Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

A Triarylboron-Based Fluorescent Temperature Indicator: Sensitive both in Solid Polymers and in Liquid Solvents

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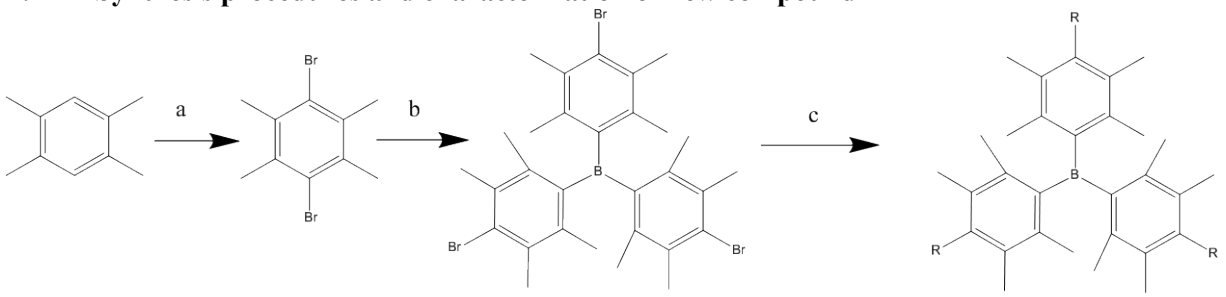
I. Experimental details

General information. Solvents for chemical synthesis and morpholine were purified or freshly distilled prior to use according to standard procedures. All the other chemicals and reagents were used as received from commercial sources without further purification. MALDI-TOF-MS spectra were measured by a Bruker BIFLEX III spectrometer. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. Elemental analysis was performed by a Carlo Erba 1106.

Spectrum measurements. The absorption spectra were recorded on a Hitachi UV-3010 spectrometer. The fluorescence spectra were collected on a Hitachi F-4500 spectrometer. The concentration of the MPG solution was 1.0×10^{-5} mol/L. A quinine sulfate (Φ_F=0.546 in 0.1N H_2SO_4) was used as a reference standard for the measurement of the fluorescence quantum yield. The temperature of the sample was controlled with the help of a heating and cooling stage (HCS) from INSTEC. The fluorescence decay curves were performed on an Edinburgh FLS-920 instrument by using single photon counting measurement (Samples were irradiated by Picoquant LDH-D-C-375 pulsed diode laser). Solvents used in spectrum measurements were HPLC grade reagent (Beijing Chemical Reagents).

II. Synthesis procedures and characterization of new compound



Scheme S1. Reagents and conditions: (a) Br_2, Al, CCl_4; (b) n-BuLi, $BF_3\cdot Et_2O$, Et_2O, -78°C, inert atmosphere; (c) morpholine, $Pd_2(dba)_3$, BINAP, Sodium tert-butoxide, toluene, inert atmosphere.

Tris(2,3,5,6-tetramethyl-4-morpholinophenyl)borane (MPB).

1 and 2 were synthesized according to the reference. The synthetic procedure for the catalytic reaction c is as follows. A suitable Schlenk tube was first charged with 4.5 equiv. of NaOtBu, 50 mL of toluene, 0.09 equiv. of BINAP and 0.045 equiv. of $Pd_2(dba)_3$ under argon. After stirred for 15 min, 5.0 mmol of 2 and 3.6 equiv. of morpholine was added. The reaction mixture was then stirred at 90 °C for 2 h. The resulting solution was added with excess of CH_2Cl_2 and washed with water, dried by $MgSO_4$, and purified with silica gel column (ethyl acetate/petroleum ether = 1:3). The obtained product was a white solid (1450mg, 43%). m. p. 299-302°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.81 (t, *J*=4.28, 12H), 3.11 (t, *J*=3.92, 12H), 2.16 (s, 18H), 1.89 (s, 18H) ppm. MALDI-TOF: *m/z* = 666.5; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.8, 147.7, 137.0, 132.5, 68.2, 50.4, 20.3, 15.7 ppm. Elemental analysis (%) calcd for $C_{42}H_{60}BN_3O_3$: C 75.77 H 9.08 N 6.31; found: C 75.49 H 9.04 N 6.21.

III. Fluorescence lifetime, fluorescence quantum yields and temperature effects experiments

Table S1: The fluorescence lifetime of MPB at three emission wavelengths in hexane, ether, ethyl acetate, THF, ethanol and acetonitrile (λ_{ex} =375 nm)

solvents	470 nm				520 nm				570 nm			
	τ1 (ns)	τ2 (ns)	Bτ1/Bτ2	χ2	τ1(ns)	τ2 (ns)	Bτ1/Bτ2	χ2	τ1(ns)	τ2 (ns)	Bτ1/Bτ2	χ2
hexane	1.6	4.0	1.75	1.15	1.6	4.0	1.12	0.97	1.6	4.0	1.02	1.13
ether	5.7	7.8	1.23	1.11	5.7	7.8	0.582	1.12	5.7	7.8	0.427	0.91
EA	6.7	8.9	1.02	0.98	6.7	8.9	0.957	1.04	6.7	8.9	0.796	1.00
THF	9.2	12.0	1.44	1.06	9.2	11.9	1.21	1.07	9.2	11.9	0.861	1.11
ethanol	8.9	11.1	1.60	1.03	8.9	11.1	1.31	1.21	8.9	11.1	1.06	1.14
acetonitrile	9.6	12.1	1.22	1.05	9.6	12.1	1.12	1.12	9.6	12.1	1.03	1.11

Table S2: The fluorescence lifetime of MPB at three emission wavelengths in 2-methoxyethyl ether (MOE) between -50°C and 30°C (λ_{ex} =375 nm)

t(°C)	470nm				520nm				570nm			
	τ1(ns)	τ2(ns)	Bτ1/Bτ2	χ2	τ1(ns)	τ2(ns)	Bτ1/Bτ2	χ2	τ1(ns)	τ2(ns)	Bτ1/Bτ2	χ2
-50	7.2	18.6	0.601	1.06	7.2	18.6	0.128	0.97	-	18.7	-	0.95
-30	8.0	17.8	0.637	1.07	8.1	17.8	0.272	1.09	8.1	17.8	0.133	1.11
-10	8.9	16.8	0.663	1.26	8.9	16.7	0.364	1.21	8.9	16.7	0.279	1.17
10	9.6	15.3	0.826	1.07	9.6	15.3	0.638	1.23	9.6	15.3	0.490	1.12
30	10.2	13.5	1.22	0.89	10.2	13.5	0.897	0.85	10.2	13.5	0.629	1.24

Table S3: Fluorescence quantum yields of MPB in hexane, ether, EA, THF,ethanol and acetonitrile.

Solvent	hexane	ether	EA	THF	acetonitrile	ethanol
Φ(MPB)	0.13	0.28	0.30	0.36	0.29	0.34

Table S4: Fluorescence quantum yields of MPB in MOE between -50°C and 100°C.

t(°C)	-50	-40	-30	-20	-10	0	10	20
Φ(MPB)	0.51	0.49	0.47	0.45	0.44	0.43	0.41	0.39
t(°C)	30	40	50	60	70	80	90	100
Φ(MPB)	0.36	0.35	0.33	0.32	0.30	0.29	0.28	0.27

Table S5: Fluorescence quantum yields of MPB in THN between -30°C and 110°C.

t(°C)	-30	-10	10	30	50	70	90	110
Φ(MPB)	0.20	0.18	0.17	0.16	0.15	0.14	0.13	0.12

Table S6: Fluorescence quantum yields Φ of MPB in PEG200 between -50°C and 100°C.

t(°C)	-50	-40	-30	-20	-10	0	10	20
Φ(MPB)	0.20	0.19	0.23	0.36	0.37	0.36	0.35	0.34
t(°C)	30	40	50	60	70	80	90	100
Φ(MPB)	0.34	0.33	0.33	0.32	0.31	0.30	0.29	0.29

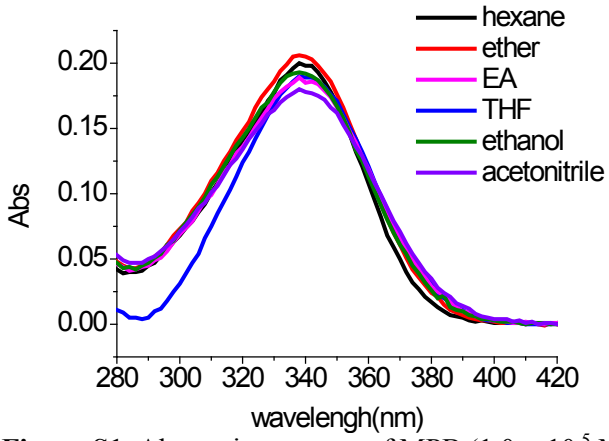


Figure S1. Absorption spectra of MPB (1.0×10^{-5} M) in hexane, ether, ethyl acetate(EA), THF, ethanol and acetonitrile.

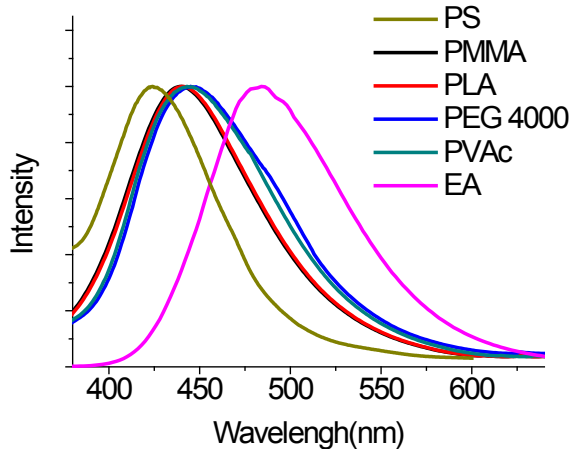


Figure S2. Normalized emission spectra of MPB in PS, PMMA, PLA, PEG 4000, PVAc glassy-state polymers (1.0×10^{-5} M and 1.4×2.5 cm^2), and ethyl acetate (λ_{ex} = 335 nm).

MPB-PEG4000 systems were obtained by dissolving MPB solid in the polymer melt (80°C, above melting point), and then the PEG 4000 system was gradually cooled and solidified. MPB-PVAc, MPB-PLA and other polymer systems were obtained by dissolving both polymers and MPB solid in dichloromethane, and then evaporate the organic solvent.

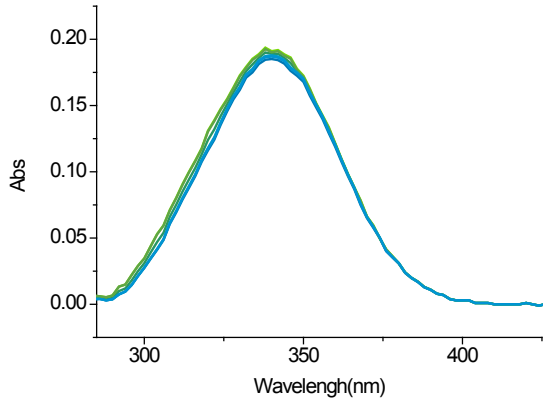


Figure S3. Absorption spectra of MPB (1.0×10^{-5} M) in MOE between -50°C and 100°C (λ_{ex} = 335 nm).

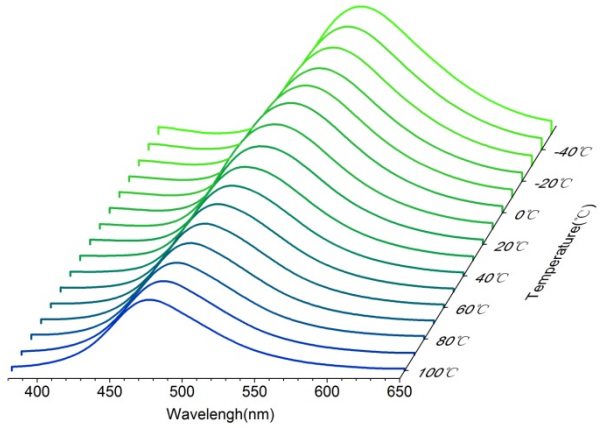


Figure S4. Corrected emission spectra of MPB (1.0×10^{-5} M) in MOE between -50°C and 100°C (λ_{ex} =335 nm).

a)

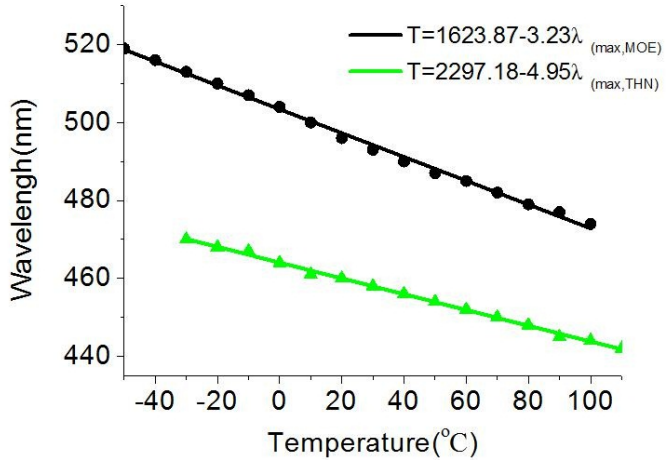


Figure S5. Temperature dependence of the emission maximum of MPB in MOE and THN (λ_{ex} = 335 nm).

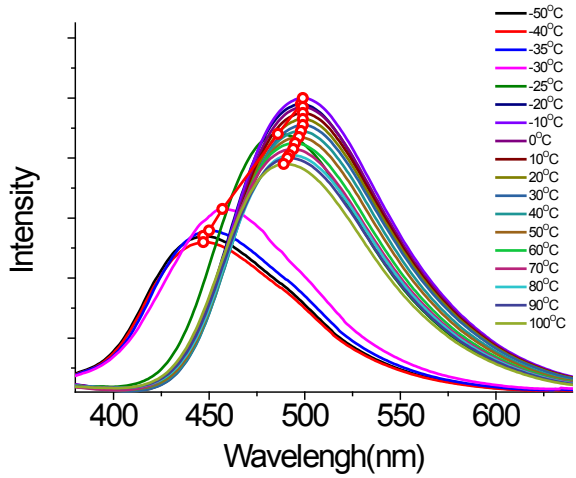


Figure S6. Corrected emission spectra of MPB (1.0×10^{-5} M) in PEG 200 between -50°C and 100°C (λ_{ex} = 335 nm), the symbol(○) is used to mark the maxima of spectra.

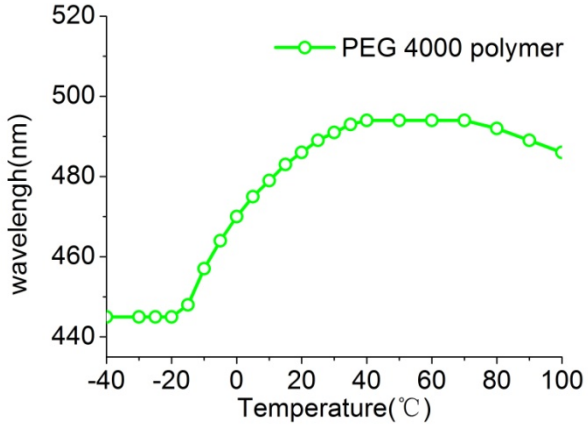


Figure S7. Temperature dependence of the emission maximum of MPB in PEG 4000 (λ_{ex} = 335 nm).

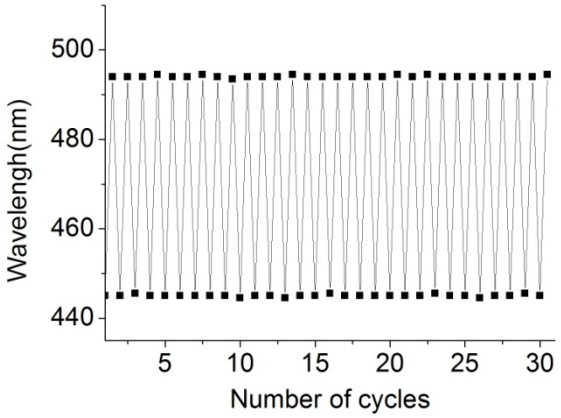


Figure S8. The emission spectra measured at -20°C and 40°C in 30 cycles reversibility experiments (λ_{ex} = 335 nm).

For evaluation of the reversibility of the MPB-PEG4000 system, 30 cycles of the temperature-dependent emission were conducted between -20°C and 40 °C with cycling rates of 30 °C. min^{-1} heating and 10 °C.min^{-1} cooling. The temperature of the sample was controlled with the help of a heating and cooling stage (HCS) from INSTEC INC.

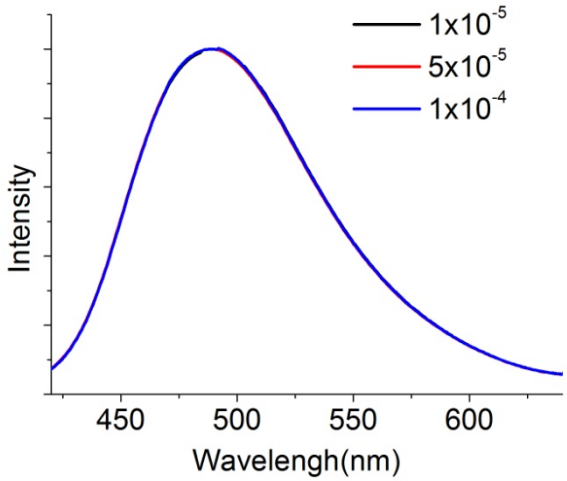


Figure S9. Normalized emission spectra of MPB in PEG 4000 with concentrations 1.0×10^{-5}, 5.0×10^{-5} and 1.0×10^{-4} M at room temperature (λ_{ex} = 335 nm).

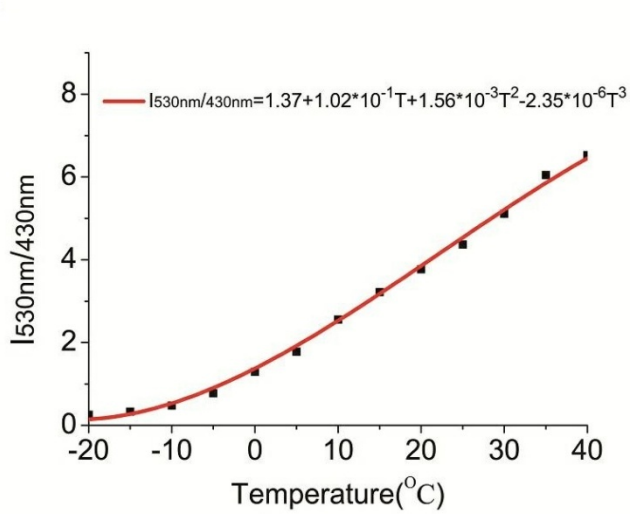


Figure S10. Temperature dependence of the ratio of fluorescence intensity (I_{530nm} /$I_{430\,nm}$) of MPB-PEG 4000 polymer. (λ_{ex} = 335 nm).

Free volume estimation

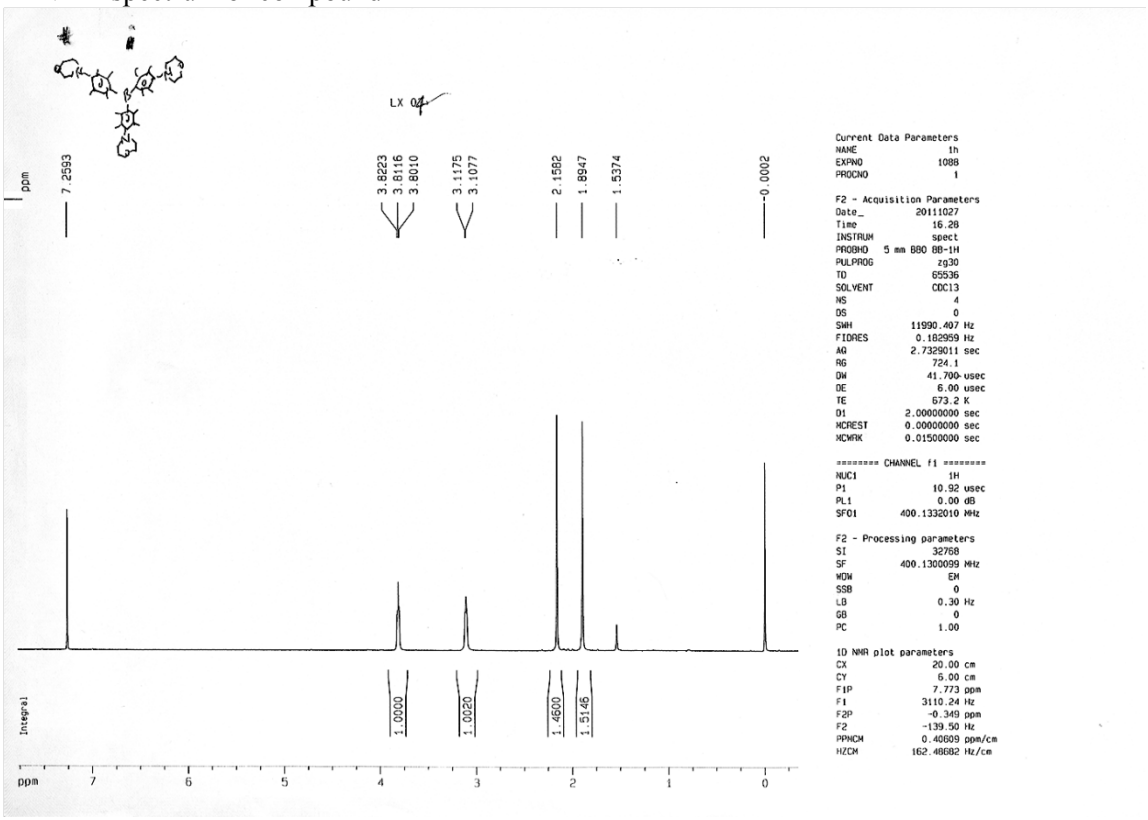
Bueche has developed general expressions for the variation of V_f, T_g of a polymer diluent system[9]:

$$V_f = 0.025+\alpha_p(T-T_{gp})V_p+\alpha_d(T-T_{gd})V_d \quad (1)$$

Here, α is the expansion coefficient, T_g is the glass transition temperature, V is the volume fraction and T is the temperature. The subscripts p and d stand for the polymer and diluent, respectively. The value of α is close to 4.8×10^{-4} per °C for most polymers and 1.0×10^{-3} per °C for most diluents. In this paper, there is no mixture, only pure dilute (V_p=0, V_d=1) or pure polymer system (V_p=1, V_d=0). PEG 200 (dilute) and PEG 4000 (polymer) are structurally similar. The free volume in the paper is calculated based on the equation. For example, PEG 200 is diluents with T_{gd} at -50 °C, and therefore we estimated its free volume is larger than 10.5% when temperature is higher than 30 °C.

^{1}H NMR and ^{13}C NMR spectra of new compound MPB

^{1}H NMR spectrum of compound MPB



^{13}C NMR spectrum of compound MPB