

Electronic Supplementary Information

For

Pyrene Boronic Acid Cyclic Ester: A New Fast Self-Recovering Mechanoluminescence Material at Room Temperature

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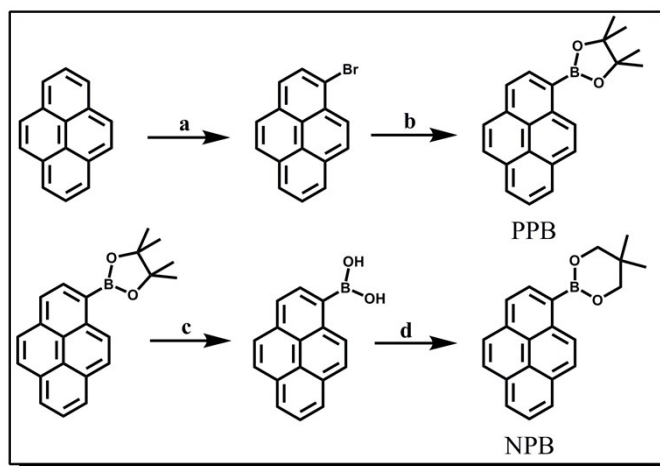
Experimental Section

1. Materials and measurements

Et₃N and 1,4-Dioxane were freshly distilled over appropriate drying agents. Reactions that required oxygen-free conditions were carried out under nitrogen atmosphere using standard Schlenk techniques. All the other reagents were purchased and used without further purification.

¹H NMR was recorded on 400 MHz (Bruker ARX400) and ¹³C NMR spectra were recorded on Bruker 100 MHz spectrometer at room temperature with CDCl₃ as the solvents and tetramethylsilane (TMS) as the internal standard. Differential scanning calorimetry (DSC) measurements were carried out on TA Instruments DSC Q2000. Fluorescence spectra measurements were performed on a Shimadzu RF-5301PC spectrofluorophotometer. Absorption spectra were determined on a Pgeneral UV-Vis TU-1901 spectrophotometer. Small and wide angle X-ray scattering (SWAXS) experiments were carried out with a SAXS instrument (SAXSess, Anton Paar) containing Kratky block-collimation system. Indentation experiments were performed on Triboindenter of Hysitron, Minneapolis, USA. The machine continuously monitors and records the load, *P*, and displacement, *h*, of the indenter with force and displacement resolutions of 1 nN and 0.2 nm, respectively. A three-sided pyramidal Berkovich diamond indenter (tip radius ≈ 100 nm) was used to indent the crystals. Loading and unloading rates of 0.6 mN/s and a hold time of 30 s at peak load were employed. A minimum of 7 indentations were performed to ensure reproducibility. The indentation impressions were captured immediately after unloading so as to avoid any time-dependent elastic recovery of the residual impression. The *P-h* curves obtained were analyzed using the standard Oliver-Pharr method¹ to extract the elastic modulus, *E*, of the crystal in that orientation.

2. Synthesis of the PPB and NPB



Scheme S1. Reaction conditions: (a) Br_2 , room temperature, overnight; (b) bis(pinacolato)–diborane, KOAc, Pd(dppf) Cl_2 , 90 °C, 12h; (c) NaIO_4 , HCl, room temperature, 24h; (d) neopentyl glycol, room temperature, 8h.

Synthesis of 1-bromopyrene

To a stirred solution of pyrene (1.01 g, 5 mmol) and hydrobromic acid (0.62 mL of a 48% aqueous solution, 5.5 mmol) in methanol-ethyl ether (10 mL, 1 : 1 (v/v)) was slowly added hydrogen peroxide (30%, 0.20 g, 10 mmol) over a period of 20 min below 12 °C. Then the mixture was left at 30 °C for 12 h. After the completion of mono-bromination, the solvent was removed under reduced pressure and the crude product was extracted by 100 mL ethyl acetate and washed with 5% potassium bromide water solution 3 times (3×100 mL). Organic phase was dried over anhydrous sodium sulfate overnight.² The pure product was isolated by flash column chromatography on silica gel eluted by ethyl acetate to give pure 1-bromopyrene as a light brown solid; yield is 90%. ^1H NMR (400 MHz, CDCl_3): δ 8.12 (s, 1H), 8.01-7.99 (m, 2H), 7.88-7.82 (m, 2H), 7.71 (m, 4H).

Synthesis of PPB

Pd(dppf) Cl_2 (0.33 g, 0.44 mmol), bis(pinacolato)diborane (3.39 g, 13.3 mmol) and KOAc (2 g, 20.4 mmol) were added to a solution of 1-bromopyrene (2.5 g, 8.9 mmol) in dioxane. Reaction mixture was degassed with nitrogen and stirred at 90 °C overnight. After the completion of the reaction, the mixture was poured into water, extracted with chloroform. The solvent was removed after drying the organic layer with Na_2SO_4 . The residue was subjected to column chromatography on silica gel (gradient elution with hexanes–ethyl acetate mixtures from 1:0 to 1000:5) to give 80% of 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane. ^1H NMR (400 MHz, CDCl_3): 1.51 (s, 12H), 8.02 (t, 1H), 8.07-8.24 (m, 6H), 8.56 (d, 1H), 9.09 (d, 1H). ^{13}C NMR (100MHz, CDCl_3): δ 136.4, 133.9, 133.5, 131.1, 130.8, 128.5, 128.0, 127.8, 127.5, 125.7, 125.4, 125.2, 124.6, 124.4, 124.1, 83.9, 25.1.

Synthesis of Pyren-1-ylboronic Acid

To the solution of PPB (2 g, 6.10 mmol) in THF (24 mL) and water (6 mL) sodium periodate (3.90 g, 18.3 mmol) was added. The cloudy suspension was stirred overnight at room temperature. Hydrochloric acid (2M, 0.5 mL) was added and the mixture stirred for another 24 hours. After the completion of the reaction, the mixture was poured into water, extracted with ethyl acetate. The

organic solvent was removed after drying it with Na₂SO₄. The pure product was obtained by washing residue with benzene twice. Yield is 85%. ¹H NMR (400 MHz, DMSO-d₆): δ 8.79 (d, 1H), 8.66 (s, 2 H), 8.35 (d, 1H), 8.14-8.30 (m, 6 H), 8.04 (t, 1H). ¹³C NMR (100 MHz, DMSO-d₆): δ 134.1, 132.6, 131.9, 131.5, 130.9, 130.5, 128.6, 127.6, 126.9, 126.0, 125.0, 124.1, 123.7, 123.1.

Synthesis of NPB

Neopentyl glycol (0.507 g, 4.9 mmol) was added to a suspension of pyren-1-ylboronic Acid (1 g, 4.1 mmol) in diethyl ether. The solution was stirred at room temperature for 8h. After the reaction completed, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel (CH₂Cl₂) to give 90% of **NPB**. ¹H NMR (400MHz, CDCl₃): δ 9.09 (d, 1H), 8.53 (d, 1H), 7.99-8.23 (m, 7H), 4.01 (s, 4H), 1.18 (s, 6H). ¹³C NMR (100MHz, CDCl₃): δ 135.9, 133.0, 131.2, 130.8, 128.2, 128.0, 127.6, 127.4, 125.6, 125.1, 125.0, 124.8, 124.6, 124.1, 72.7, 31.9, 22.0.

Table S1. The recovery property of the shearing sample in different solvents

Solvent	Dichloromethane	Chloroform	Tetrahydrofuran	Acetonitrile	Toluene	Acetone
FL Recovery	Y ^a	Y	Y	Y	Y	Y
Solvent	Ethyl acetate	Hexane	Ethanol	Methanol	Benzene	Petroleum ether
FL Recovery	Y	Y	N	N	Y	Y

^a “Y” indicates that the solvent can restore the shearing powders from green to blue, while “N” denotes that the solvent cannot restore the blue luminescence.

Table S2. Photophysical parameters of **PPB** and **NPB** in THF solution

Compound	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi_{\text{f}}^{\text{a}}$	$\tau_{\text{f}}^{\text{b}}/\text{ns}$
PPB	351	37410	382	0.24	3.2
NPB	350	35680	380	0.22	3.4

^a Quinine bisulfate in 0.05 M H₂SO₄ solution was used as the standard.

^b Excitation at 350 nm, data collected at 380 nm for **PPB** and **NPB**.

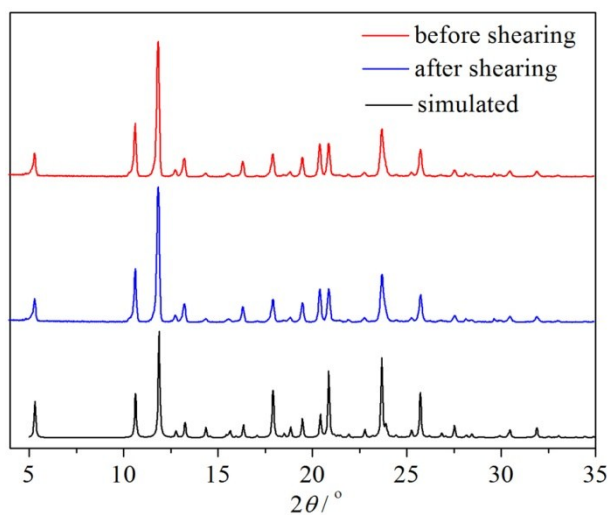


Figure S1. The powder XRD patterns of NPB.

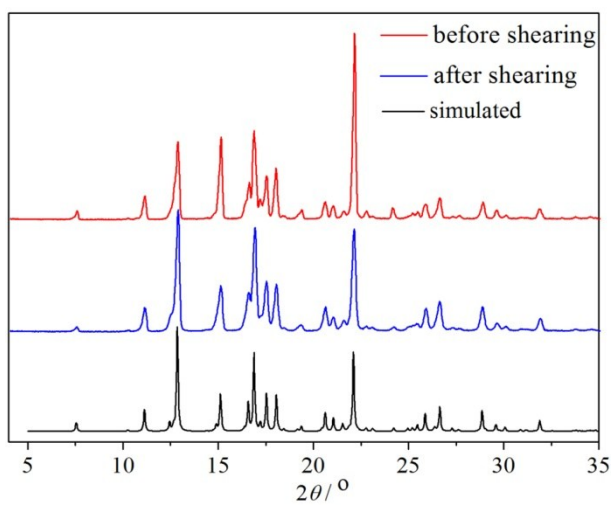


Figure S2. The powder XRD patterns of PPB.

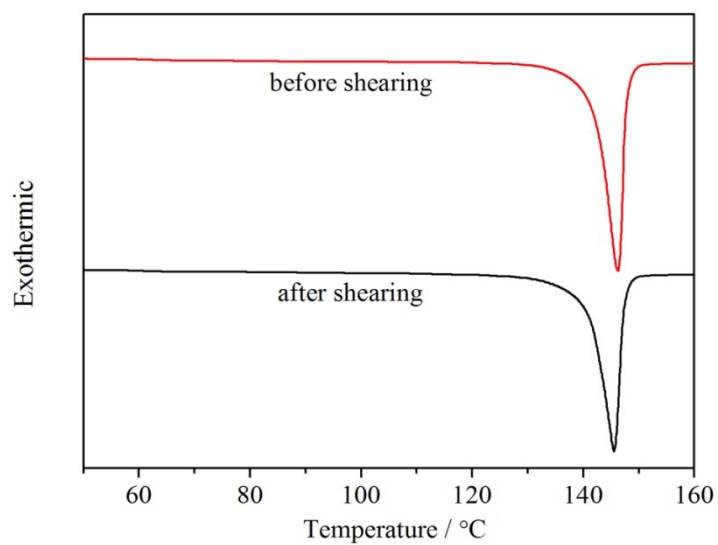


Figure S3. The DSC profiles of NPB before and after mechanical shearing.

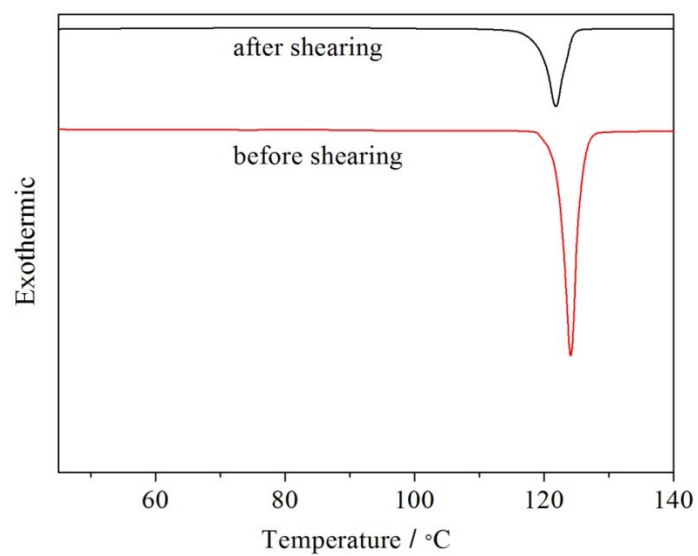


Figure S4. The DSC profiles of **PPB** before and after mechanical shearing.

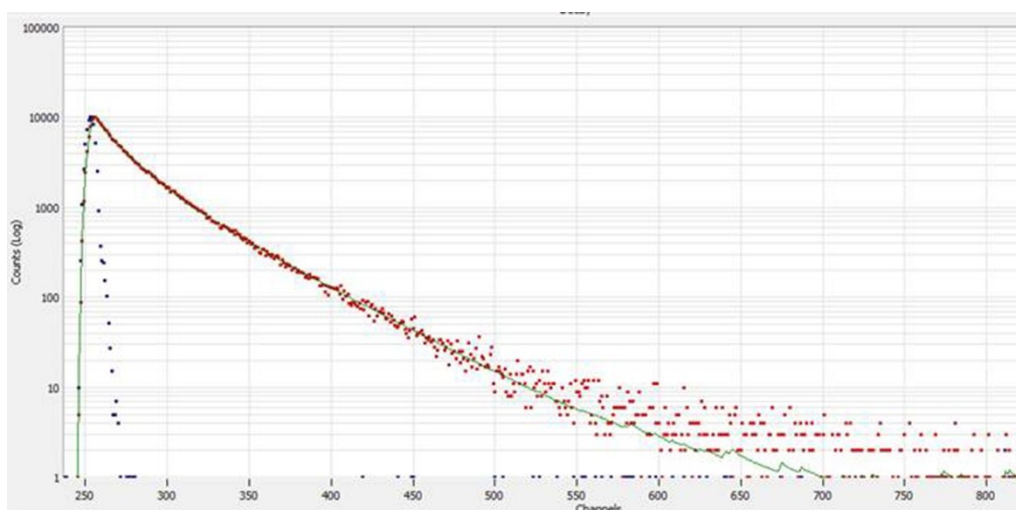


Figure S5. Fluorescence decay of **PPB** before mechanical shearing.

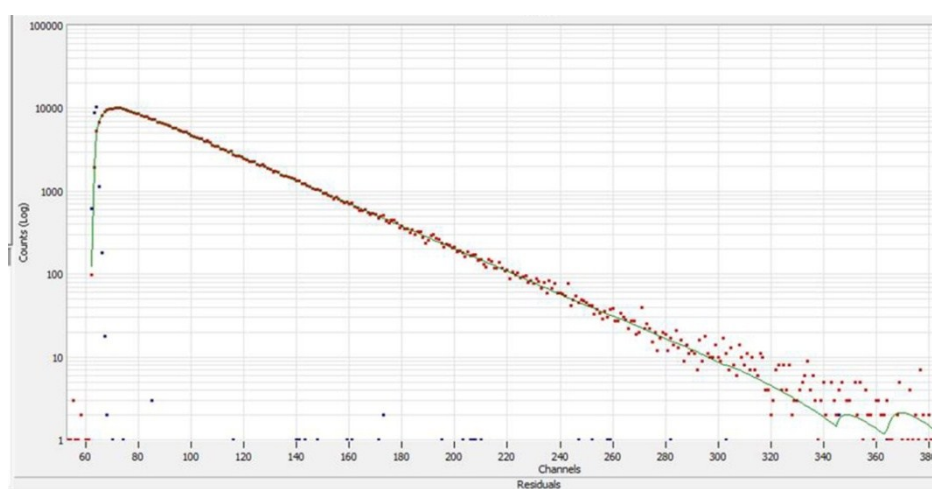


Figure S6. Fluorescence decay of **PPB** after mechanical shearing.

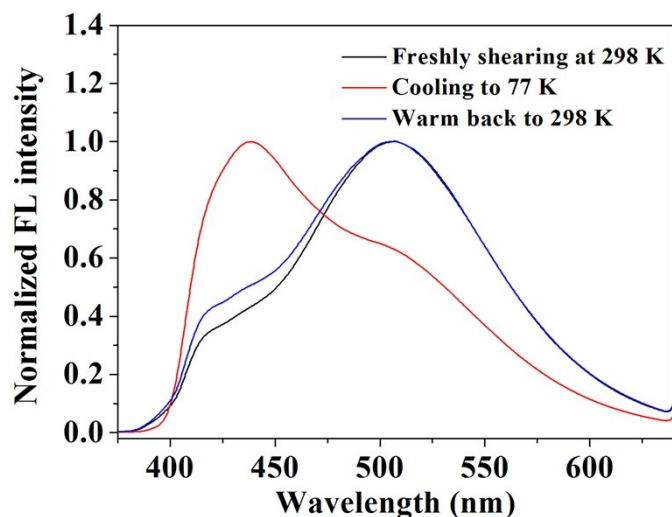


Figure S7. The fluorescent spectra of PPB powder: freshly shearing at room temperature of 298 K (black); cooling to 77 K (red) and warm back to room temperature (blue).

Table S3. Mechanical properties of **PPB** and **NPB** crystals obtained using nanoindentation with a Berkovich tip

Compound	Elastic modulus, E^a	Hardness, H^a
	[GPa]	[MPa]
PPB	6.1 ± 0.1	220 ± 40
NPB	8.7 ± 1.1	280 ± 10

^a The error bars correspond to the standard deviations on the ten measurements that were made on each face.

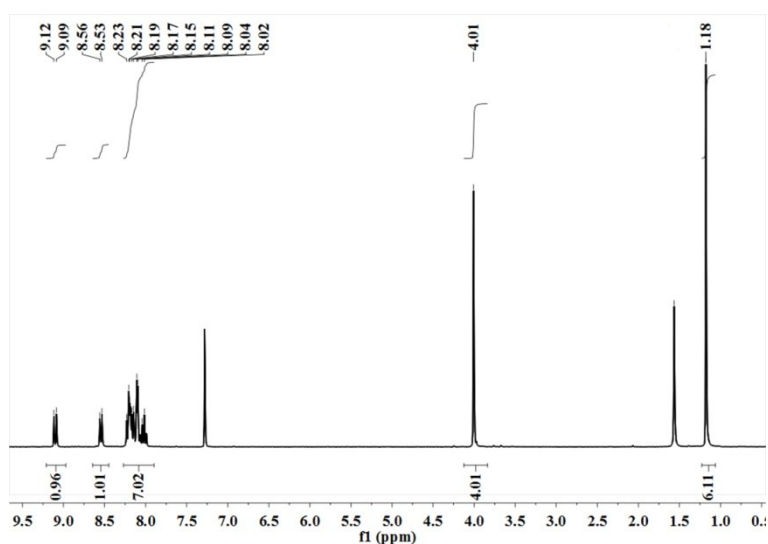


Figure S8. ^1H NMR spectrum of NPB.

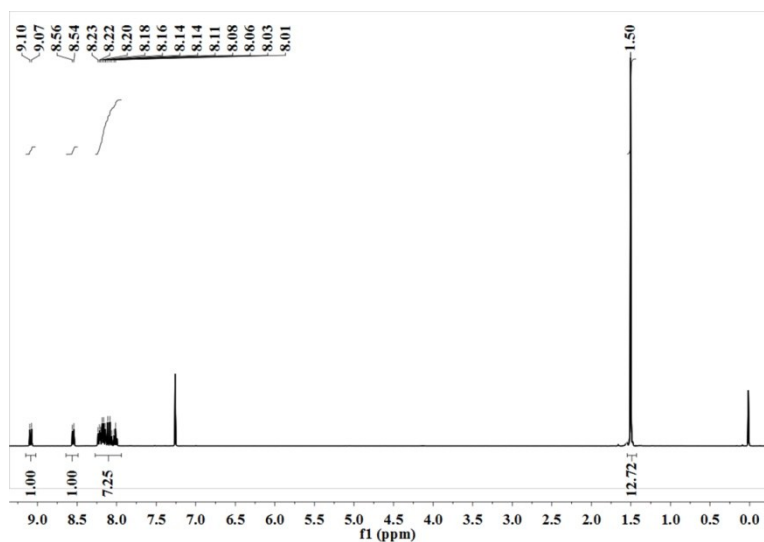


Figure S9. ^1H NMR spectrum of PPB.

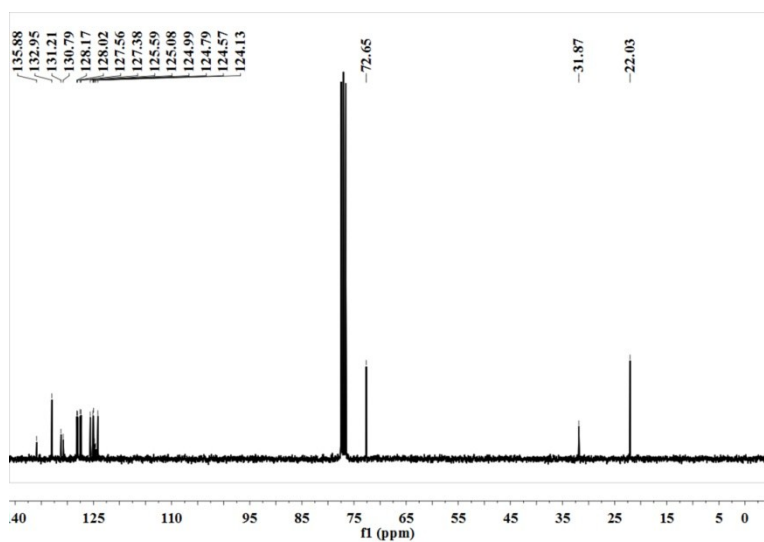


Figure S10. ^{13}C NMR spectrum of NPB.

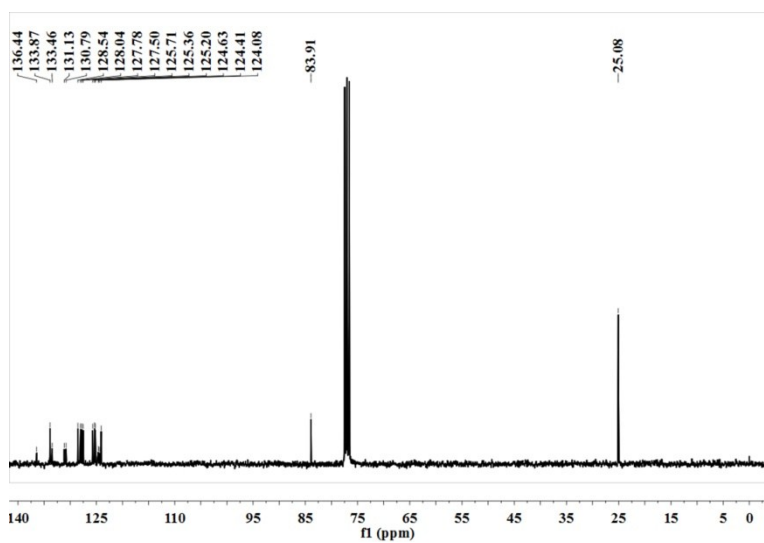


Figure S11. ^{13}C NMR spectrum of PPB.

Table S4. Crystal data and structure refinement for **NPB**

Bond precision:	C-C = 0.0022 Å	Wavelength=1.54184
Cell:	a=14.9097(4) b=6.6345(2) c=16.6553(4)	
	alpha=90 beta=92.822(2) gamma=90	
Temperature:	290 K	
	Calculated	Reported
Volume	1645.52(8)	1645.52(8)
Space group	P 21/a	P 21/a
Hall group	-P 2yab	?
Moiety formula	C21 H19 B O2	?
Sum formula	C21 H19 B O2	C21 H19 B O2
Mr	314.17	314.17
Dx,g cm-3	1.268	1.268
Z	4	4
Mu (mm-1)	0.620	0.620
F000	664.0	664.0
F000'	665.87	
h,k,lmax	17,7,19	17,7,19
Nref	2644	2626
Tmin,Tmax	0.785,0.830	0.794,0.836
Tmin'	0.785	
Correction method=	MULTI-SCAN	
Data completeness=	0.993	Theta(max)= 62.710
R(reflections)=	0.0457(2239)	wR2(reflections)= 0.1389(2626)
S =	1.048	Npar= 219

Table S5. Crystal data and structure refinement for **PPB**

Bond precision:	C-C = 0.0035 Å	Wavelength=0.71073
Cell:	a=11.7096(13) b=10.8168(11) c=14.2151(15)	

	alpha=90	beta=91.551(10)	gamma=90
Temperature:	290 K		
	Calculated		Reported
Volume	1799.8(3)		1799.8(3)
Space group	P 21/c		P 21/c
Hall group	-P 2ybc		?
Moiety formula	C22 H21 B O2		?
Sum formula	C22 H21 B O2		C22 H21 B O2
Mr	328.20		328.20
Dx,g cm-3	1.211		1.211
Z	4		4
Mu (mm-1)	0.075		0.075
F000	696.0		696.0
F000'	696.30		
h,k,lmax	14,13,17		14,13,17
Nref	3679		3638
Tmin,Tmax	0.969,0.976		0.969,0.976
Tmin'	0.969		
Correction method=	MULTI-SCAN		
Data completeness=	0.989	Theta(max)=	26.370
R(reflections)=	0.0627(2137)	wR2(reflections)=	0.1360(3638)
S =	1.009	Npar=	230

Reference

- [1] W. C. Oliver, G. M. Pharr, *J. Mater. Res.*, **1992**, *7*, 1564.
 [2] S. Yang, A. Elangovan, K. Hwang and T. Ho, *J. Phys. Chem. B*, **2005**, *109*, 16628.