Electronic Supporting Information

Resemblances of experiment and theory on aryl substituted luminogenic polypyrazolines

Tirumalachetty Vandana[a], Arumugam Karuppusamy[a], Rasu Arulkumar[b],

PonnambalamVenuvanalingam*[b] and Palaninathan Kannan*[a]

Table of Content

FigureS1. ^{1}H-NMR spectrum of **PPB.**

PPB : ^{1}H NMR(400 MHZ, CDCl$_3$) δ (ppm) 7.89-7.10(m, 15H, Ar-H), 6.9-6.8 (t, 1H, pyrazoline CH), 4.4 -4.2 (m, 2H, pyrazoline CH$_2$).
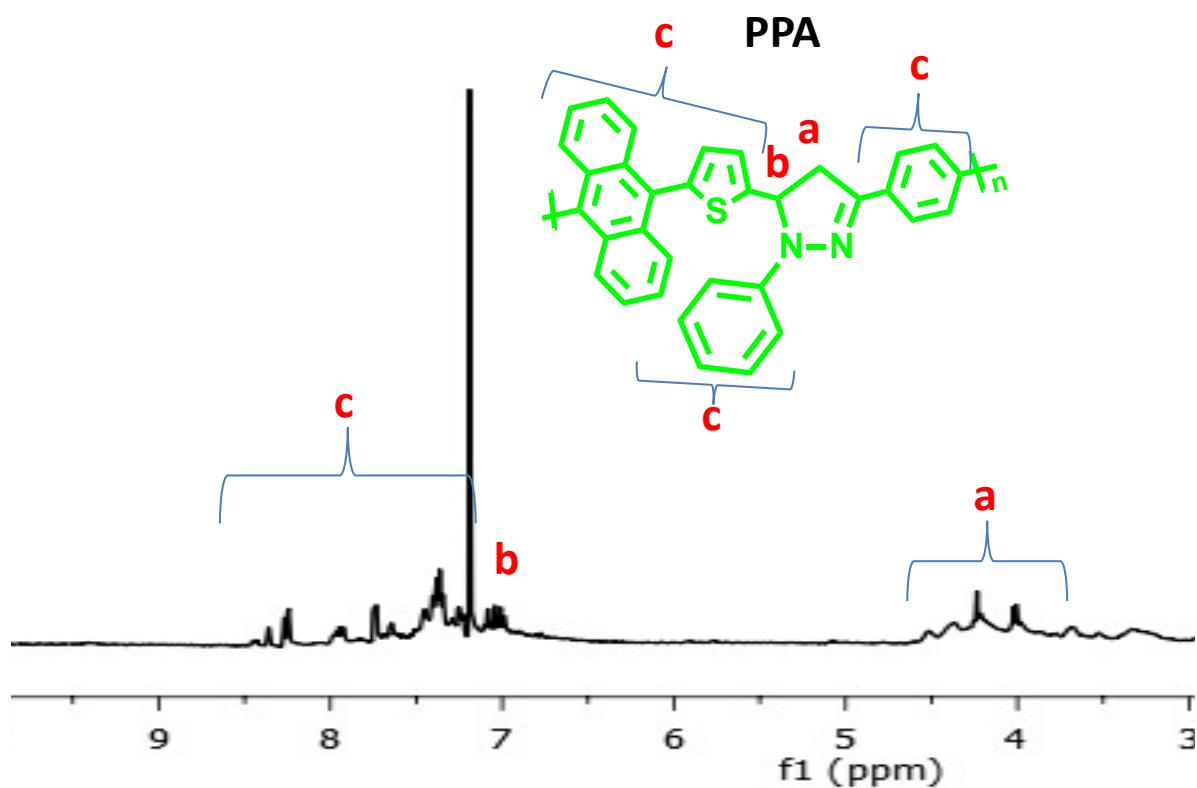
FigureS2. ^{1}H-NMR spectrum of**PPA.**

PPA: ^{1}H NMR(400 MHZ, CDCl$_3$) δ (ppm) 7.89-7.10(m, 19H, Ar-H), 6.9-6.8 (t, 1H, pyrazoline CH), 4.4 -4.2 (m, 2H, pyrazoline CH$_2$).
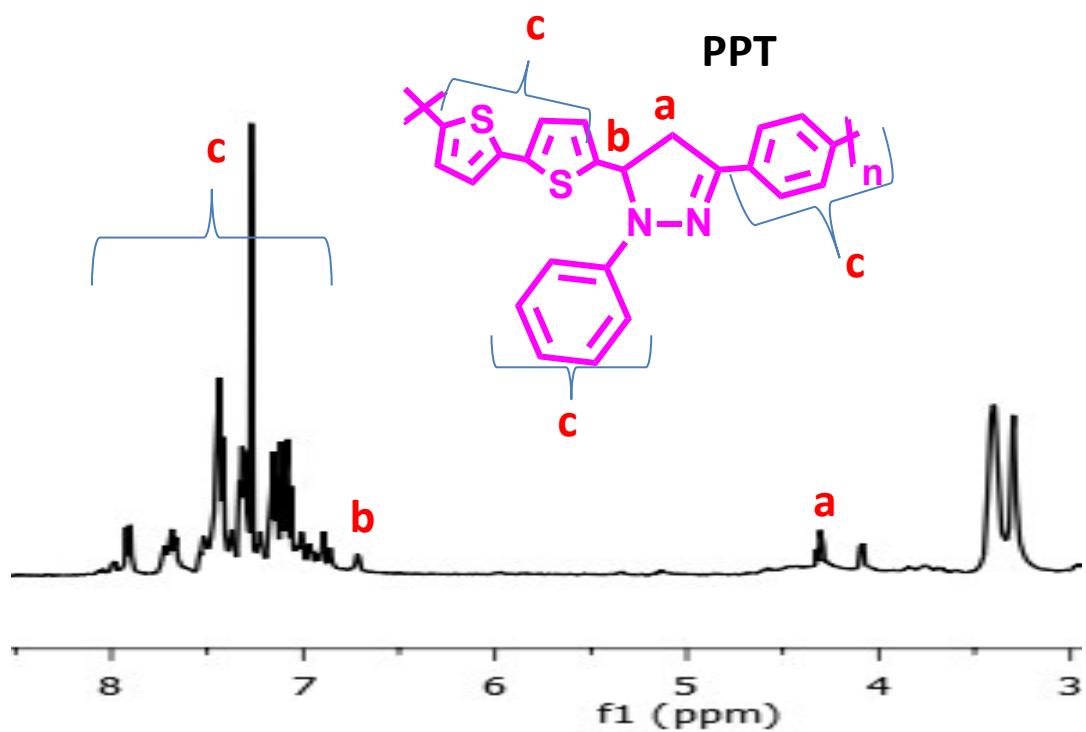
FigureS3.^{1}H-NMR spectrum of**PPT.**

PPT: ^{1}H NMR(400 MHZ, CDCl$_3$) δ (ppm) 7.89-7.10(m, 13H, Ar-H), 6.9-6.8 (t, 1H, pyrazoline CH), 4.4 -4.2 (m, 2H, pyrazoline CH$_2$).
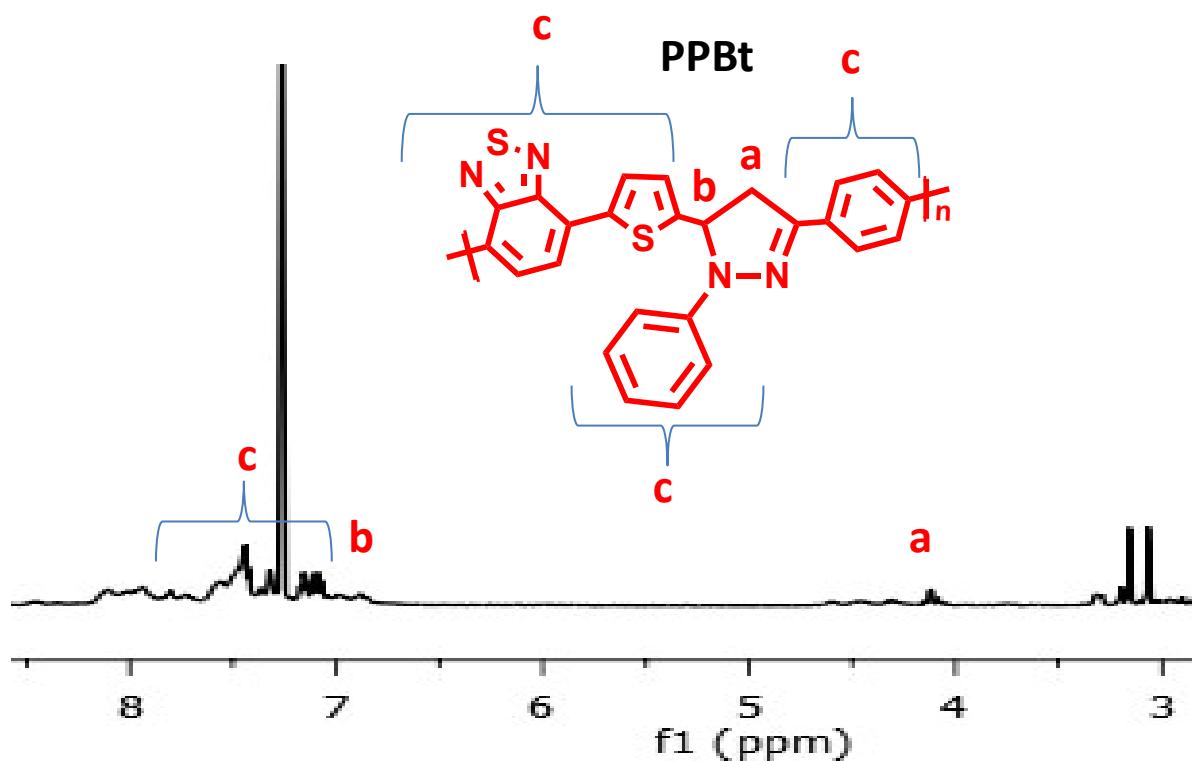
FigureS4. ^{1}H-NMR spectrum of **PPBt.**

PPBt: ^{1}H NMR(400 MHZ, CDCl$_3$) δ (ppm) 7.89-7.10(m, 13H, Ar-H), 6.9-6.8 (t, 1H, pyrazoline CH), 4.4 -4.2 (m, 2H, pyrazoline CH$_2$).
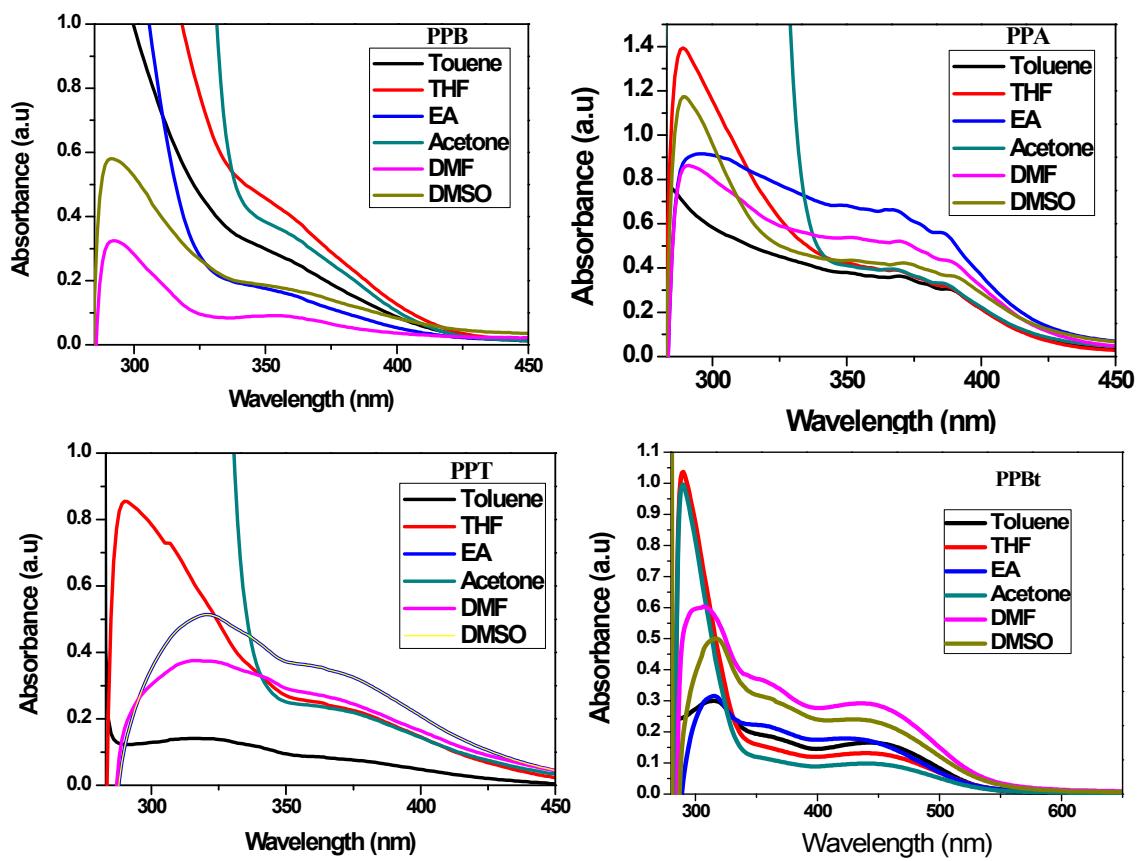
**FigureS5.** Absorption spectra of PPB, PPA,PPT and PPBt in various solvents
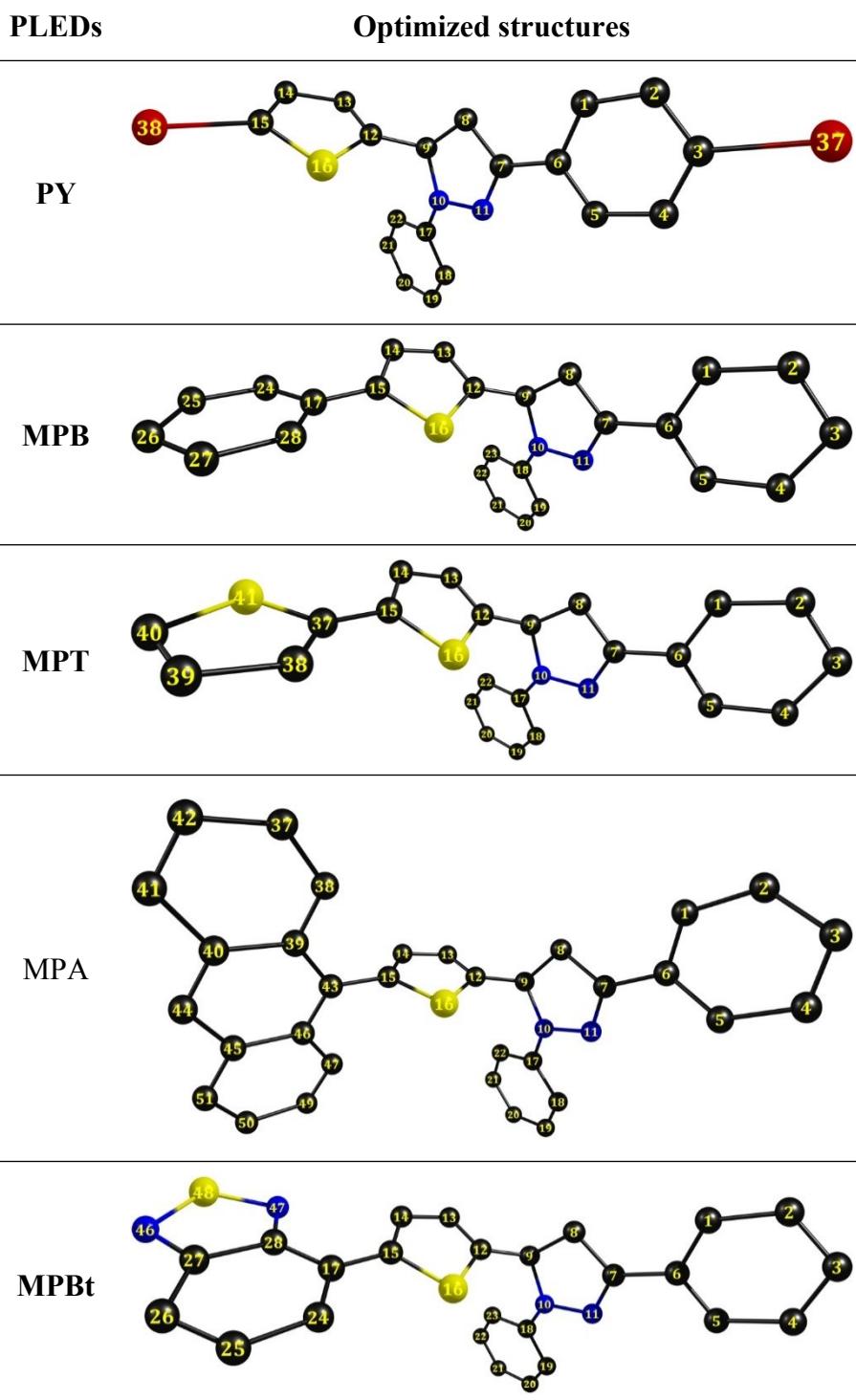
Figure S6. Ground state optimized structures of the monomer units calculated at B3LYP/ 6-311+G(d,p) level in CHCl$_3$ medium. (H atoms has been omitted for clarity)

Table S1. Thermal properties of polymers**.**

Material	T_g/T_m (˚C)	$T_{5\%}$ (˚C)	$T_{50\%}$ (˚C)	$T_{d\ max}$ (˚C)
PPB	75	282	401	658
PPA	111	300	408	516
PPT	113	310	422	530
PPBt	127/158	311	390	558

Table S2. Selected dihedral angles (degree) of designed monomeric units of PLEDs. S_0 geometries had been optimised both in gas phase and $CHCl_3$ medium at B3LYP/ 6-311+G (d, p) level. S_1 and T_1 geometries are optimized using TDA method. The atom numbers are given in the Fig.S6.

Model PLEDs	Dihedral Angle	S_0		TDA	
		Gas Phase	$CHCl_3$	S_1*	T_1*
PY	16S-12C-9C-10N (ϕ_a)	37.3	37.7	57.8	51.0
MPB	16S-12C-9C-10N (ϕ_a)	38.3	39.2	60.8	49.3
	24C-17C-15C-16S (ϕ_b)	-150.0	-151.8	-178.6	-151.8
MPT	16S-12C-9C-10N (ϕ_a)	38.2	38.6	61.3	41.7
	41S-37C-15C-16S (ϕ_b)	-154.0	-155.5	-178.6	-180.0
MPA	16S-12C-9C-10N (ϕ_a)	41.6	41.8	52.9	40.5
	39C-43C-15C-16S (ϕ_b)	97.4	95.6	89.4	117.1
MPBt	16S-12C-9C-10N (ϕ_a)	37.9	38.2	54.9	35.7
	28C-17C-15C-16S (ϕ_b)	-173.1	-171.7	-176.8	-179.7