Gamma rays as innovative tool towards synthesizing conducting copolymers with improved properties

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Table SI1- *Homopolymers and copolymers preparation starting from aqueous or dichloromethane (DCM) solutions containing monomers. The concentrations in monomers along with the environments used for irradiation are specified. The notations for all homopolymers and copolymers synthesized in this work are defined.*

Monomers	**Py (10 mM)**		**TAA (10 mM)**		**EDOT (10 Mm)**		**3HT (10 mM)**
Solvents	H_2O	DCM	H_2O	DCM	H_2O	DCM	DCM
Gas	N_2O	N_2	N_2O	N_2	N_2O	N_2	O_2
Homopolymers	**PPy_{H2O}**	**PPy_{DCM}**	**$PTAA_{H2O}$**	**$PTAA_{DCM}$**	**$PEDOT_{H2O}$**	**$PEDOT_{DCM}$**	**$P3HT_{DCM}$**

Monomers	**Py/TAA (5/5 mM)**		**Py/EDOT (5/5 mM)**		**Py/3HT (5/5 mM)**
Solvents	H_2O	DCM	H_2O	DCM	DCM
Gas	N_2O	N_2	N_2O	N_2	O_2
Copolymers	**$PPy/PTAA_{H2O}$**	**$PPy/PTAA_{DCM}$**	**$PPy/PEDOT_{H2O}$**	**$PPy/PEDOT_{DCM}$**	**$PPy/P3HT_{DCM}$**

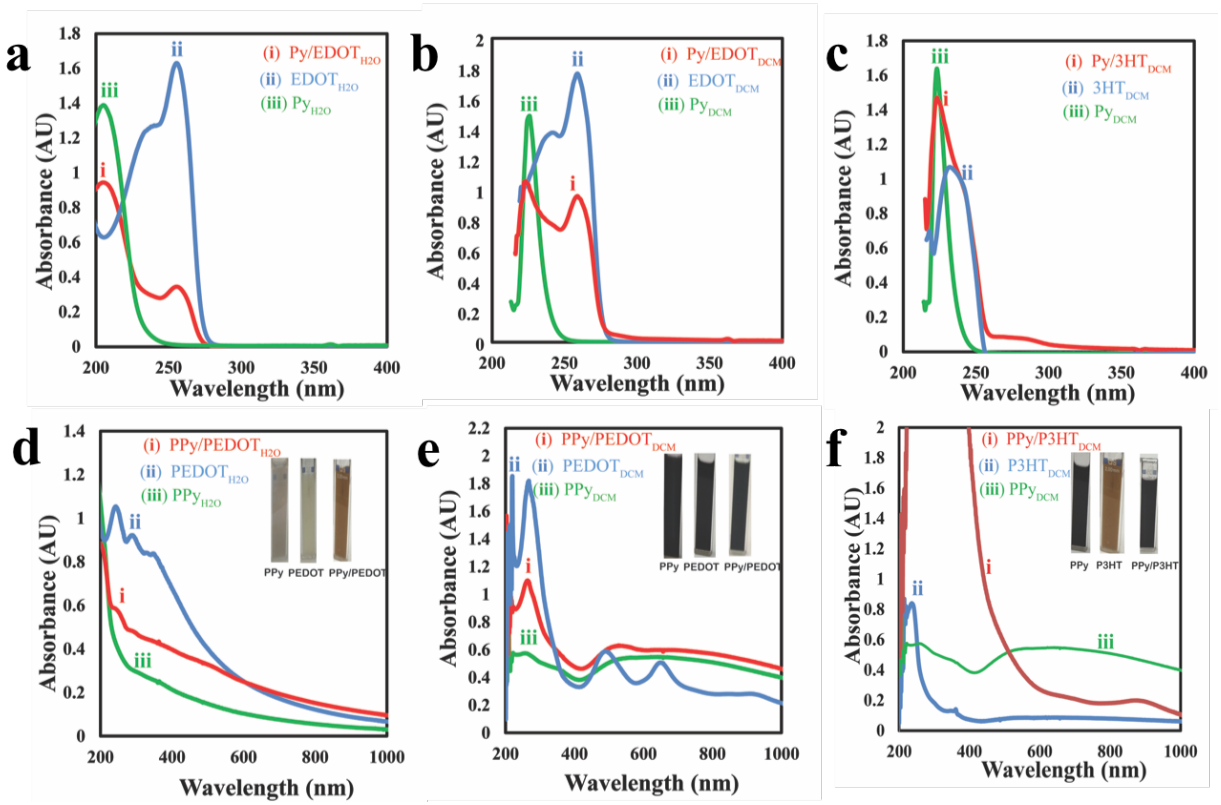

Figure SI1- *UV-Vis absorption spectra of* ***a)*** *Py, EDOT and Py/EDOT aqueous solutions,* ***b)*** *Py, EDOT, Py/EDOT dichloromethane (DCM)* solutions, **c)** *Py, 3HT, Py/3HT dichloromethane (DCM)* solutions, **d)** Aqueous solutions of Py, EDOT and Py/EDOT irradiated at 36 kGy **e)** DCM solutions of Py, EDOT and Py/EDOT irradiated at 36 kGy and **f)** DCM solutions of Py, 3HT and Py/3HT irradiated at 36 kGy. ***Inserts:*** *photographs of polymer suspensions obtained after irradiation. The total concentration in monomers was 10 mM in all cases. The optical path length was 0.2 cm and reference was pure solvent. All solutions were diluted 10 times*.

Table SI2- *Calculated molar extinction coefficients of Py, TAA, EDOT and 3HT monomers in aqueous and dichloromethane solutions from UV-Vis absorption spectra by using Beer-Lambert's Law.*

Monomers	Solvent	Absorption Maxima (λ_{max}) (nm)	Molar extinction coefficients (ε) ($L.mol^{-1}.cm^{-1}$)
Py	H_2O	205	7272
Py	DCM	222	7332
TAA	H_2O	235	7772
TAA	DCM	235	7160
EDOT	H_2O	235 255	6259 8179
EDOT	DCM	242 259	6590 8878
3HT	DCM	237	5963

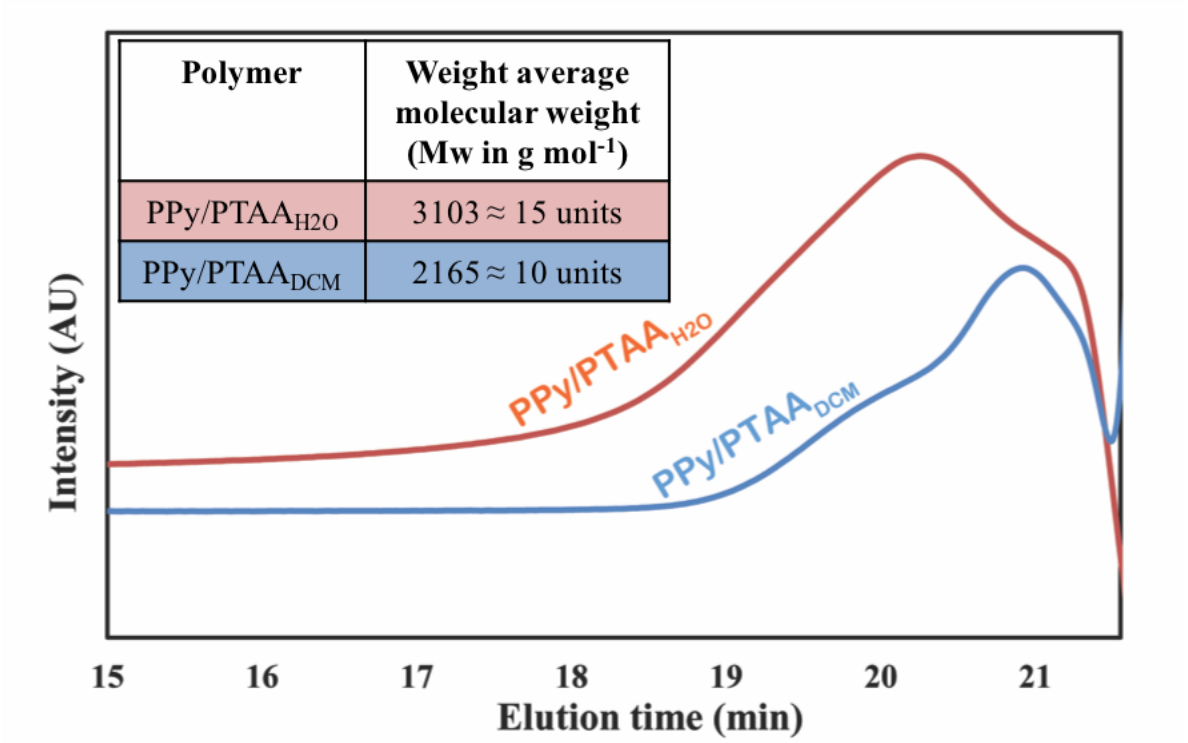

Figure SI2- *SEC chromatograms of PPy/PTAA$_{H2O}$ and PPy/PTAA$_{DCM}$ radiosynthesized at 36 kGy and solubilized in THF (used as eluent).* ***Insert:*** *Average molecular weights and calculated chain lengths of both PPy/PTAA$_{H2O}$ and PPy/PTAA$_{DCM}$ copolymers as determined by using polystyrene as standard. Note that the number of units is the number of monomers in a copolymer chain (**see Scheme 1**).*

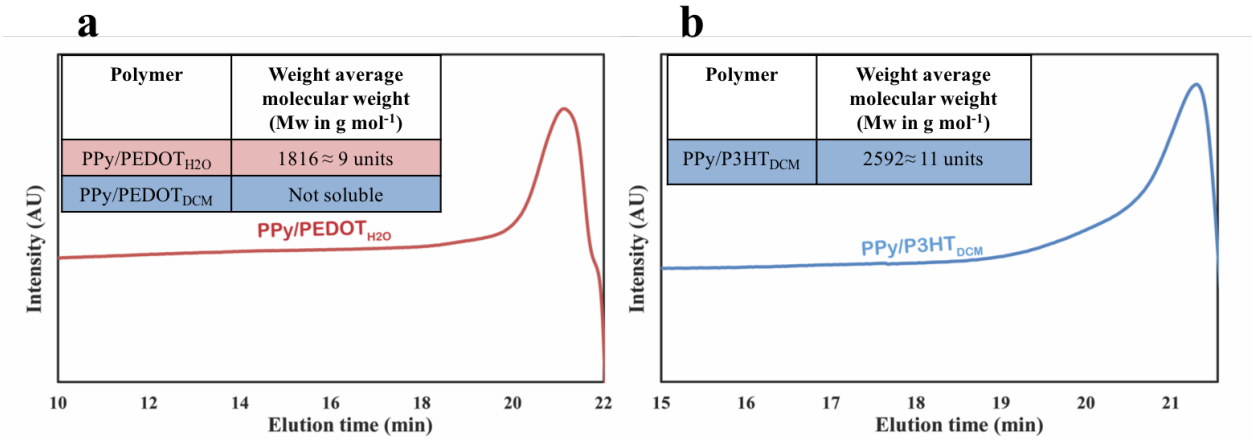

Figure SI3- *SEC chromatograms of* ***a)*** *PPy/PEDOT$_{H2O}$ and* ***b)*** *PPy/P3HT$_{DCM}$ radiosynthesized at 36 kGy and solubilized in THF (used as eluent).* ***Inserts****: Average molecular weights and calculated chain lengths of both PPy/PEDOT$_{H2O}$ and PPy/P3HT$_{DCM}$ copolymers as determined by using polystyrene as standard. Note that the number of units is the number of monomers in a copolymer chain (****see Scheme 1****). Note also that PPy/PEDOT$_{DCM}$ was found insoluble in DCM.*

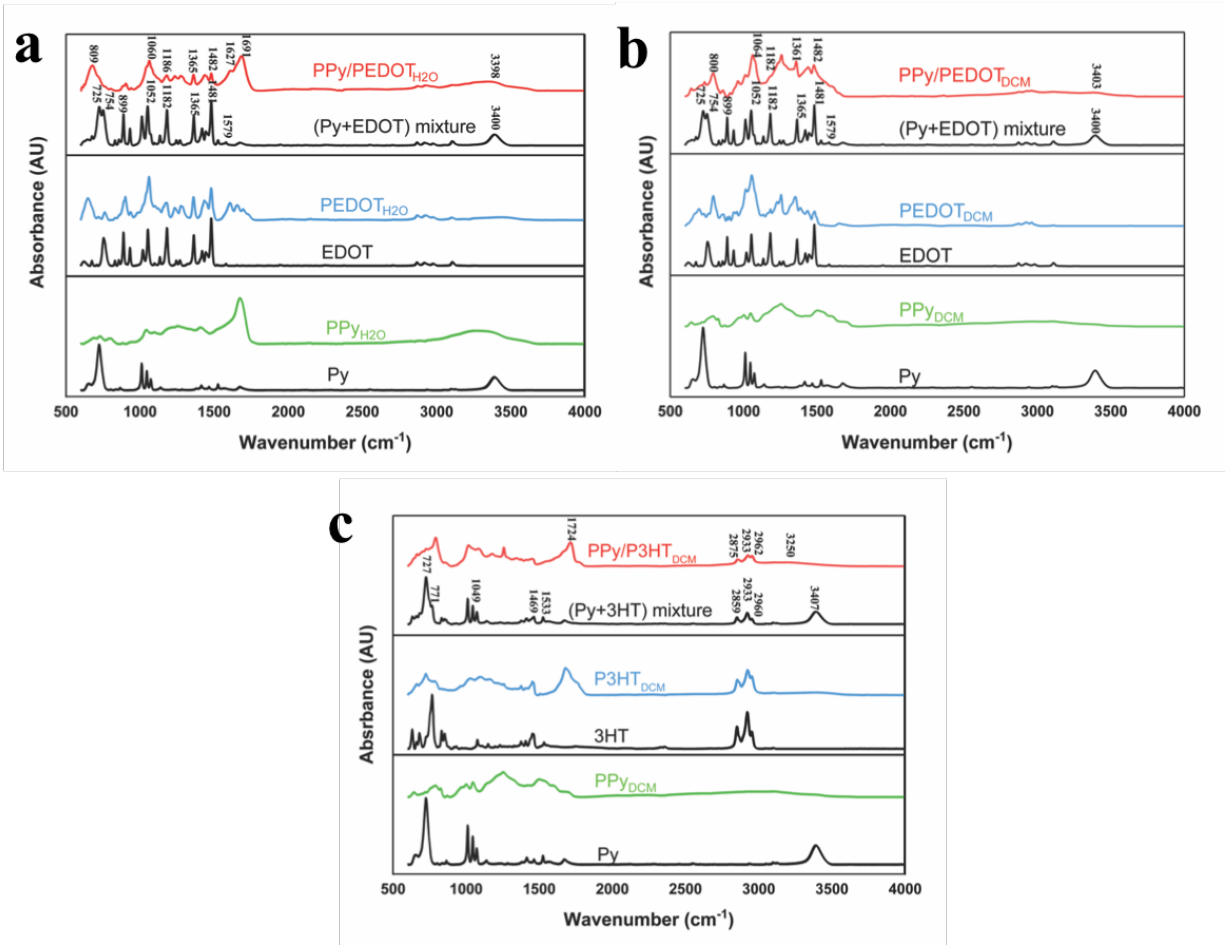

Figure SI4- *ATR-FTIR spectra of* ***a)*** *PPy$_{H2O}$, PEDOT$_{H2O}$ and PPy/PEDOT$_{H2O}$ polymers prepared in water at 36 kGy,* ***b)*** *PPy$_{DCM}$, PEDOT$_{DCM}$ and PPy/PEDOT$_{DCM}$ polymers prepared in dichloromethane (DCM) solution at 36 kGy and* ***c)*** *PPy$_{DCM}$, P3HT$_{DCM}$ and PPy/P3HT$_{DCM}$ polymers prepared in dichloromethane (DCM) solution at 36 kGy along with the spectra of their respective pure monomers. The spectra of pure Py, pure EDOT, pure 3HT as well as their mixtures were also displayed for clarity.*

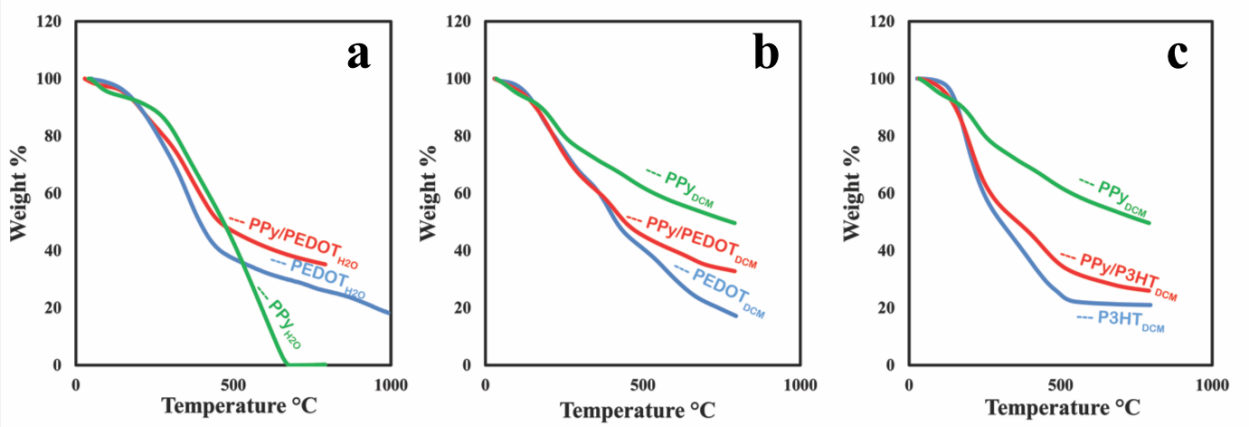

Figure SI5- *TGA analysis curves of dried processed* ***a)*** PPy_{H2O}, $PEDOT_{H2O}$ *and* $PPy/PEDOT_{H2O}$, ***b)*** PPy_{DCM}, $PEDOT_{DCM}$ *and* $PPy/PEDOT_{DCM}$ *and* ***c)*** PPy_{DCM}, $P3HT_{DCM}$ *and* $PPy/P3HT_{DCM}$ *polymers synthesized at 36 kGy .*

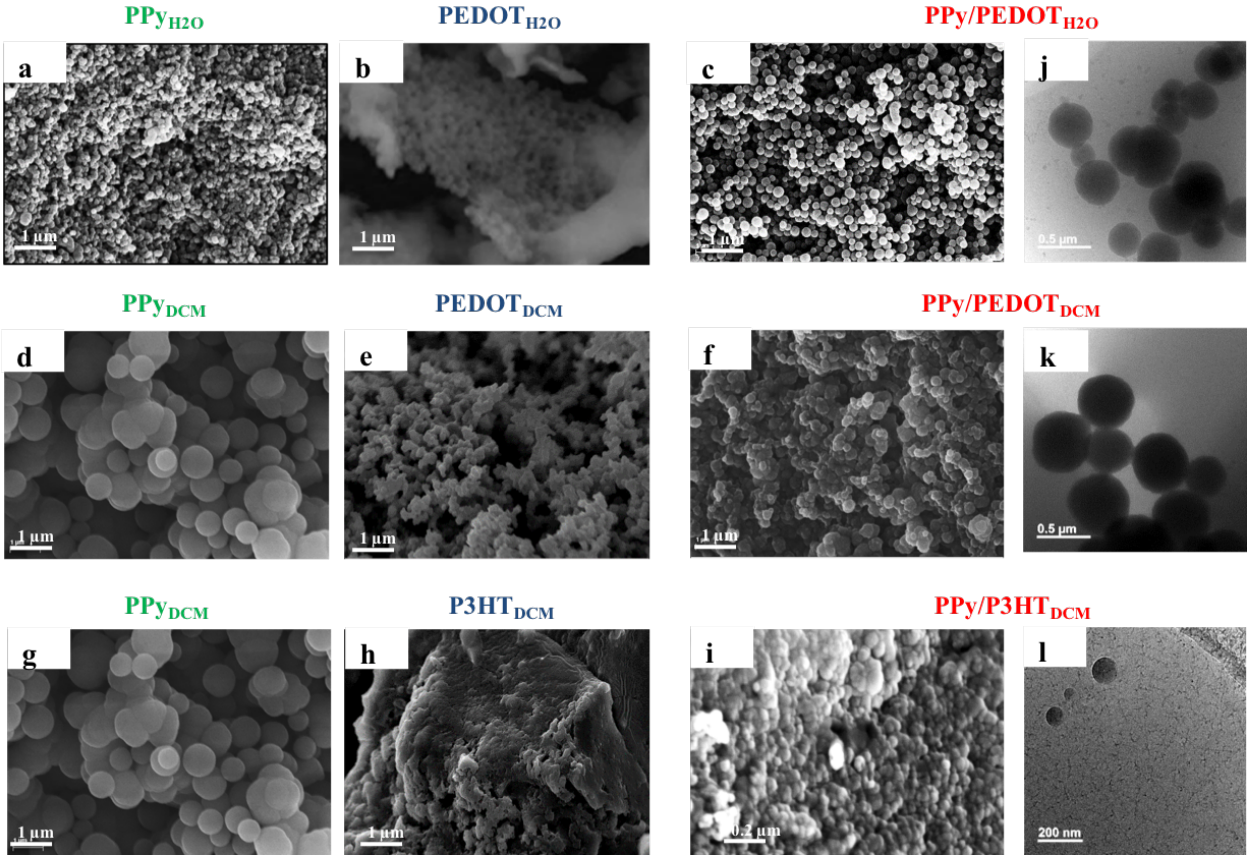

Figure SI6- SEM images *of dried polymers* ***a)*** *PPy_{H2O}* ***b)*** *$PEDOT_{H2O}$* ***c)*** *$PPy/PEDOT_{H2O}$* ***d)*** *PPy_{DCM}* ***e)*** *$PEDOT_{DCM}$* ***f)*** *$PPy/PEDOT_{DCM}$* ***g)*** *PPy_{DCM}* ***h)*** *$P3HT_{DCM}$* ***i)*** *$PPy/P3HT_{DCM}$ (after deposition on carbon tapes adhered to aluminium mounts with gold coating) together with* ***Cryo-TEM images*** *of* ***j)*** *$PPy/PEDOT_{H2O}$* ***k)*** *$PPy/PEDOT_{DCM}$ and* ***l)*** *$PPy/P3HT_{DCM}$. Polymers were obtained after irradiation at 36 kGy. SEM image of PPy_{DCM} was displayed twice for clarity.*

Table SI3- *Morphologies and mean sizes of all homopolymers and copolymers synthesized at 36 kGy in this work either in water or DCM.*

Polymer	Morphology	Mean size (nm)
PPy_{H2O}	Spheres	150-250
PPy_{DCM}	Spheres attached together	750-1000
$PTAA_{H2O}$	Spheres	200-700
$PTAA_{DCM}$	Aggregates of spheres	80-400
$PEDOT_{H2O}$	Aggregates of spheres	180-220
$PEDOT_{DCM}$	Closely packed spheres	100-1500
$P3HT_{DCM}$	Aggregates	-
$PPy/PTAA_{H2O}$	Homogeneous spheres	450-700
$PPy/PTAA_{DCM}$	Spheres attached together	470-900
$PPy/PEDOT_{H2O}$	Spheres	200-500
$PPy/PEDOT_{DCM}$	Closely packed sphere	200-600
$PPy/P3HT_{DCM}$	Spheres	180-200

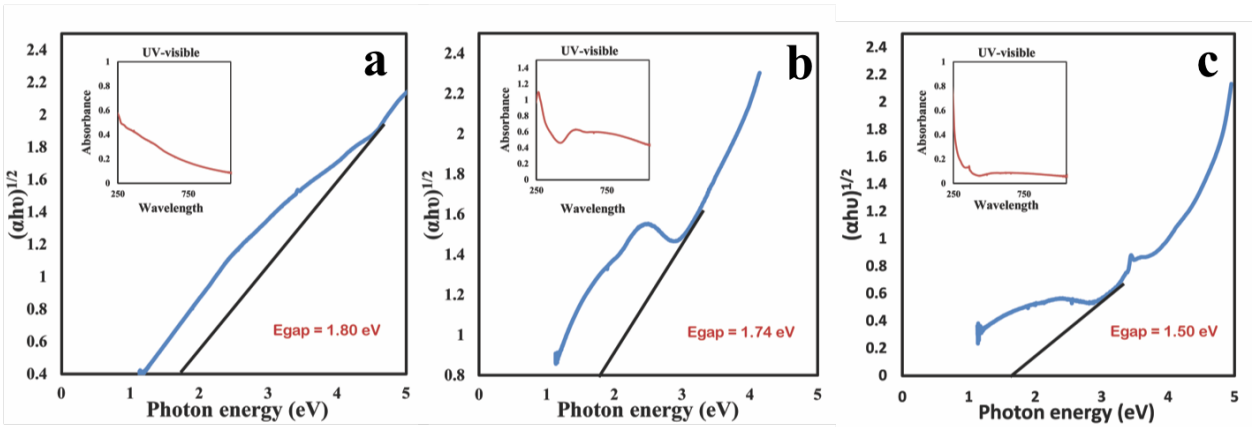

Figure SI7- *Tauc's plot analysis of UV-Vis absorption spectra of* ***a)*** *PPy/PEDOT$_{H2O}$* ***b)*** *PPy/PEDOT$_{DCM}$ and* ***c)*** *PPy/P3HT$_{DCM}$ dissolved in THF solvent for optical band gap assessment.* ***Inserts****: UV-Vis absorption spectra of respective polymers in THF. The optical path length was 0.2 cm and reference was pure THF solvent.*

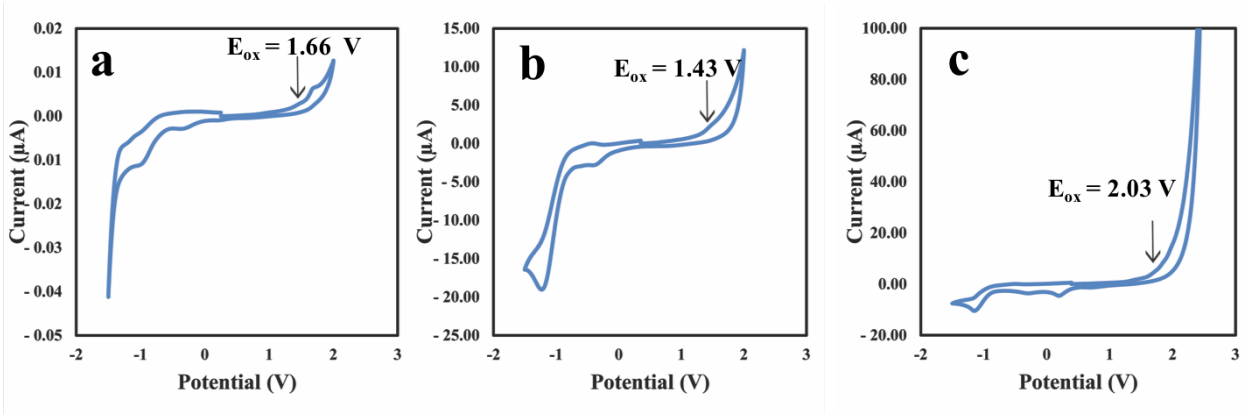

Figure SI8- *Cyclic voltammograms of* ***a)*** *PPy/PEDOT$_{H2O}$* ***b)*** *PPy/PEDOT$_{DCM}$ and* ***c)*** *PPy/P3HT$_{DCM}$ dissolved in THF and recorded in acetonitrile containing 0.1 M of TBAClO$_4$ at a scan rate of 100 mV.s^{-1}. The polymers were synthesized at 36 kGy either in water or in DCM. Redox potential of ferrocenium/ferrocene (Fc$^+$/Fc) was measured to calibrate the pseudo-reference electrode (0.53 V vs. the pseudo-reference electrode used in the present study). The HOMO energetic levels of polymers were calculated from oxidation potentials as follows: E_{HOMO} (eV) = – 4.80 – e(E_{ox} – 0.53) where e is the elementary charge.*