Supporting Information

Emission and surface properties of main-chain type polybenzoxazine with pyridinyl moieties

Ching Hsuan Lin,*[a] Yu Sin Shih,[a] Meng Wei Wang,[a] Chun Yu Tseng,[a] Tzong Yuan Juang,[b] Chih Feng Wang*[c]

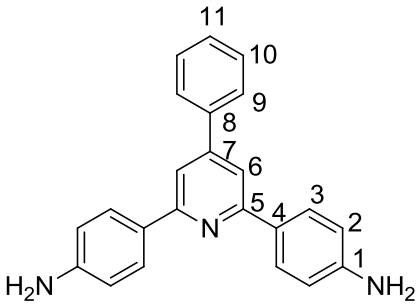
[a]Department of Chemical Engineering, National Chung Hsing University, Taichung, Taiwan

[b]Department of Applied Chemistry, National Chiayi University, Chiayi, Taiwan

[c]Department of Materials Science and Engineering, I-Shou University, Kaohsiung, Taiwan

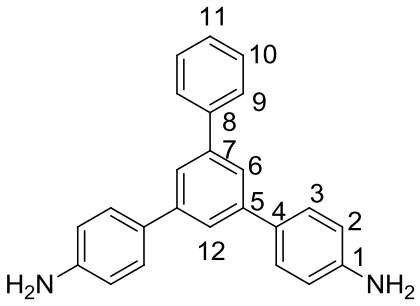
Preparation of diamine (2). Diamine **(2)** was prepared by a two-step procedure (Scheme 1).[1] In the first step, benzaldehyde 3.20 g (0.03 mole), p-nitroacetophenone 10.00 g (0.06 mole), and ammonium acetate 30.00 g (0.39 mole) , and glacial acetic acid 75 mL were introduced into a round-bottom 250 mL glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer. The reaction mixture was stirred at reflux for 12 h. The precipitate was filtered and washed with 50% acetic acid solution and then with ethanol. After drying in a vacuum oven, deep yellow powder **(1)** with 67% yield was obtained. In the second step, **(1)** 10.00 g (0.024 mole), palladium on carbon 10 % (0.40 g), and ethanol 400 mL were introduced into a round-bottom 500 mL glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer. The reaction mixture was warmed to 80 ^{o}C. Hydrazine hydrate 80% (20 mL) in ethanol (40 mL) was added dropwise over a 2

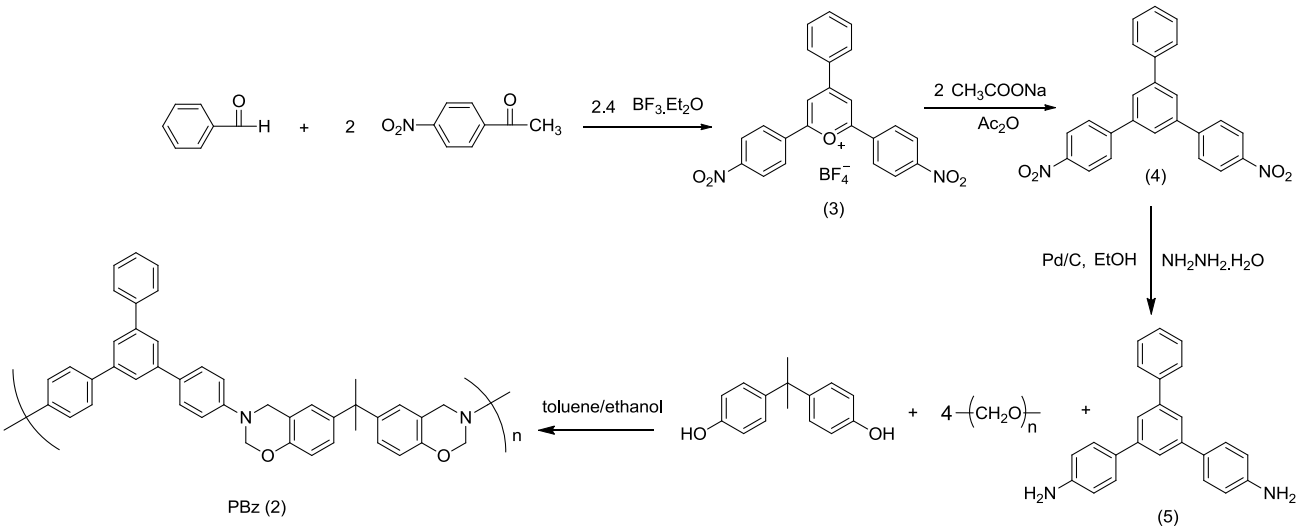
h period through the dropping funnel, and stirred constantly for another 12 h. The solution was filtered, and the filtrate was cooled slowly to room temperature. Yellow crystal **(2)** with 90% yield was obtained after filtering and vacuum drying at 100 ^{o}C. ^{1}H-NMR (ppm,DMSO-d_6), δ=5.42 (4H, NH_2), 6.72 (4H, H^2), 7.48 (1H, H^{11}), 7.54 (2H, H^{10}), 7.81 (2H, H^6), 7.94 (2H, H^9), 8.04 (4H, H^3). Melting point from DSC thermogram: 200.8 ^{o}C. Melting enthalpy 88.6 J/g.



Preparation of diamine (5). Diamine **(5)** was prepared by a three-step procedure (Scheme S1).[25] In the first step, benzaldehyde 5.00 g (47.12 mmol), 4-nitroacetophenone (15.56 g, 94.23 mmol), and toluene (30 mL) were introduced into a round-bottom 150 mL glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer. Boron trifluoride etherate 14.20 mL (113.09 mmol) diluted with toluene (5 mL) was added dropwise over a 1 h period through a dropping funnel. The mixture was stirred at reflux for 3 h. The dark solution obtained was concentrated by a rotary evaporator, and the residue was washed with 1,4-dioxane and then with ether. After vacuum dried at 105 ^{o}C, 2,6-bis(4-nitrophenyl)-4-phenylpyrylium tetrafluoroborate **(3)** with 63% yield was obtained. In the second step, **(3)** 11.00 g (23.51 mmol), sodium acetate 3.86 g, (47.02 mmol), and acetic anhydride 40 mL) introduced into a round-bottom 150 mL glass flask equipped with a nitrogen inlet, a condenser,

and a magnetic stirrer. The mixture was refluxed for 12 h. The resulting solution was subsequently cooled at -10 °C for several hours. The precipitate was filtered and washed with methanol. After being vacuum dried at 105 ^{o}C, 4,4-dinitro-5-phenyl-*m*-terphenyl **(4)** with 70% yield was obtained. In the third step, **(4)** 7.00 g (0.016 mole), palladium on carbon 10 % (0.28 g), and ethanol 20 mL were introduced into a round-bottom 150 mL glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer. The reaction mixture was warmed to 80 ^{o}C. Hydrazine hydrate 80% (8 mL) in ethanol (16 mL) was added dropwise over a 2 h period through the dropping funnel, and keep stirred for another 12 h. The solution was filtered, and the filtrate was cooled slowly to room temperature. Brown crystal **(5)** with 85% yield was obtained after being filtered and vacuum dried at 100 ^{o}C. ^{1}H-NMR (ppm,DMSO-d_6) δ=5.2 (4H, NH_2), 6.7 (4H, H^{2}), 7.4-7.5 (7H, $H^{3,10,11}$), 7.5-7.8 (5H, $H^{6,9,12}$). Melting point from DSC thermogram: 229.3 ^{o}C. Melting enthalpy 77.5 J/g.





Scheme S1. Synthesis of PBz **(2)**

Table S1. Solvent effects on PBz **(1)** and PBz **(2)** synthesis

Run	Sample ID	Temp (^{o}C)	Time (hr)	Solvent	Reaction Status
1	PBz **(1)**	80	24	1,4-dioxane	A lot of gelatin
2	PBz **(1)**	60	24	chloroform	A lot of gelatin
3	PBz **(1)**	80	24	xylene	A lot of gelatin
4	PBz **(1)**	80	24	toluene	A lot of gelatin
5	PBz **(1)**	80	24	toluene/ethanol (2/1)	Precipitate in slurry form during polymerization
6	PBz **(1)**	80	24	toluene/ethanol (1/1)	Homogeneous with high yield (82%)
7	PBz **(1)**	80	24	toluene/ethanol (1/2)	Homogeneous but low yield (less than 40%)
8	PBz **(2)**	60	24	chloroform	Powder precipitation during polymerization
9	PBz **(2)**	80	24	toluene/ethanol (2/1)	Powder precipitation during polymerization
10	PBz **(2)**	80	24	toluene/ethanol (1/1)	Powder precipitation during polymerization

Table S2. Solubility data of PBz **(1)** and PBz **(2)**[a]

Sample ID	Solvent							
	NMP	DMAc DMF DMSO	Dioxane	CH_2Cl_2	$CHCl_3$	THF	Toluene	Xylene
PBz **(1)**	+	+	+	±	+h	+	±	±
PBz **(2)**	+h	±	-	±	±	±	-	-

[a] Solubility was tested with a 10 mg sample in 1 mL of solvent.

+, soluble; +h, soluble on heating; ±, partially soluble on heating; -, insoluble on heating.

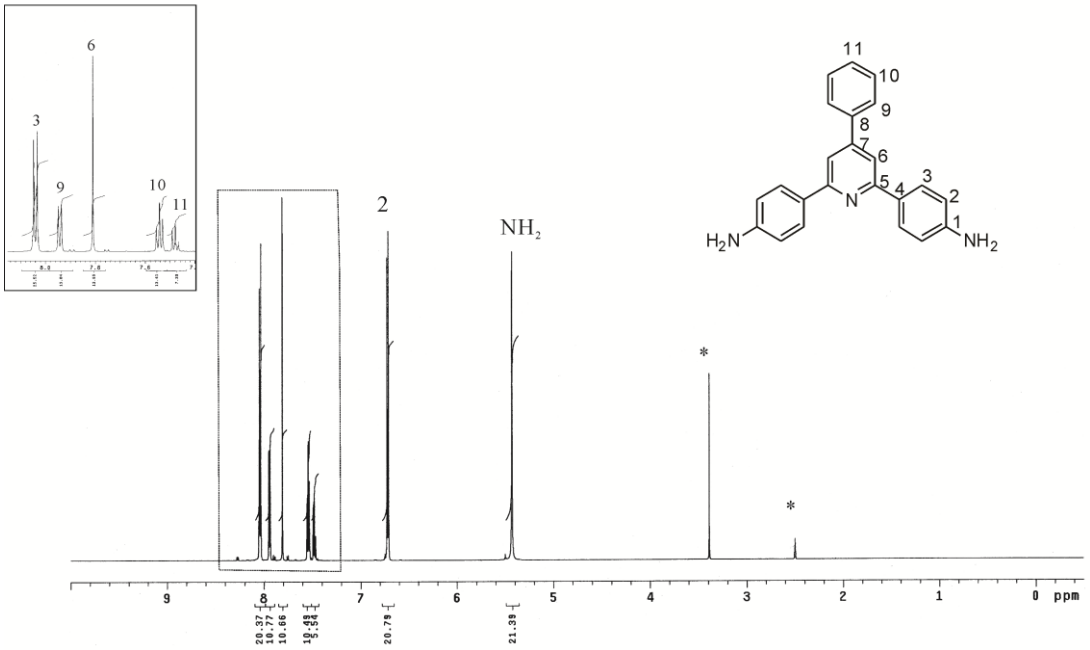


Figure S1. ^{1}H NMR spectrum of **(2)** in DMSO-d_6.

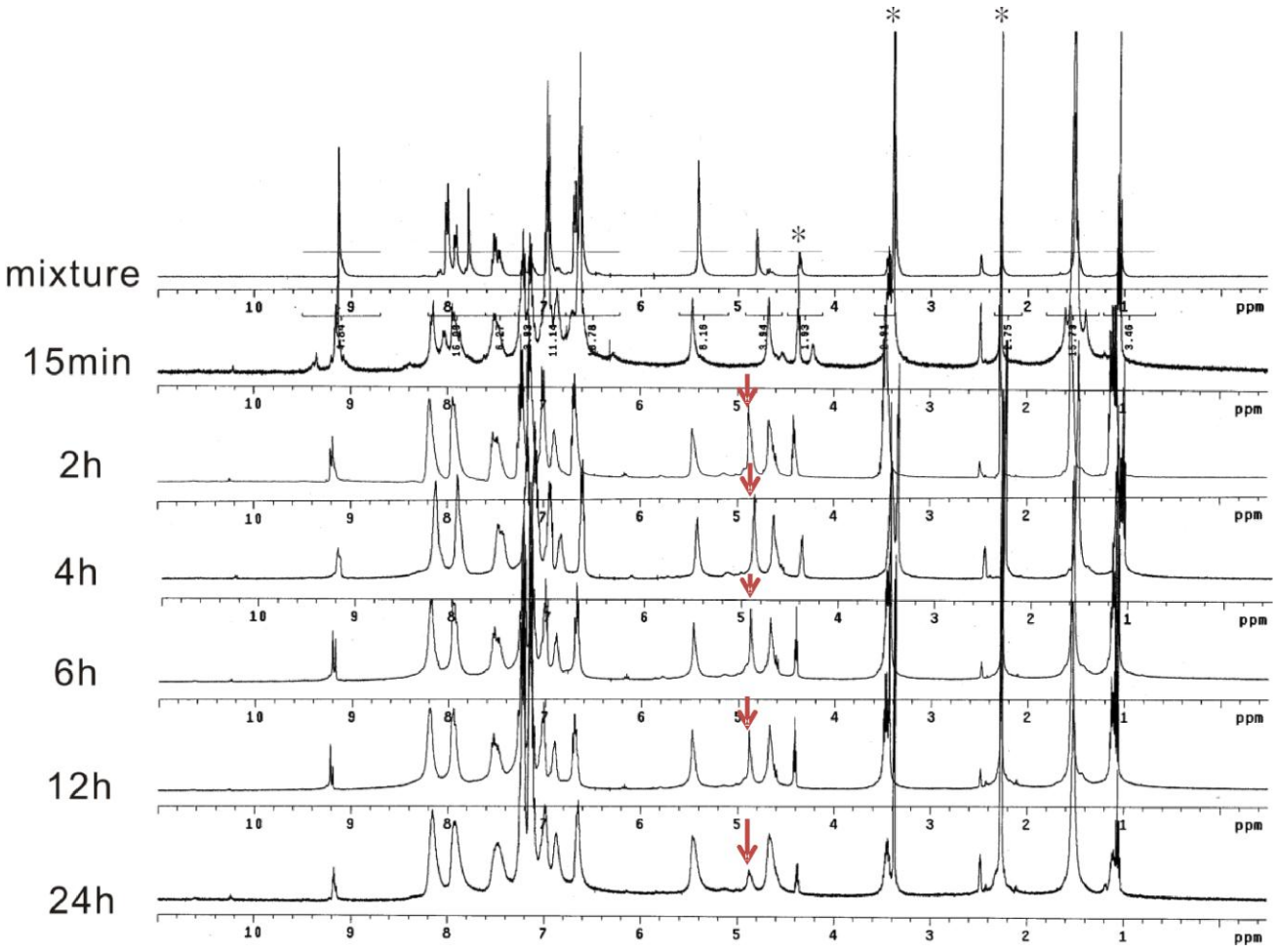


Figure S2. ^{1}H NMR spectra of vacuum-dried reaction mixture at various reaction time for PBz **(1)** synthesized in Run 5. Note that the triazine peak (4.88 ppm) did not disappear completely after 24 h.

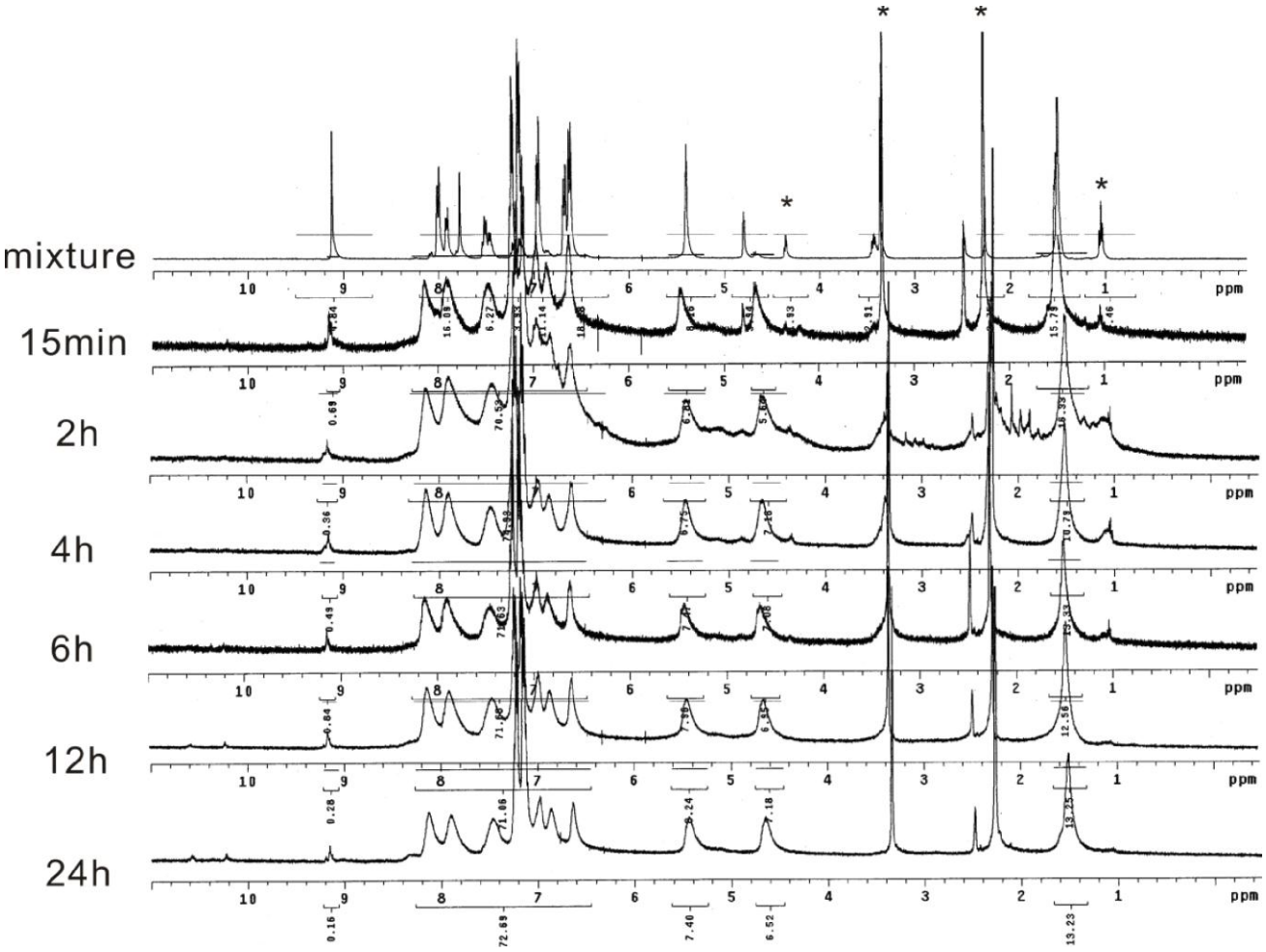


Figure S3. ^{1}H NMR spectra of vacuum-dried reaction mixture at various reaction time for PBz **(1)** synthesized in Run 6. Note that no triazine peak was observed during the synthesis.

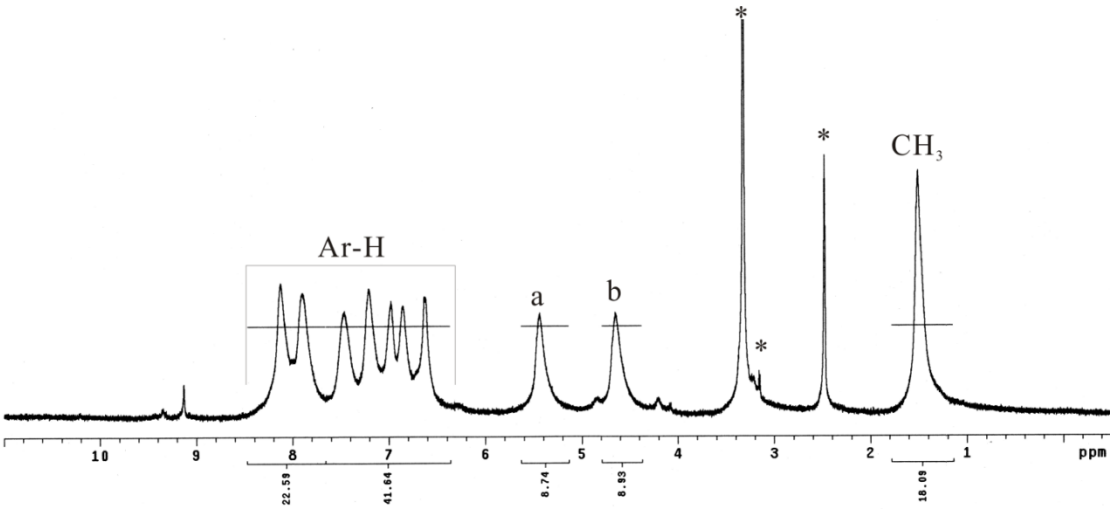


Figure S4. ^{1}H NMR spectrum of (a) PBz **(1)** in DMSO-d_6.

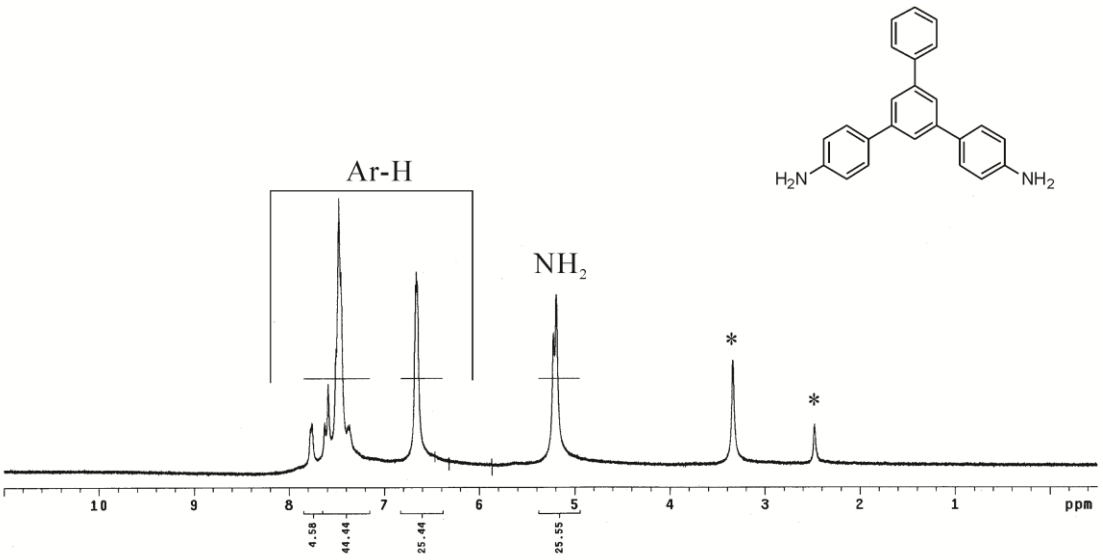


Figure S5. ^{1}H NMR spectrum of **(5)** in DMSO-d_6.

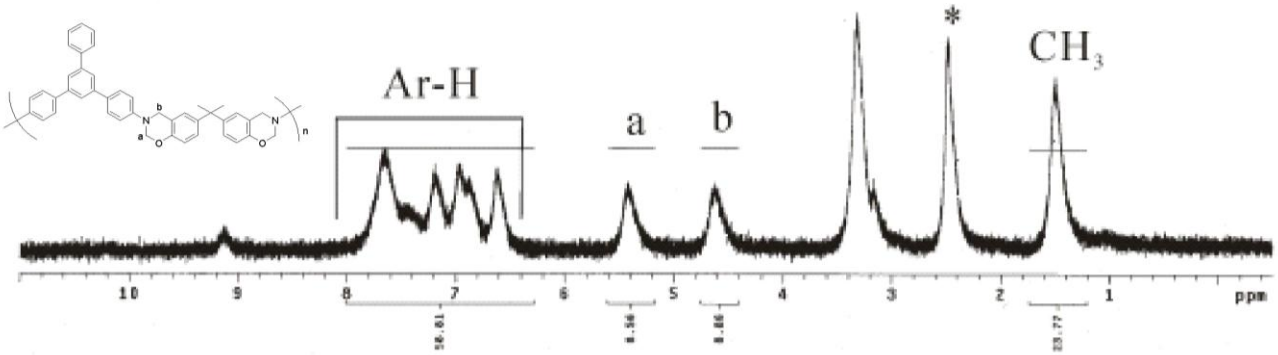


Figure S6. ^{1}H NMR spectrum of (a) PBz **(2)** in DMSO-d_6. Note that the early precipitation lowers the purity of PBz **(2)**.

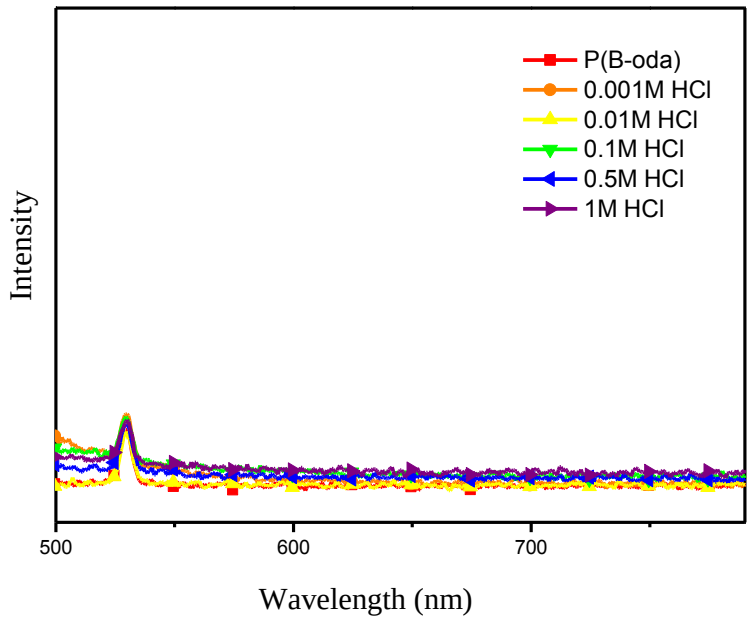


Figure S7. Emission spectra of THF dilute solution of P(B-oda) and protonated PBz (B-oda) after being excited at 458 nm.

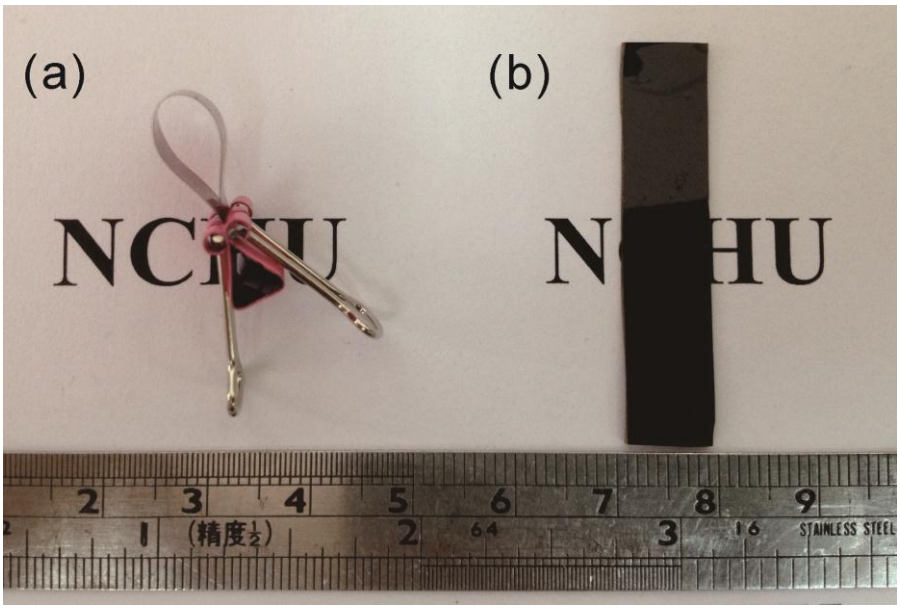


Figure S8. A photo of PBz **(1)**-T at a thickness of (a) 60μm (b) 550μm

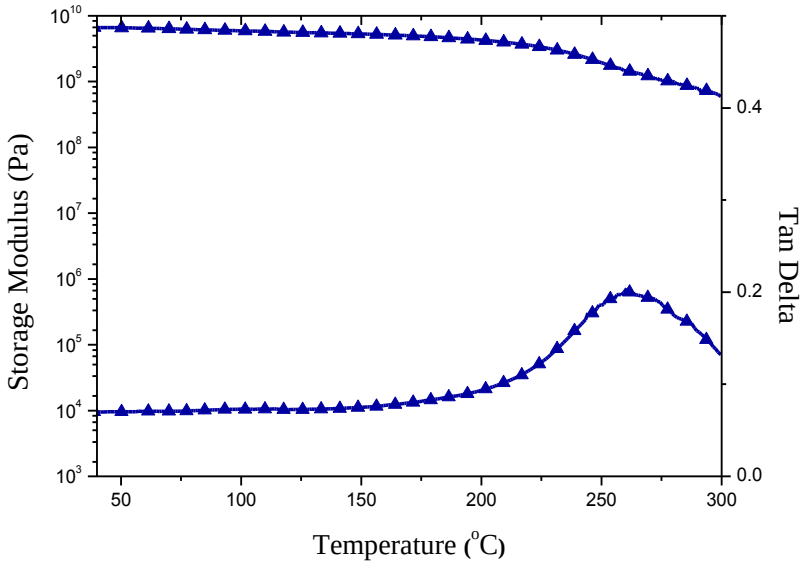


Figure S9. DMA thermogram of PBz **(1)**-T.

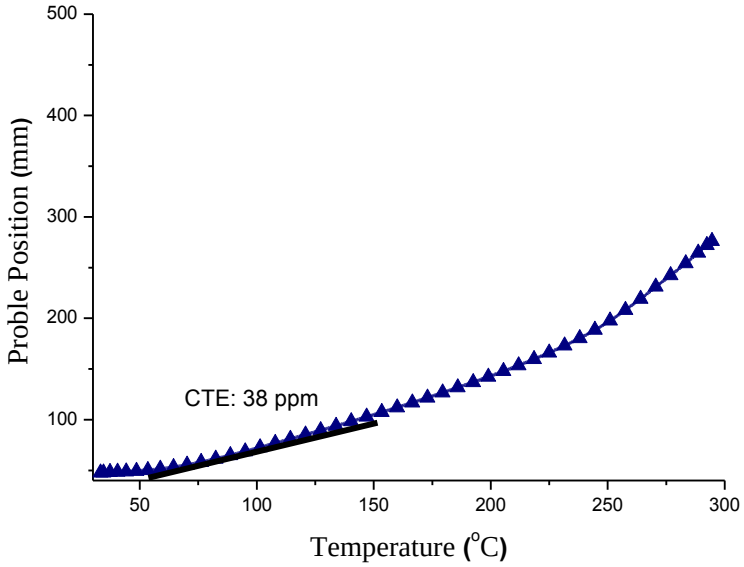


Figure S10. TMA curve of PBz **(1)**-T

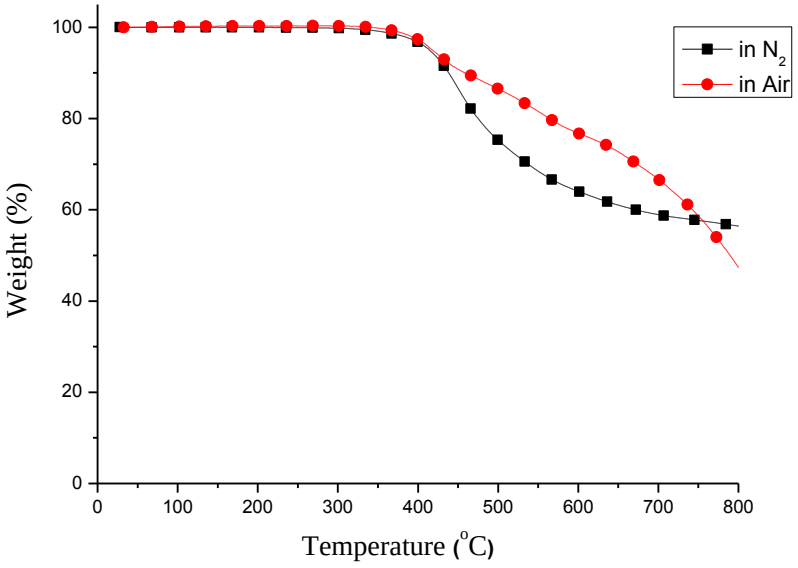


Figure S11. TGA thermograms of PBz **(1)**-T in N_2 and air.