III) 50 mg and (IV) 70 mg; (b) Microcapsule with different concentration of PANI-JNPs-1 (I) 10 mg, (II) 25 mg (III) 50 mg and (IV) 70 mg; (c) Optical properties of Microcapsule obtained with different types of nanoparticles at the same concentration 50 mg and with 0.5 APS/EDOT molar ratio: (I) PANI-JNPs-1, (II) PANI-HNPS.
From the literature it is known that the typical absorption band of (PANI\(^+\)) emeraldine salt (ES) is at 340 nm can be ascribed to the $\pi-\pi^*$ in the benzoid ring, polaron band transitions appear at 450 nm; meanwhile, the localized polaron bands transitions appear in the range of 700–800 nm.\(^3\) The UV-Vis-NIR absorption spectra of microcapsule of PEDOT obtained with different concentration of nanoparticles from 10 mg to 70 mg of PANI-HNPs and PANI-JNPs-1 are reported in Figure S9. The absorption bands related to $\pi-\pi^*$ transition exhibited a substantial red shift in the absorption spectrum from 590 in the Microcapsule with 10 mg PANI-HNPs to 684 nm for 70 mg and in the microcapsule obtained with PANI-JNPs-1 by increase the concentration from 10 to 70 mg the red-shift is from 601 to 683, owing to a decrease in the band-gap energy as a result of the doping process.\(^4\) The absorption of bipolaronic PEDOT\(^{2+}\) band can be also observed a red-shift in both cases by using PANI-HNPs and PANI-JNPs-1 in the microcapsule of PEDOT and this indicates a transition toward the more quinoid structure with increase the concentration of nanoparticles, which translates in a higher electrical conductivity.

**REFERENCES**

(1) Mihali, V.; Honciuc, A. Semiconductive Materials with Tunable Electrical Resistance and Surface Polarity Obtained by Asymmetric Functionalization of Janus Nanoparticles. *Adv. Mater. Interfaces* 2017, 4, 1700914:1-11.

(2) Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K. J.; Samuelson, L. Enzymatically Synthesized Conducting Polyaniline. *J. Am. Chem. Soc.* 1999, 121, 71–78.

(3) Dennany, L.; Innis, P. C.; McGovern, S. T.; Wallace, G. G.; Forster, R. J. Electronic Interactions within Composites of Polyanilines Formed under Acidic and Alkaline Conditions. Conductivity, ESR, Raman, UV-Vis and Fluorescence Studies. *Phys. Chem. Chem. Phys.* 2011, 13, 3303-3310.
(4) Bredas, J. L.; Street, G. B. Polarons, Bipolarons, and Solitons in Conducting Polymers. Acc. Chem. Res. 1985, 18, 309–315.