

Electronic Supplementary Information (ESI)

Aromatic Bi-, Tri- and Tetracarboxylic Acid doped Polyaniline Nanotubes: Effect of Morphology and Electrical Transport Properties.

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1) Table S1: Preparation of polyaniline using different aromatic acids.

Name of the Composite	Aniline (mmol)	Acid (mmol)	APS (mmol)	[Ani]/[APS]	[Acid]/[Ani]	Yield (%)
BA/PANI (0.25)	102 mg (1.096)	31.72 mg (0.26)	232.56 mg (1.02)	1:1	0.25:1	72.5
BDA-1/PANI (0.50)	102 mg (1.096)	83.0 mg (0.50)	232.56 mg (1.02)	1:1	0.50:1	73.2
BDA-1/PANI (0.25)	102 mg (1.096)	43.19 mg (0.26)	232.56 mg (1.02)	1:1	0.25:1	75.6
BDA-2/PANI (0.25)	102 mg (1.096)	43.19 mg (0.26)	232.56 mg (1.02)	1:1	0.25:1	76.4
BDA-3/PANI (0.25)	102 mg (1.096)	43.19 mg (0.26)	232.56 mg (1.02)	1:1	0.25:1	72.8
BTA-1/PANI (0.33)	102 mg (1.096)	69.3 mg (0.33)	232.56 mg (1.02)	1:1	0.33:1	71.1
BTA-1/PANI (0.25)	102 mg (1.096)	54.68 mg (0.26)	232.56 mg (1.02)	1:1	0.25:1	80.2
BTA-1/PANI (0.10)	102 mg (1.096)	21.42 mg (0.10)	250 mg (1.096)	1:1	0.10:1	73.2
BTA-1/PANI (0.01)	102 mg (1.096)	2.14 mg (0.010)	250 mg (1.096)	1:1	0.01:1	74.1
BTA-2/PANI (0.25)	102 mg (1.096)	54.68 mg (0.26)	250 mg (1.096)	1:1	0.25:1	82.8
BTA-3/PANI (0.25)	102 mg (1.096)	54.68 mg (0.26)	250 mg (1.096)	1:1	0.25:1	86.0
BTCA/PANI (0.25)	102 mg (1.096)	66.06 mg (0.26)	250 mg (1.096)	1:1	0.25:1	69.7
BPCA/PANI (0.25)	55.8 mg (0.60)	43.79 mg (0.15)	139.2 mg (0.60)	1:1	0.25:1	67.9
TPCA/PANI (0.25)	102 mg (1.096)	113.99 mg (0.26)	250 mg (1.096)	1:1	0.25:1	51.60

^1H NMR spectra of BPCA^{S1}:

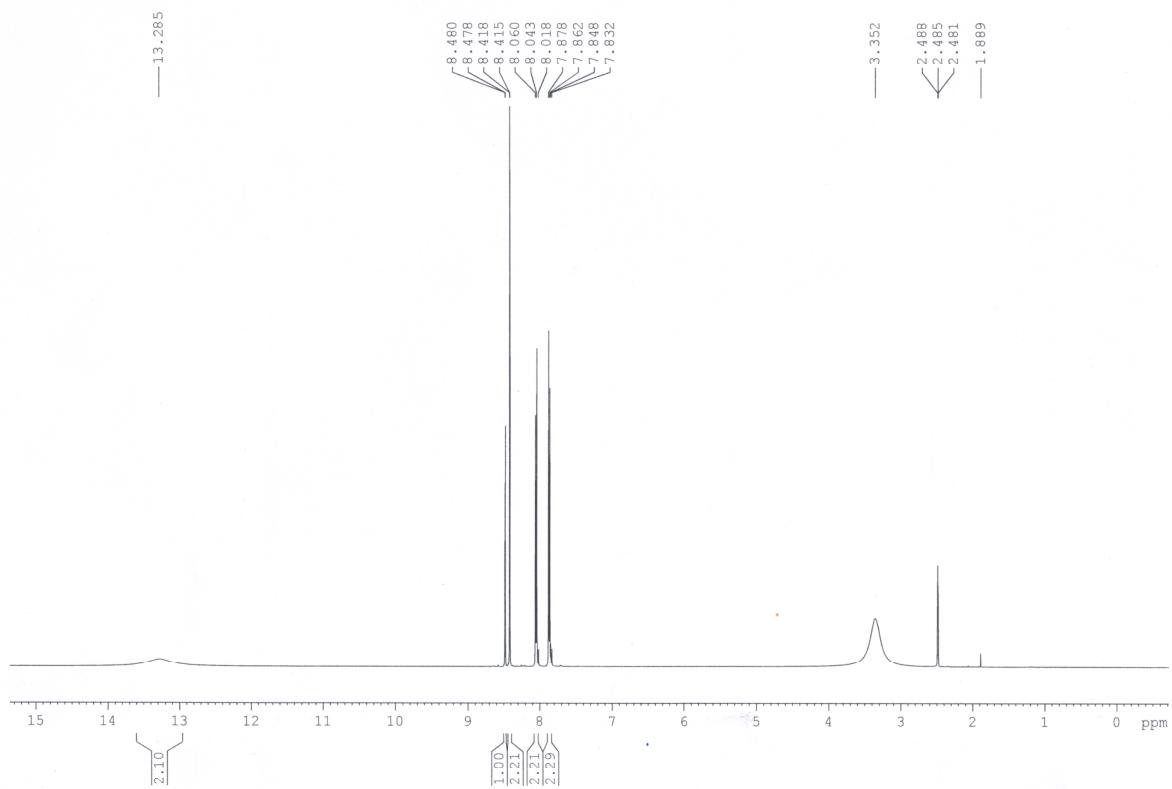


Fig. S1: ^1H -NMR of BPCA in DMSO-d_6 solvent, 300 MHz

¹³C-NMR of BPCA:

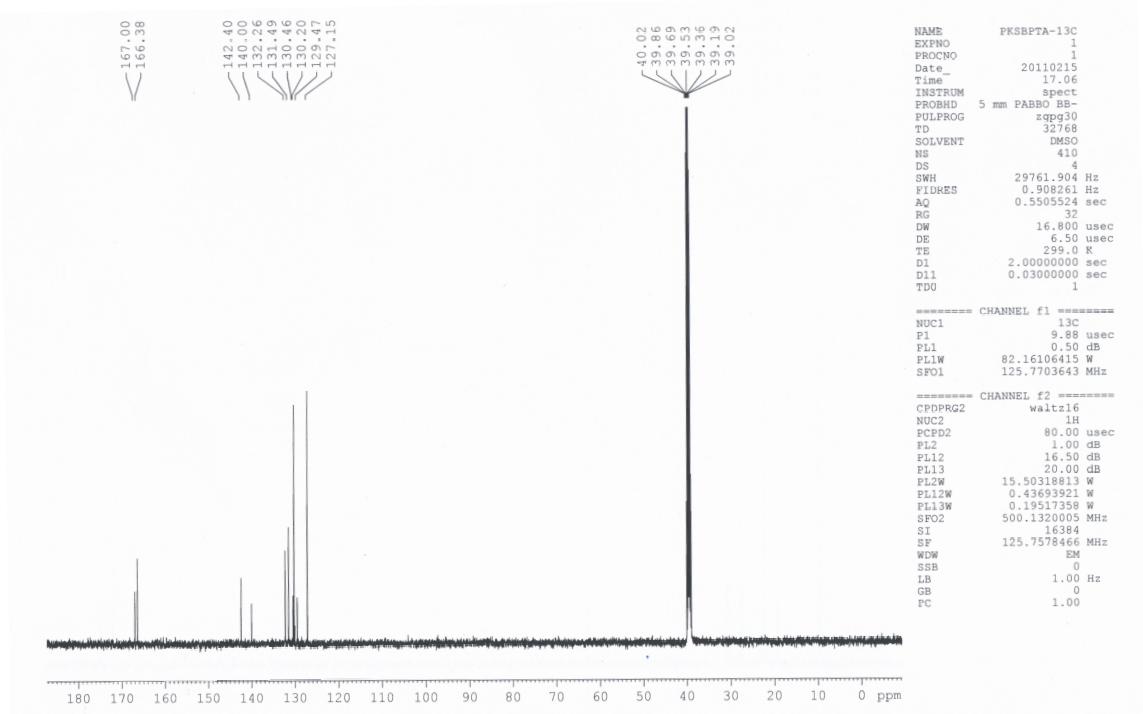


Fig. S2. ¹³C-NMR of BPCA in DMSO-d₆ solvent, 300 MHz

$^1\text{H-NMR}$ of TPCA^{S1}:

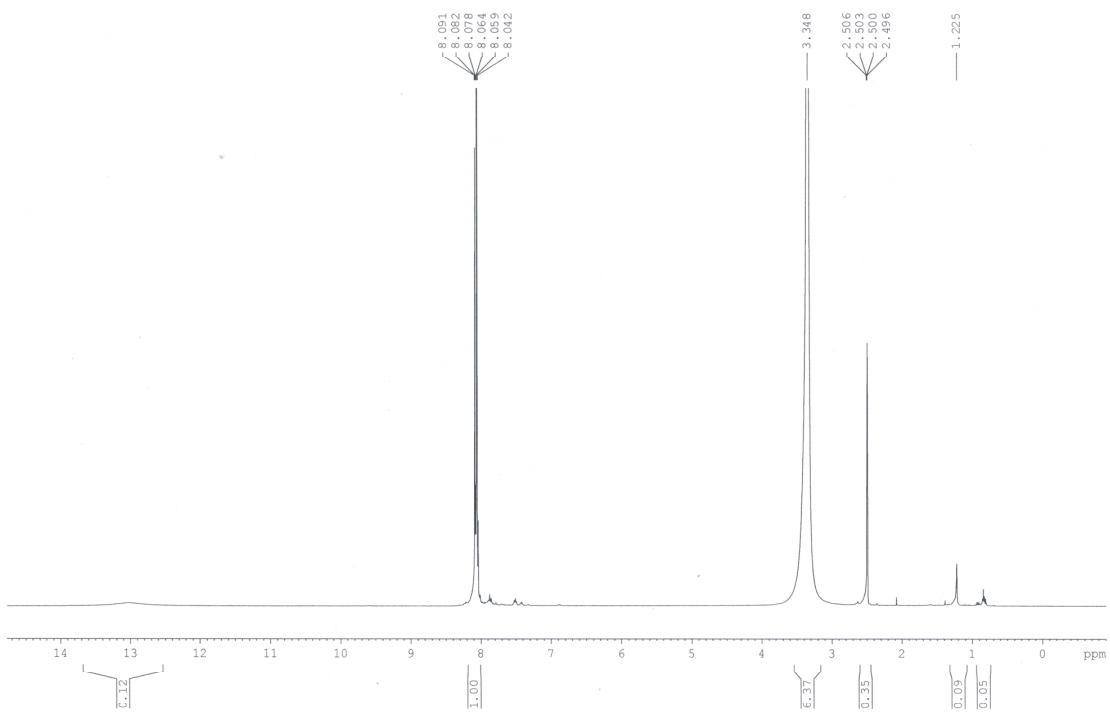


Fig S3: $^1\text{H-NMR}$ of TPCA in DMSO-d_6 solvent, 300 MHz

¹³C-NMR of TPCA

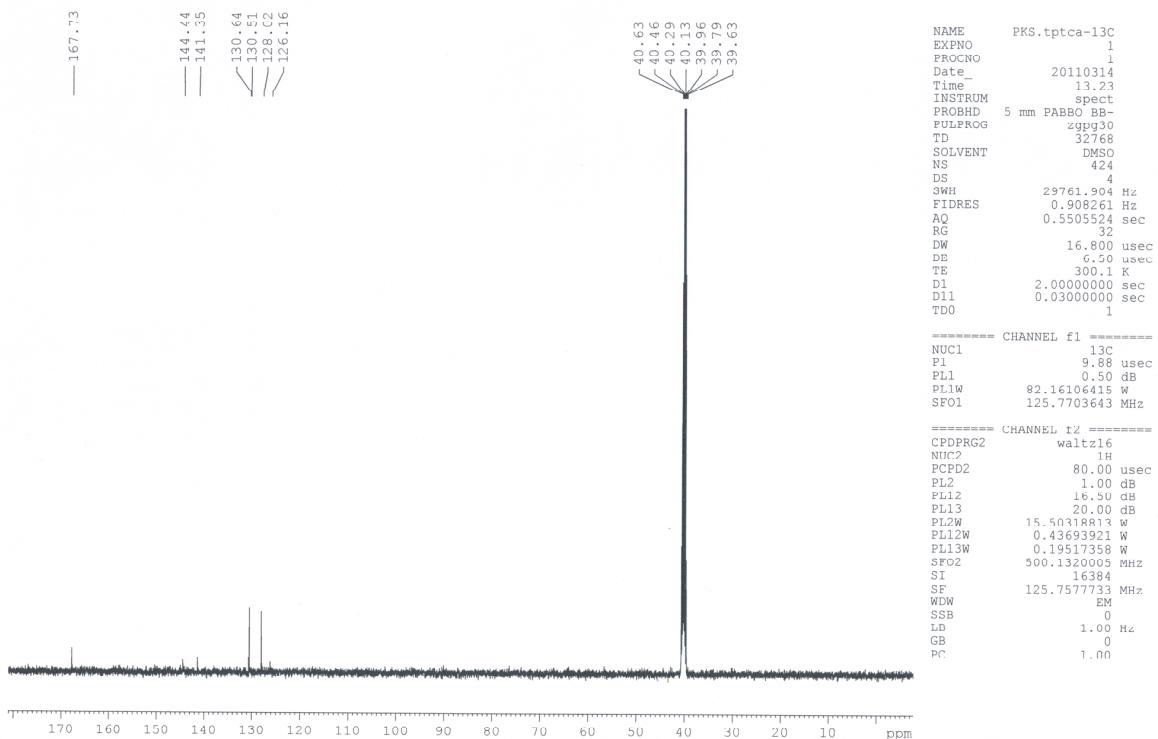


Fig. S4: ¹³C-NMR of TPCA in DMSO-d₆ solvent, 300 MHz

3) ^1H -NMR spectra of the PANI nanocomposite:

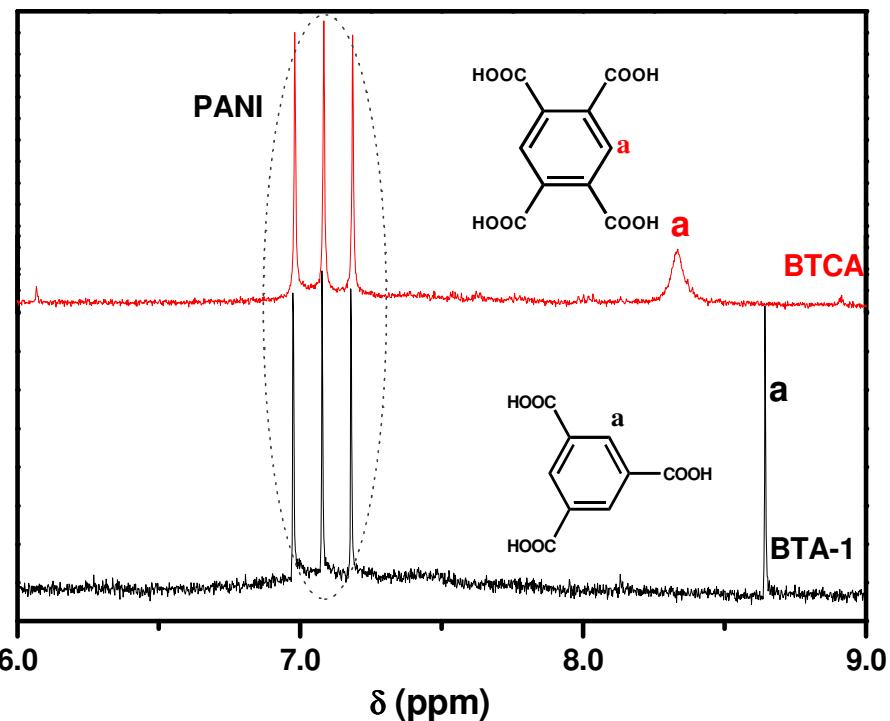
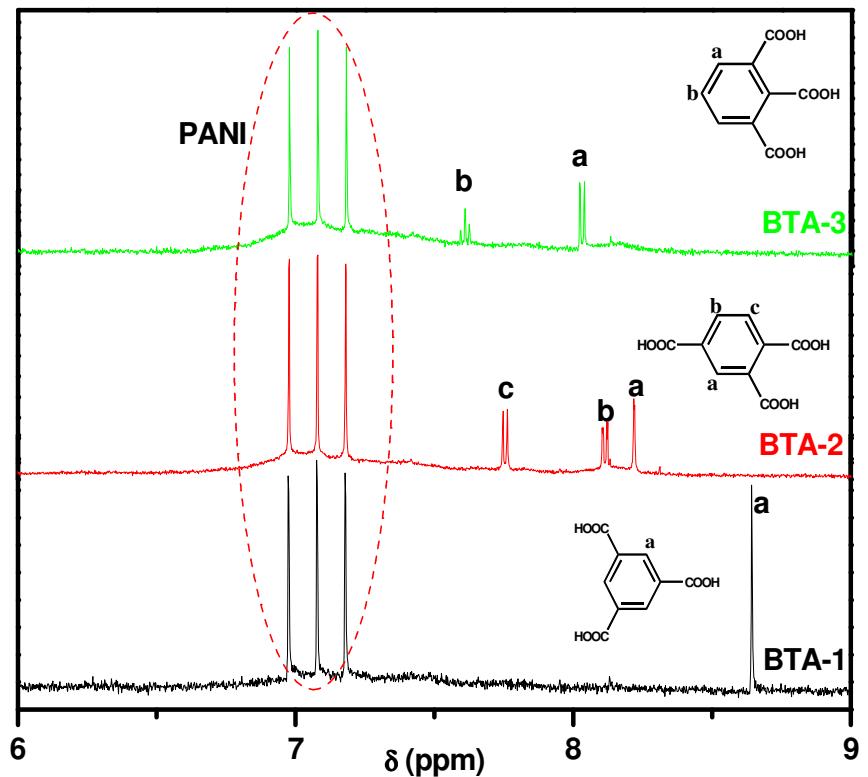


Fig. S5: ^1H -NMR spectra of PANI nanostructure doped by different aromatic tricarboxylic acids in solvent DMSO- d_6 , 500 MHz.

4) FT-IR. Spectra of PANI nanocomposites

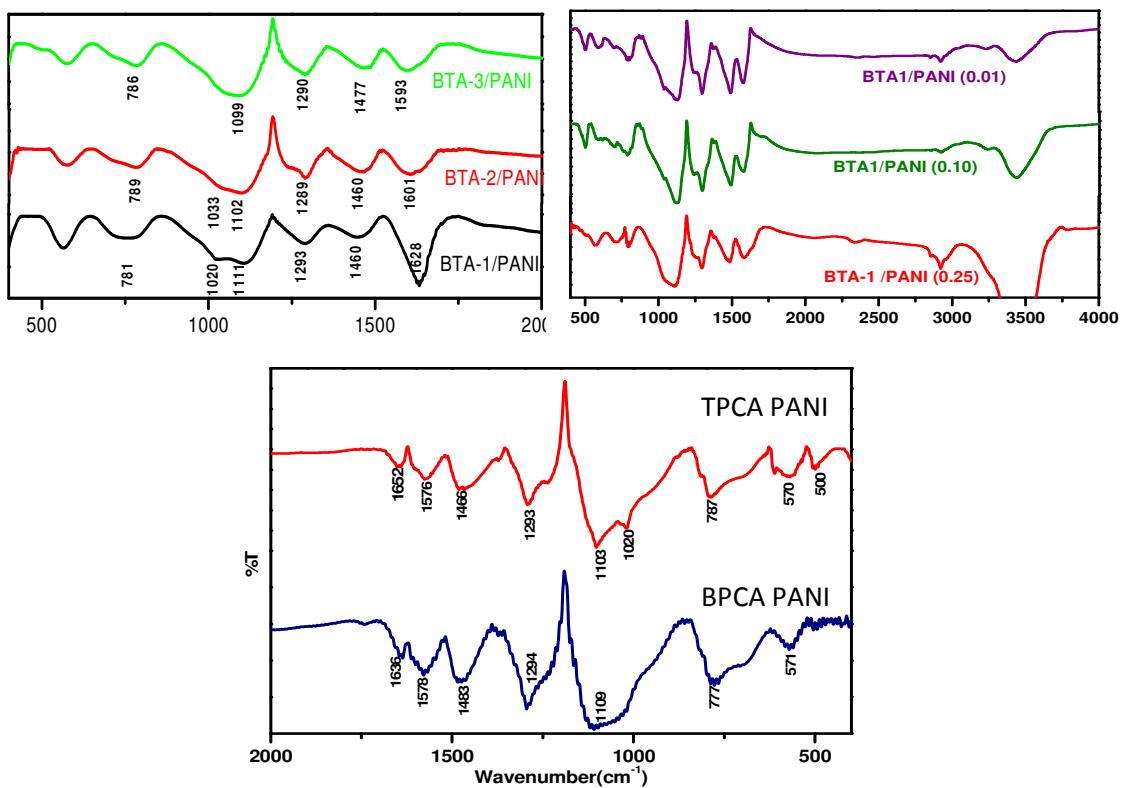


Fig. S6: FT-IR spectra of PANI nanostructure doped by different aromatic tricarboxylic acids.

5) UV-Vis spectra of PANI nanocomposites:

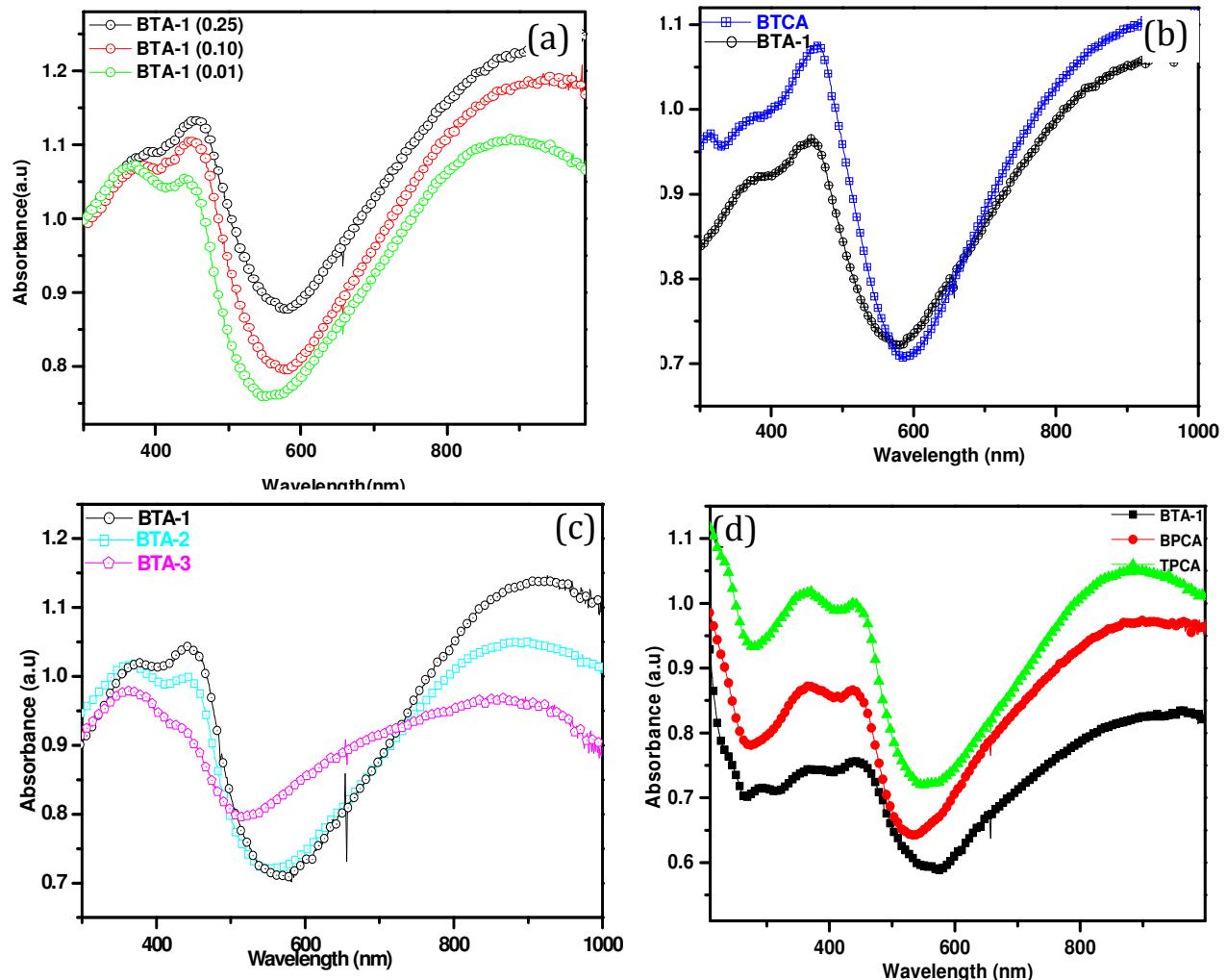


Fig. S7: UV-Vis spectra of PANI nanostructure doped by different aromatic tricarboxylic acids.

FESEM image di and monocarboxylic acid PANI composite:

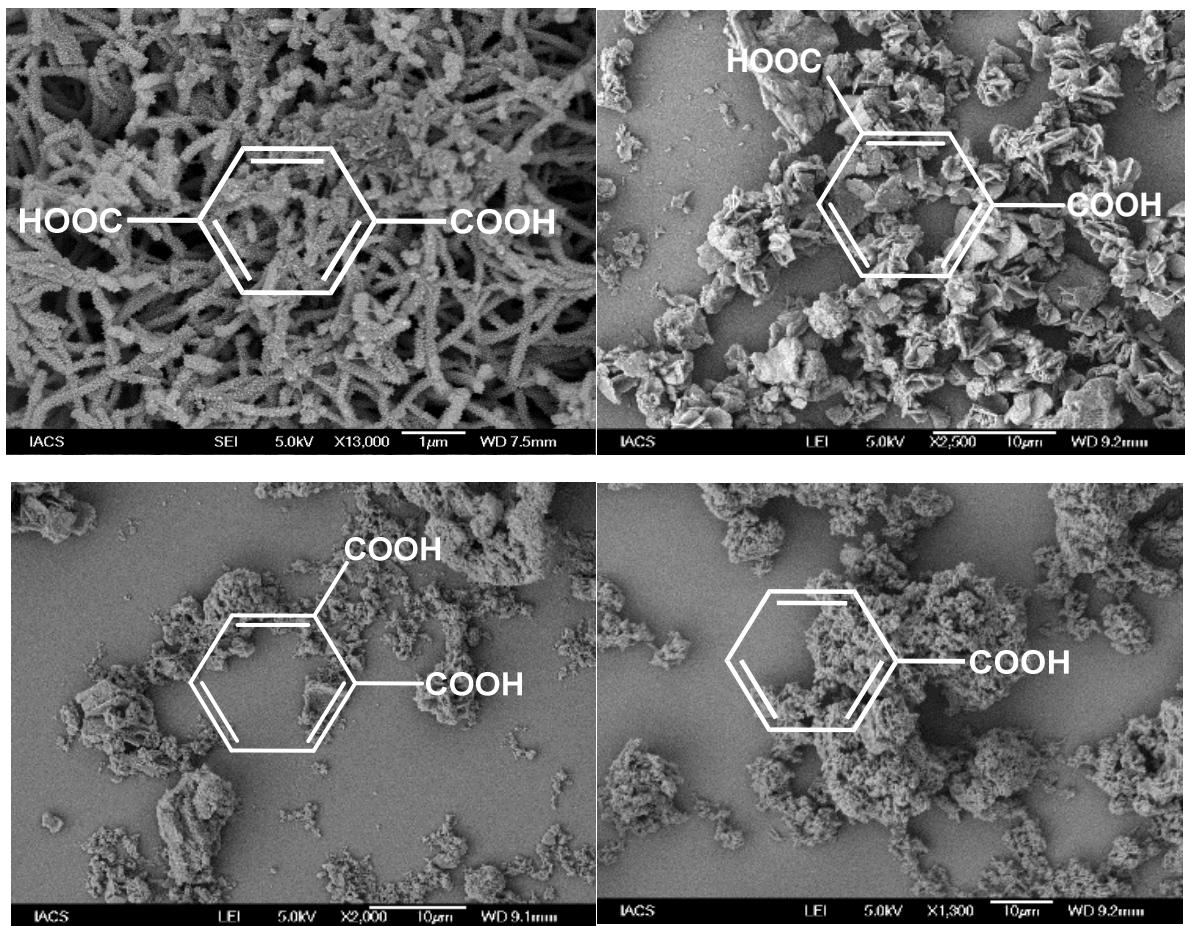


Fig. S8: FESEM-images of BDA-1/PANI, BDA-2/PANI, BDA-3/PANI and BA/PANI.
Synthetic condition, [acid]/ [aniline] = 0.25, [aniline]/[APS]=1.00.

Morphological study of bi-, tri-, tetracarboxylic acid doped PANI:

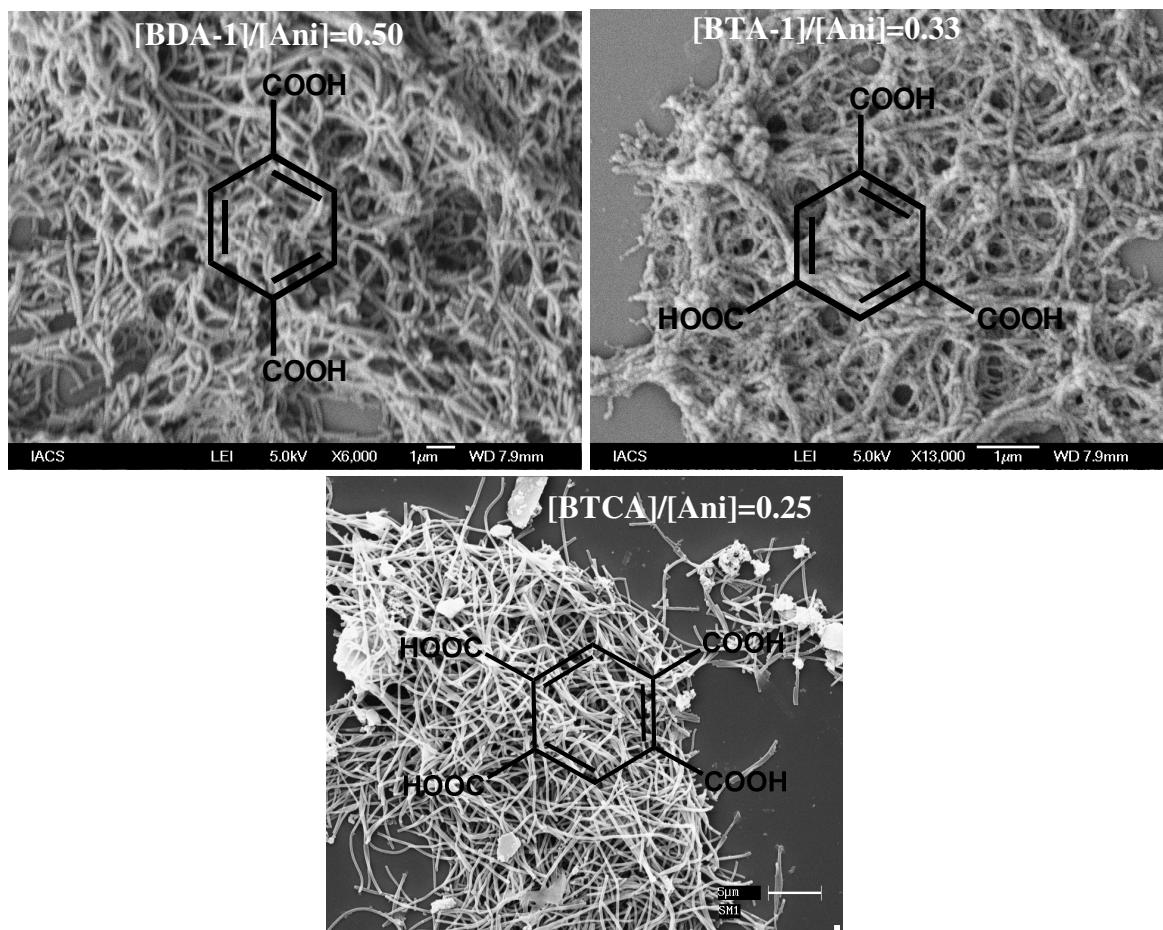


Fig. S9: FESEM-images of BDA-1/PANI, BTA-1/PANI, and BTCA/PANI under same stoichiometric condition (mole ratio of carboxylic acid unit to aniline) and [aniline]/[APS]=1.00.

pH Study:

pH profile of the polymerization of aniline in presence of three symmetrical acids BDA-1/PANI, BTA-1/PANI and BTCA/PANI under same stoichiometric condition (mole ratio of carboxylic acid unit to aniline) shown in Fig. S10. The curve indicates that the pH changes with respect to time for all acids. The same trend is followed because all acids are weak in nature and starting stoichiometric ratios of all systems are same.^{S2} In three cases, final pH of the medium is ~2.8 as we have carried out all the reaction in [aniline]/[APS]=1:1 ratio. Excess APS that should not be present in the reaction medium will generate the excess H₂SO₄ which decreases the pH of the medium more.^{S3}

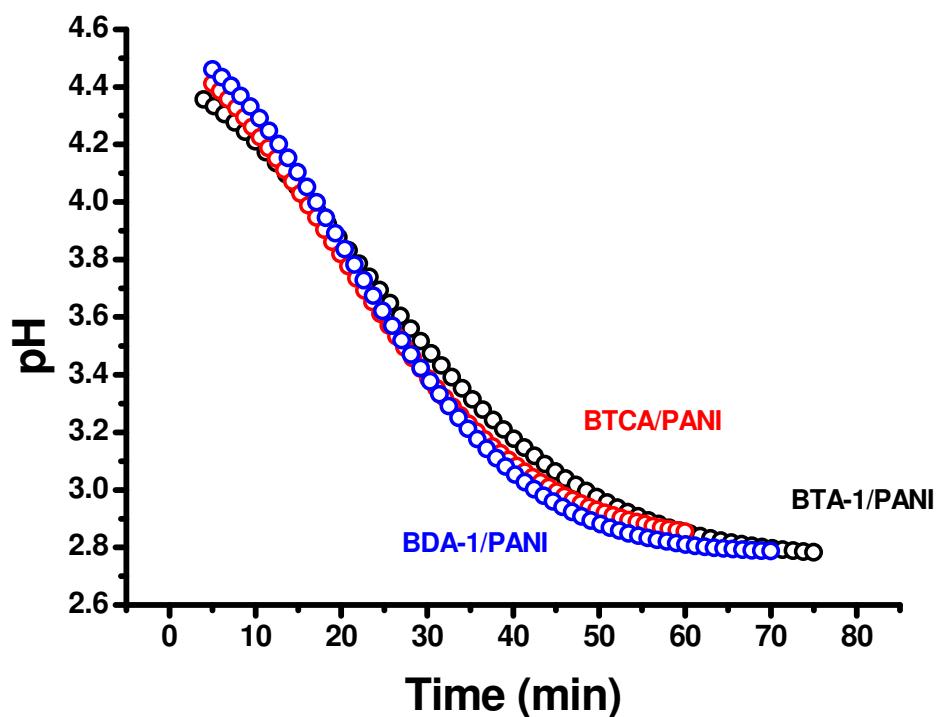


Fig. S10: pH –profile of all three symmetrical dopant acids under same stoichiometric condition.

2) Table S2: Room temperature and characteristic temperature (T_0) conductivity of different aromatic acid doped PANI. (The electrical conductivity was calculated as the inverse of resistivity. For measurement, PANI sample was pelletized under 2.5 torr pressure to give it a disk type shape. Then four probe connections were made by copper wire using silver epoxy. The measurement was done three times taking three different pellets. These measurements were consistent to each other).

Sample Name	$T_0(\times 10^7)$	Conductivity at room temperature ($\times 10^{-3}$ S/cm)
BDA-1(0.25)	2.88	10.7
BTA1 (0.25)	3.49	10.4
BTA1 (0.1)	6.53	0.503
BTA1 (0.01)	4.54	2.01
BTA2 (0.25)	2.61	4.2
BTA3 (0.25)	3.26	3.99
BPCA (0.25)	12.28	588
TPCA (0.25)	1.95	3.15

4. References:

- S1. P. K. Sukul and Sudip Malik, *RSC Adv.*, 2013, **3**, 1902.
- S2. R. L. Lundblad and F. M. MacDonald, *Handbook of Biochemistry and Molecular Biology*, 4th Ed., 2010, 595.
- S3. J. Stejskal, I. Sapurina, M. Trchová and E. N. Konyushenko, *Macromolecules*, 2008, **41**, 3530.