Supplementary Information for

Synthesis and polymerization of polyelectrolyte-based conductive inks: the protagonism of the coadjutant oxidizing salt.

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SI-1. Dynamic Light Scattering (DLS)

The measurements were carried out in a quartz cuvette of a 10 mm optical path, with four polished sides, using a Litesizer™ 500 DLS equipment provided with a Laser diode light source (output power = 40 mW, and λ = 658 nm). The cuvette was washed in an ultrasonic bath using detergent (Merck, Extran MA 02), deionized water, and isopropyl alcohol (Synth), each step for 10 minutes, followed by drying in an oven for 2 hours. We evaluate several aqueous mixtures, as follow: an aqueous solution of a poly-salt PSS with 0.93 wt.% (PSSNa, M_w = 70 kDa, Aldrich), without the addition of OA, named the "OA-free PSSNa" sample. An aqueous solution of a poly-acid PSS of 0.93 wt.% (PSS, M_w = 75kDa, Aldrich) was also prepared without the addition of OA named the "OA-free PSS" sample. We also prepared four solutions of poly-acid PSS with addition of OA named as PSS + X (with X= 0.5P, 1P, 3P and 5P), as follows: For the PSS + 0.5P solution, in 3 mL of poly-acid PSS of 0.93 wt.%, 0.1 mg of $Fe_2(SO_4)_3.5H_2O$ (>99%, Synth) and 9.5 mg of $Na_2S_2O_8$ (>98%, Aldrich) were added to the mixture. For the solutions PSS + 1P, PSS + 3P, and PSS + 5P, the amount of $Fe_2(SO_4)_3.5H_2O$ and $Na_2S_2O_8$ varied as 0.2 mg and 18.9 mg, 0.6 mg and 56.7 mg, 1.0 mg and 94.6 mg, respectively. Additionally, two emulsions were prepared, first of EDOT, mixing 11.2 mg of EDOT (97%, Aldrich) in 3 mL of deionized water. And second of PSS with EDOT, prepared mixing 3 mL of poly-acid PSS of 0.93 wt.% with 11.2 mg of EDOT, named the "PSS + EDOT" sample. All samples were vigorously stirred for 10 min before the DLS measurement.

DLS data analysis

The electric field−field correlation functions, $g^1(\tau)$ of each sample were fitted using the multiexponential method. $g^1(\tau) = B + \sum A_i e^{-D_i q^2 t}$, as referred in the main text. This expression was used for performing multi-exponential fits for the determination of diffusion coefficients (D_i) for particles present in the solution, as follow:

PSSNa

$$g^1(\tau) = A_2 e^{D_2 q^2 \tau} + A_3 e^{D_3 q^2 \tau} + y_0 \qquad \text{(Eq. SI-1)}$$

Table SI -1. Fitting parameters of DLS measurements for free-OA PSSNa solution using Equation SI-1.

A_2	D_2	A_3	D_3	y_0
0.65 ± 0.01	$1.61E^{-6}$ ± $4E^{-8}$	0.31 ± 0.01	$2.34E^{-7}$ ± $1E^{-8}$	0.016 ± 0.001

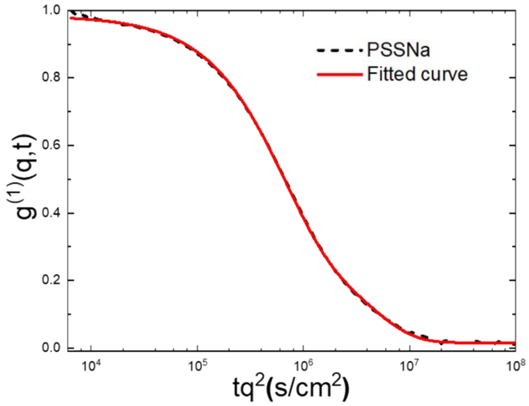


Figure SI -1. Field-correlation functions $g^1(\tau)$ and fitting curves for free-OA PSSNa solution.

PSS

$$g^1(\tau) = A_1 e^{D_1 q^2 \tau} + A_2 e^{D_2 q^2 \tau} + A_3 e^{D_3 q^2 \tau} + y_0 \quad \text{(Eq. SI-2)}$$

Table SI -2. Fitting parameters of DLS measurements for free-OA PSS solution using Equation SI-2.

y_0	A_1	D_1	A_2	D_2	A_3	D_3
0.016 ± 0.002	0.37 ± 0.02	1.13E^{-5} ± 2E^{-7}	0.30 ± 0.01	1.56E^{-6} ± 6E^{-8}	0.30 ± 0.01	1.59E^{-7} ± 1E^{-9}

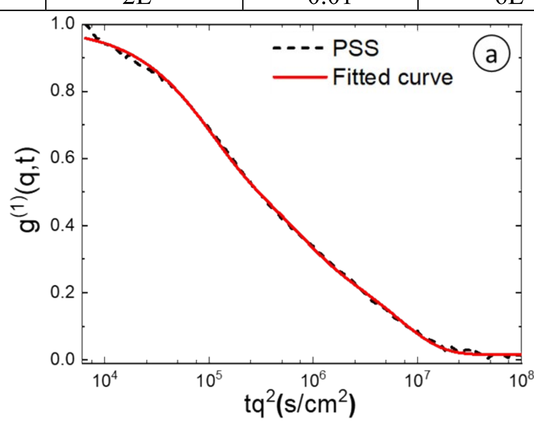


Figure SI -2. Field-correlation functions $g^1(\tau)$ and fitting curves for free-OA PSS solution.

PSS + 0.5P

Table SI -3. Fitting parameters of DLS measurements for PSS + 0.5P solution using Equation SI-1.

y_0	A_2	D_2	A_3	D_3
0.016 ± 0.001	0.61 ± 0.01	1.50E^{-6} ± 9E^{-9}	0.36 ± 0.01	3.43E^{-7} ± 4E^{-9}

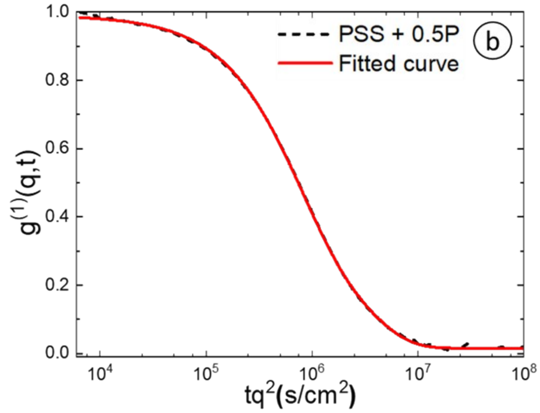


Figure SI -3. Field-correlation functions $g^1(\tau)$ and fitting curves for PSS + 0.5P solution.

PSS + 1P

Table SI -4. Fitting parameters of DLS measurements for PSS + 1P solution using Equation SI-1.

y_0	A_2	D_2	D_3	D_3
0.015 ± 0.001	0.49 ± 0.04	$1.28E^{-6}$ ± $1E^{-8}$	0.46 ± 0.04	$3.87E^{-7}$ ± $5E^{-9}$

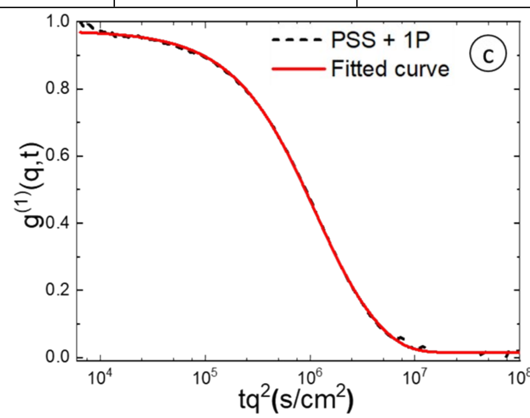


Figure SI -4. Field-correlation functions $g^1(\tau)$ and fitting curves for PSS + 1P solution.

PSS + 3P

Table SI -5. Fitting parameters of DLS measurements for PSS + 3P solution using Equation SI-1.

A_2	D_2	A_3	D_3	y_0
0.28 ± 0.04	$1.25E^{-6}$ ± $6E^{-8}$	0.70 ± 0.04	$4.34E^{-7}$ ± $7E^{-9}$	0.014 ± 0.001

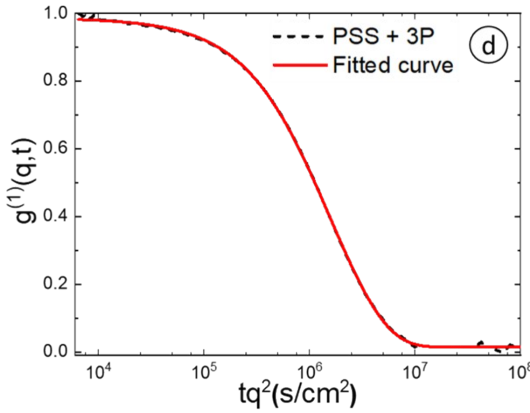


Figure SI -5. Field-correlation functions $g^1(\tau)$ and fitting curves for PSS + 3P solution.

PSS + 5P

Table SI -6 Fitting parameters of DLS measurements for PSS + 5P solution using Equation SI-1.

A_2	D_2	A_3	D_3	y_0
0.17 ± 0.03	$1.44E^{-6} \pm 1E^{-7}$	0.80 ± 0.03	$4.59E^{-7} \pm 1E^{-8}$	0.016 ± 0.001

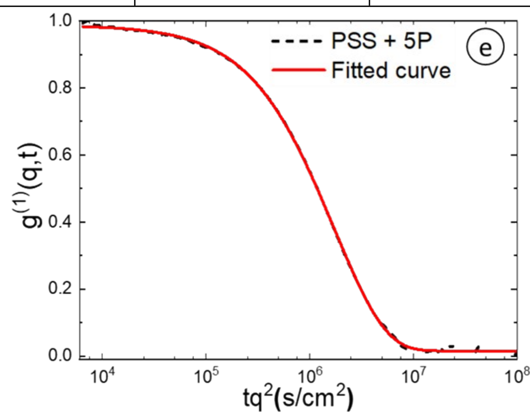


Figure SI -6. Field-correlation functions $g^1(\tau)$ and fitting curves for PSS + 5P solution.

Emulsions of EDOT and PSS + EDOT

EDOT

$$g^1(\tau) = Ae^{Dq^2\tau} + y_0 \qquad \text{(Eq. SI-3)}$$

Table SI -7 Fitting parameters of DLS measurements for EDOT aqueous emulsion using Equation SI-3.

A	D	y_0
0.958 ± 0.001	$4.73E^{-8} \pm 1E^{-10}$	0.029 ± 0.001

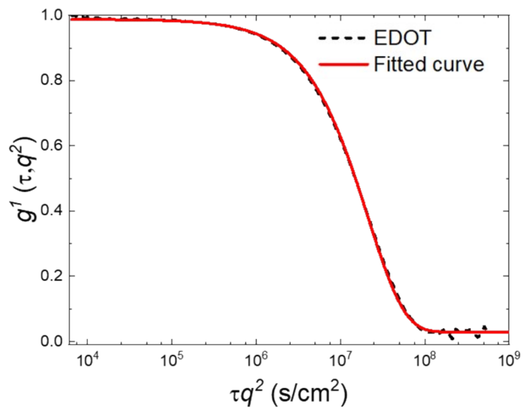


Figure SI -7. Field-correlation functions $g^1(\tau)$ and fitting curves for EDOT emulsion.

PSS + EDOT

Table SI -8 Fitting parameters of DLS measurements for PSS + EDOT aqueous emulsion using Equation SI-1.

A_2	D_2	A_3	D_3	y_0
0.68 ± 0.02	2.90E^{-8} ± 3E^{-10}	0.28 ± 0.02	7.98E^{-9} ± 2E^{-11}	0.021 ± 0.001

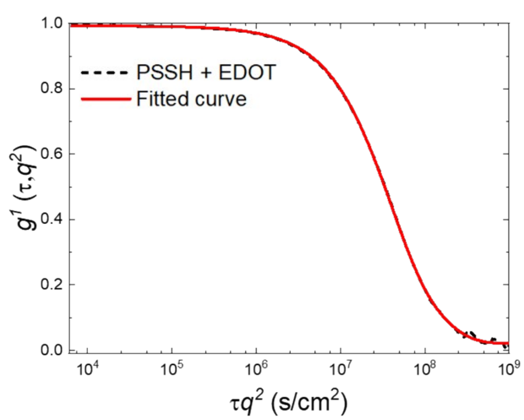


Figure SI -8. Field-correlation functions $g^1(\tau)$ and fitting curves for PSS + EDOT emulsion.

SI-2. UV-Vis absorption spectra

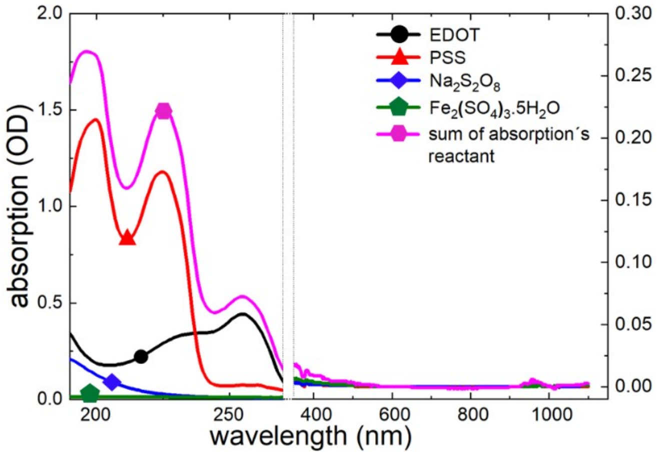


Figure SI -9. UV-Vis spectra of individual reactants for PEDOT:PSS polymerization. Here, the concentration of all reactants is the same as used in the 1P ink polymerization, then 10 µL aliquot was diluted in 2990 µL of deionized water, as reported in SI-1.

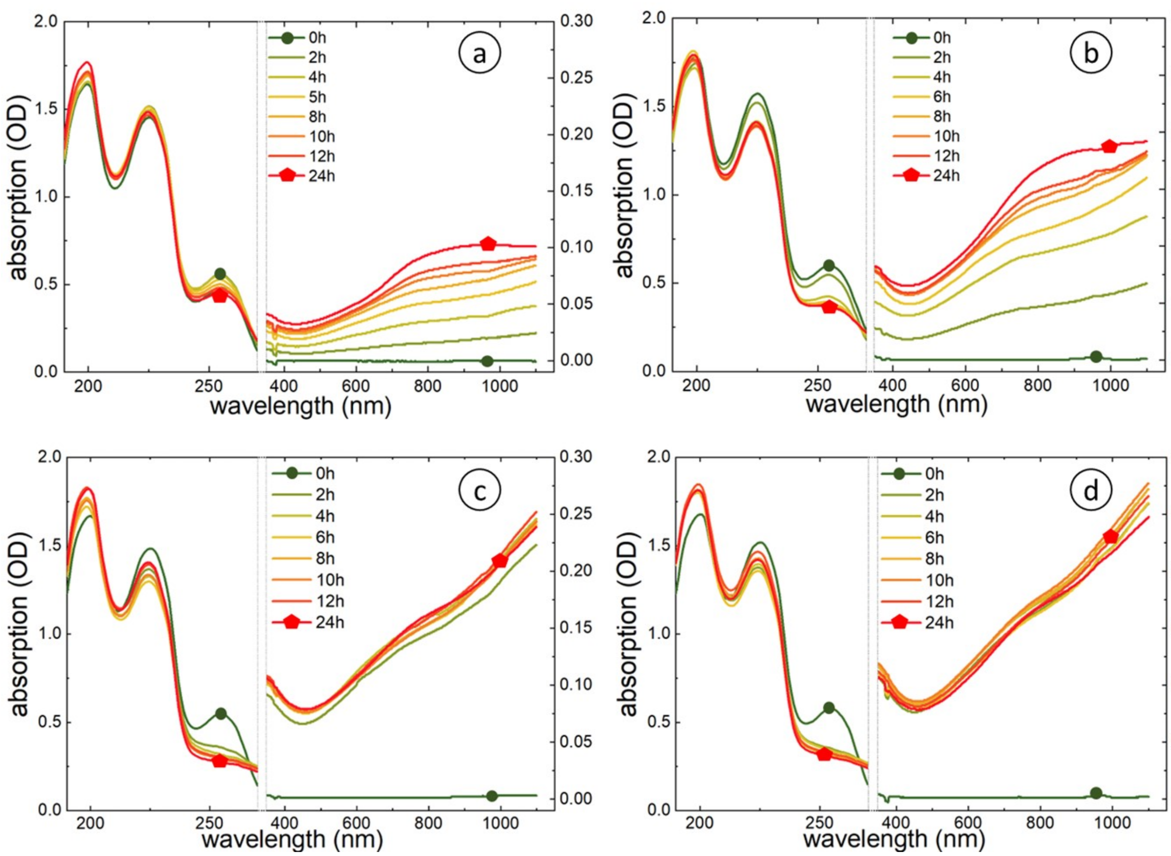


Figure SI -10. UV-Vis spectra of PEDOT:PSS inks during the polymerization. Each spectrum was taken every 2h until the first 12h of reaction; a) 0.5P; b) 1P; c) 3P and d) 5P. It is also present a final sample that was collected after 24h of reaction.

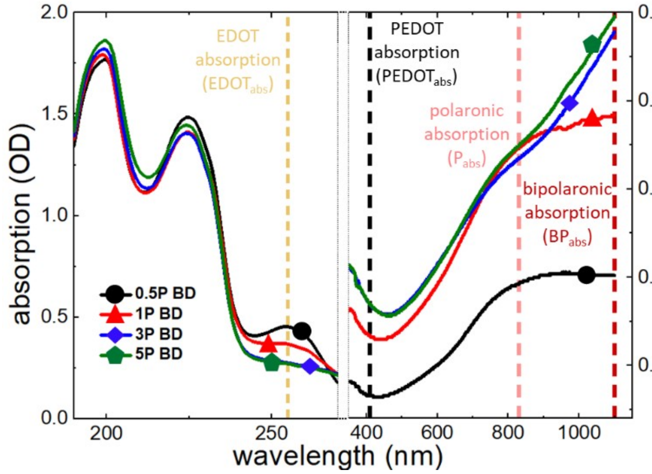
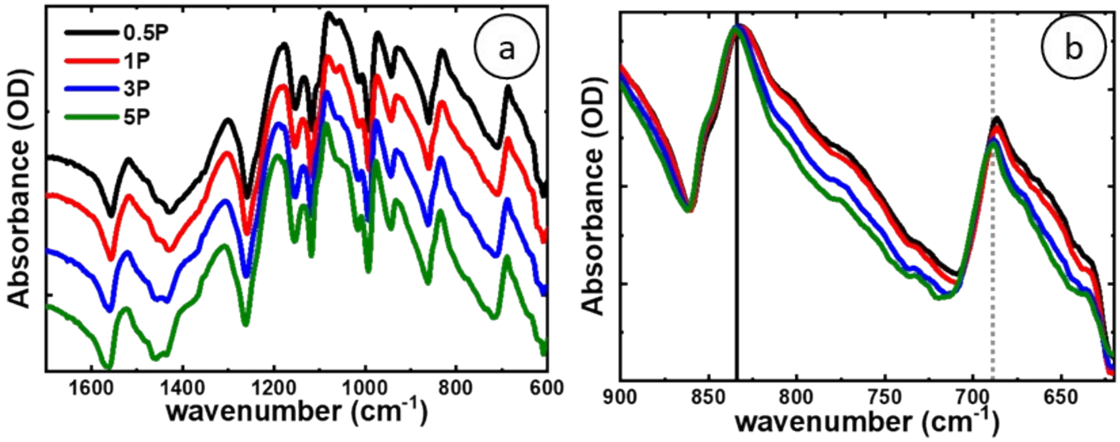


Figure SI -11. UV-Vis spectra of PEDOT:PSS inks after 24 h of polymerization, before the dialysis (BD).



SI-3. FTIR absorption and XPS spectra

Figure SI -12. a) FTIR spectra of PEDOT:PSS inks. For better presentation the individual curves are offset. b) Close view of spectrum region between 900 and 600 cm^{-1}.

Table SI -9. PEDOT:PSS inks code, FTIR absorption intensity in 835 cm^{-1} and 865 cm^{-1}, respectively and FTIR intensity ratios between 835 cm^{-1} and 665 cm^{-1}.

Code	835 cm^{-1}	685 cm^{-1}	835 cm^{-1}/685 cm^{-1}
0.5P	0.067	0.057	1.17
1P	0.053	0.043	1.23
3P	0.037	0.026	1.43
5P	0.027	0.015	1.82

SI-4. XPS fittings

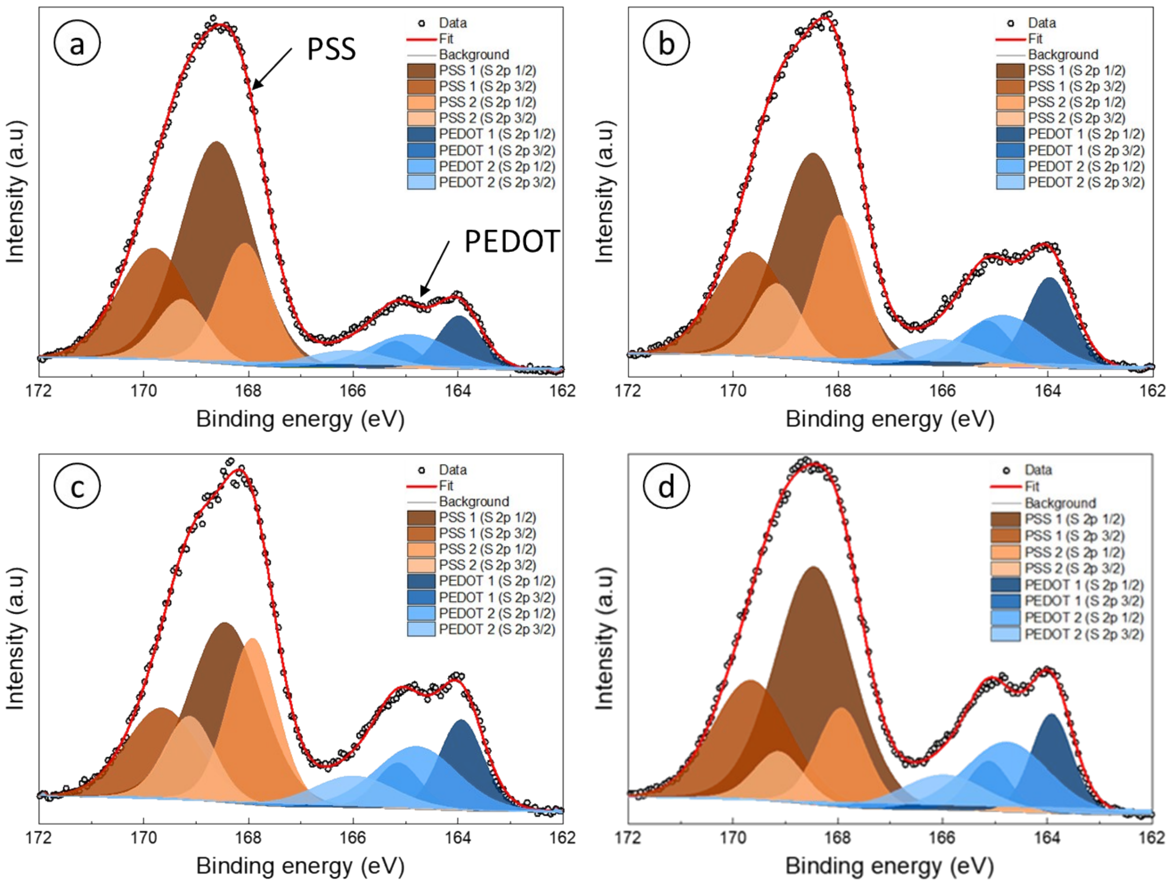


Figure SI -13. XPS spectra showing S(2p) signals for PEDOT:PSS a)0.5P, b)1P, c)3P and d)5P.

Table SI-10. XPS deconvoluted peaks areas and ratios of the PEDOT:PSS inks. PSS1+2 and PEDOT1+2 correspond to the summation of PSS_1(**S** $\mathbf{2p_{1/2}}$), PSS_1(**S** $\mathbf{2p_{3/2}}$), PSS_2(**S** $\mathbf{2p_{1/2}}$), PSS_2(**S** $\mathbf{2p_{3/2}}$) peak areas and $PEDOT_1$(**S** $\mathbf{2p_{1/2}}$), $PEDOT_1$(**S** $\mathbf{2p_{3/2}}$), $PEDOT_2$(**S** $\mathbf{2p_{1/2}}$), $PEDOT_2$(**S** $\mathbf{2p_{3/2}}$) peak areas, respectively.

Code	**PSS_1 (S $2p_{1/2}$)**	**PSS_1 (S $2p_{3/2}$)**	**PSS_2 (S $2p_{1/2}$)**	**PSS_2 (S $2p_{3/2}$)**	**$PEDOT_1$ (S $2p_{1/2}$)**	**$PEDOT_1$ (S $2p_{3/2}$)**	**$PEDOT_2$ (S $2p_{1/2}$)**	**$PEDOT_2$ (S $2p_{3/2}$)**	**Ratio**
	%Area	**%Area**	**%Area**	**%Area**	**%Area**	**%Area**	**%Area**	**%Area**	**$(PSS_1+PSS_2)/(PEDOT_1+PEDOT_2)$**
0.5P	38.96	19.47	15.29	7.64	5.62	2.81	6.81	3.40	4.4
1P	32.58	16.28	15.54	7.77	9.12	4.56	9.33	4.71	2.6
3P	28.55	14.27	18.18	9.09	8.79	4.39	11.16	5.58	2.3
5P	36.95	18.47	9.75	4.87	8.35	4.18	11.62	5.81	2.3