Supplementary Information (SI) for CrystEngComm.

Supporting Information

Engineering visible-to-ultraviolet emission switching of benzothiazole-based mechanoresponsive materials

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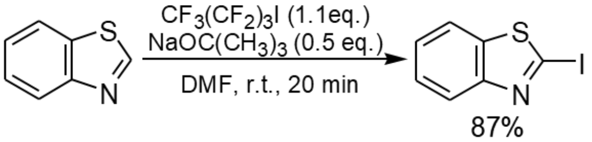
1. Experimental

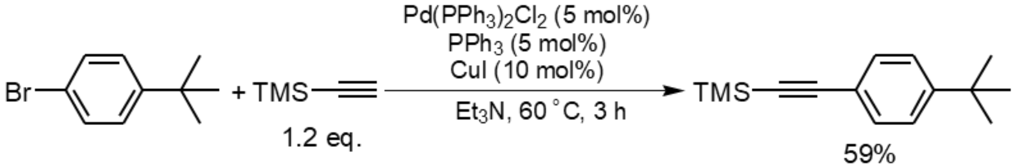
Synthesis of 2-iodobenzothiazole



Scheme S1 Synthesis of 2-iodobenzothiazole.

A mixture of benzothiazole (1.35 g, 10 mmol), perfluorobutyl iodide (3.81 g, 11 mmol), sodium tert-butoxide (0.48 g, 5 mmol), and *N*,*N*-dimethylformamide (DMF, 50 mL) was stirred for 20 min under an argon atmosphere at room temperature. After 20 min, the reaction was quenched with aqueous sodium thiosulfate. The precipitate was separated by atmospheric filtration, and DMF was washed away with water. The corrected precipitate was dissolved in ethyl acetate (EtOAc) and dried over anhydrous Na_2SO_4. After the reaction mixture was concentrated in vacuo, it was purified by silica-gel column chromatography (eluent: hexane/EtOAc = 10/1) to obtain 2-iodobenzothiazole (2.13 g, 87%) as a white powder. ^{1}H-NMR (400 MHz, $CDCl_3$) d 8.03 (dm, *J* = 8.0 Hz, 1H), 7. 85 (dm, *J* = 8.4 Hz, 1H), 7.46-7.37 (m, 2H). The NMR chemical shifts are consistent with those previously reported.[1]

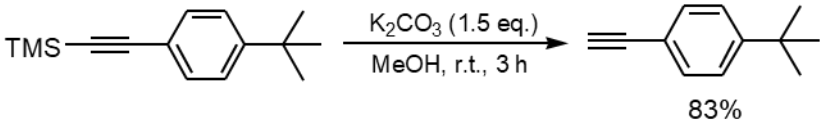
Synthesis of 1-(1,1-dimethylethyl)-4-[2-(trimethylsilyl)ethynyl]benzene



Scheme S2 Synthesis of 1-(1,1-dimethylethyl)-4-[2-(trimethylsilyl)ethynyl]benzene.

A mixture of 1-bromo-4-*tert*-butylbenzene (3.20 g, 15 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.53 g, 0.75 mmol), triphenylphosphine (0.20 g, 0.75 mmol), copper(I)iodide (0.29 g, 1.5 mmol), (trimethylsilyl)acetylene (1.77 g, 18 mmol), and Et_3N (75 mL) was stirred for 3 h under an argon atmosphere at 60 °C. After 3 h, the precipitate formed during the reaction was separated by atmospheric filtration, while the filtrate was poured into a saturated aqueous ammonium chloride solution. The crude product was extracted three times with EtOAc. The organic layer collected was dried over anhydrous Na_2SO_4, which was separated by filtration. The filtrate was evaporated in-vacuo and subjected to silica-gel column chromatography (eluent: hexane) to obtain 1-(1,1-Dimethylethyl)-4-[2-(trimethylsilyl)ethynyl]benzene (1.79 g, 59%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) d 7.40 (dm, *J* = 8.7 Hz, 2H), 7.31 (dm, *J* = 8.6 Hz, 2H), 1.30 (s, 9H), 0.24 (s, 9H). The NMR chemical shifts are consistent with those previously reported.[2]

Synthesis of 1-(1,1-dimethylethyl)-4-ethynylbenzene



Scheme S3 Synthesis of 1-(1,1-dimethylethyl)-4-ethynylbenzene.

A mixture of 1-(1,1-Dimethylethyl)-4-[2-(trimethylsilyl)ethynyl]benzene (1.74 g, 7.5 mmol), potassium carbonate (1.56 g, 11 mmol), and MeOH (40 mL) was stirred 3 h under an air atmosphere at room temperature. After 3 h, the precipitate formed during the reaction was separated by atmospheric filtration, while the filtrate was poured into water. The crude product was extracted three times with EtOAc. The organic layer collected was dried over anhydrous Na_2SO_4, which was separated by filtration. The product was then concentrated to obtain 1-(1,1-Dimethylethyl)-4-ethynylbenzene (0.99 g, 83%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) d 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 3.03 (s, 1H), 1.32 (s, 9H). The NMR chemical shifts are consistent with those previously reported.[3]

2. Absorption, PL decay spectra of crystal and powder

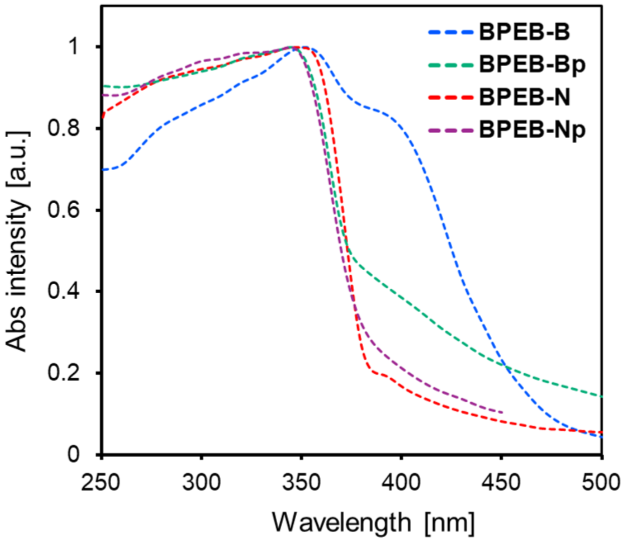


Fig. S1 Absorption spectra of **BPEB-B**, **BPEB-Bp, BPEB-N** and **BPEB-Np**.

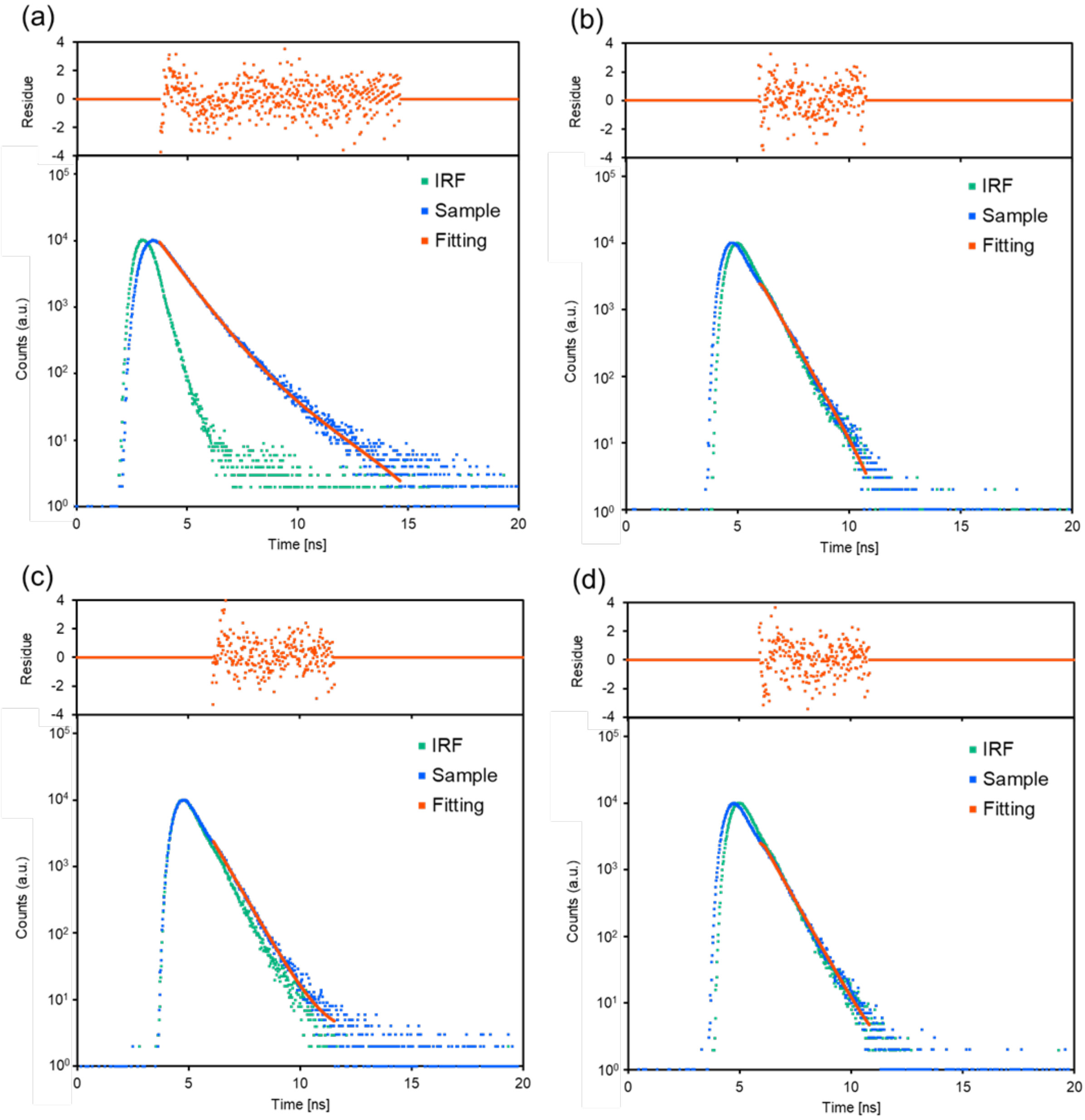


Fig. S2 PL decay profiles monitored at emission maxima of (a) **BPEB-B**, (b) **BPEB-Bp**, (c) **BPEB-N**, (d) **BPEB-Np** excited at 365 nm (**BPEB-B**),340 nm (**BPEB-Bp**, **BPEB-N**, **BPEB-Np**).

Table S1 Absorption maxima (λ_{abs}) and Fluorescence lifetime (τ) of **BPEB**.

	λ_{abs} [nm]	τ_1 [ns]	τ_2 [ns]
BPEB-B	352, 396	＜1.0	2.2
BPEB-Bp	344	＜1.0	-
BPEB-N	347, 397	＜1.0	-
BPEB-Np	344	＜1.0	-

3. X-ray single-crystal structures

Table S2 Crystallographic data of **BPEB-B** and **BPEB-N**.

crystals	**BPEB-B**	**BPEB-N**
formula	$C_{19}H_{17}NS$	$C_{19}H_{17}NS$
fw [g·mol^{-1}]	291.41	291.41
crystal color	colorless	colorless
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P\ 1\ 2_1/c\ 1$
a [Å]	9.0381(3)	17.7329(7)
b [Å]	9.7302(2)	18.9012(4)
c [Å]	10.261(4)	37.568(14)
α [°]	101.159(2)	90.00
β [°]	110.509(3)	119.525(5)
γ [°]	108.369(3)	90.00
V [Å^3]	753.79(5)	10955(8)
Z	2	28
ρ_{calcd} [g/cm^3]	1.284	1.237
μ [mm^{-1}]	0.207	0.200
T [K]	173	173
θ_{min}-θ_{max} [°]	0.998-27.48	0.999-27.48
R/wR [I > $2\sigma_{(1)}$]	0.0347/0.0962	0.0697/0.2249

4. Temperature variable powder X-ray diffraction

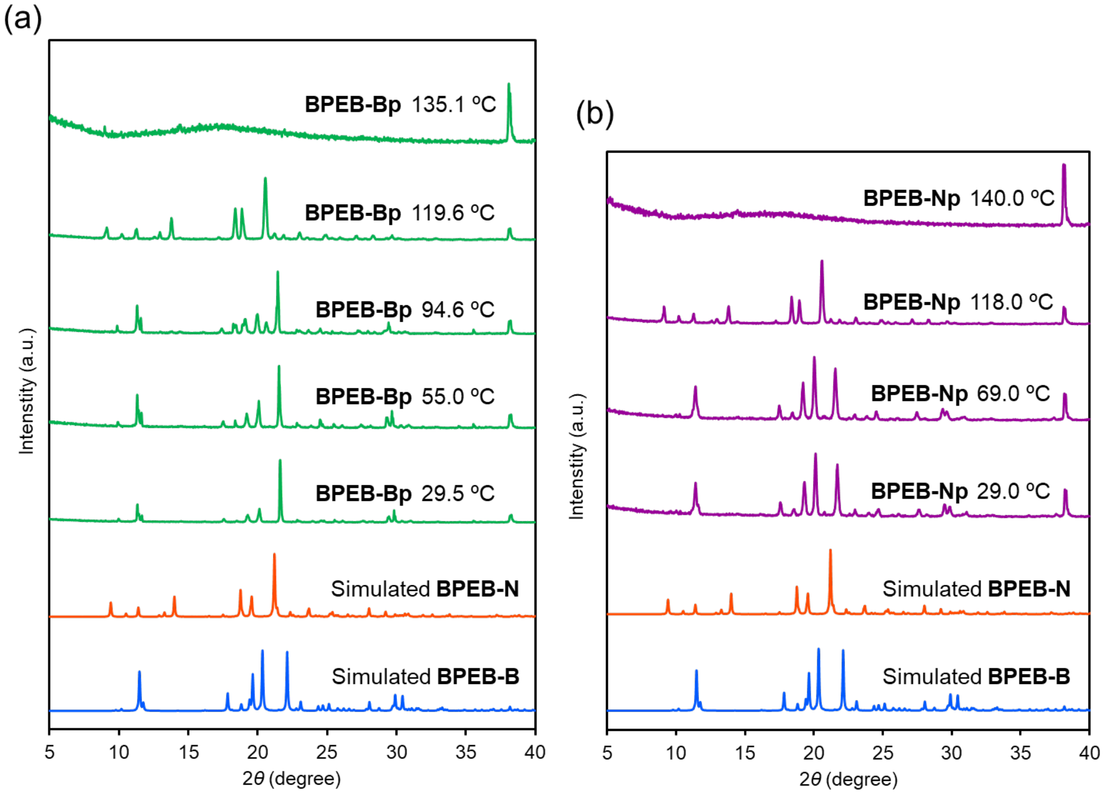


Fig. S3 Temperature variable PXRD of (a) **BPEB-Bp** (b) **BPEB-Np**.

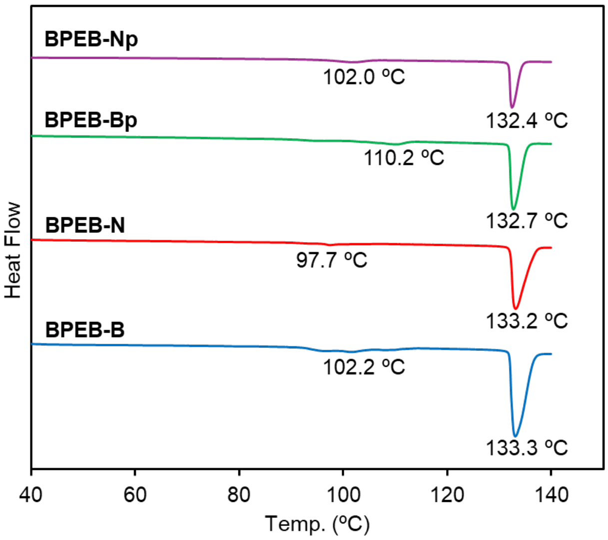


Fig. S4 DSC profiles of **BPEB**.

5. Exposure of grinding-powder to solvent vapor

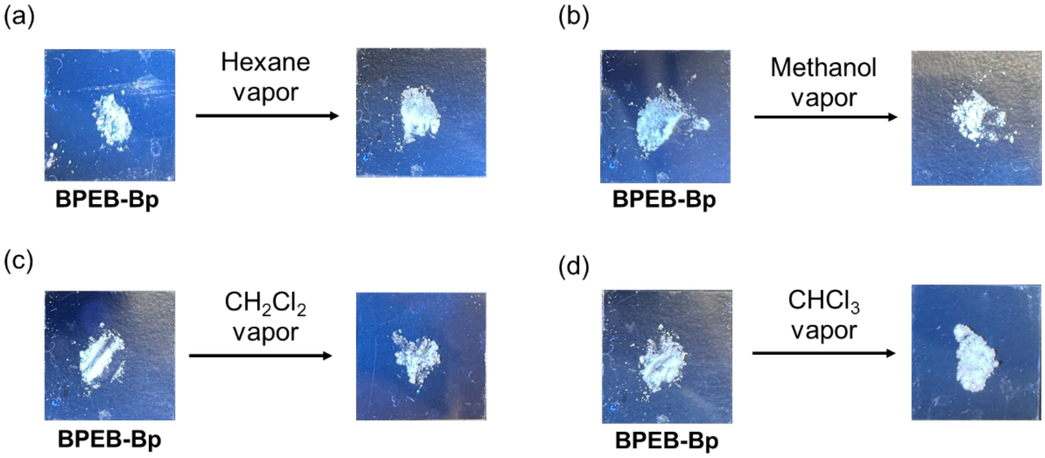


Fig. S5 UV irradiation (365 nm) of **BPEB-Bp** exposed to the vapor of (a) hexane (b) methanol (c) CH_2Cl_2 (d) $CHCl_3$.

6. ^{1}H-, ^{13}C-NMR, IR spectra and Elemental analysis data

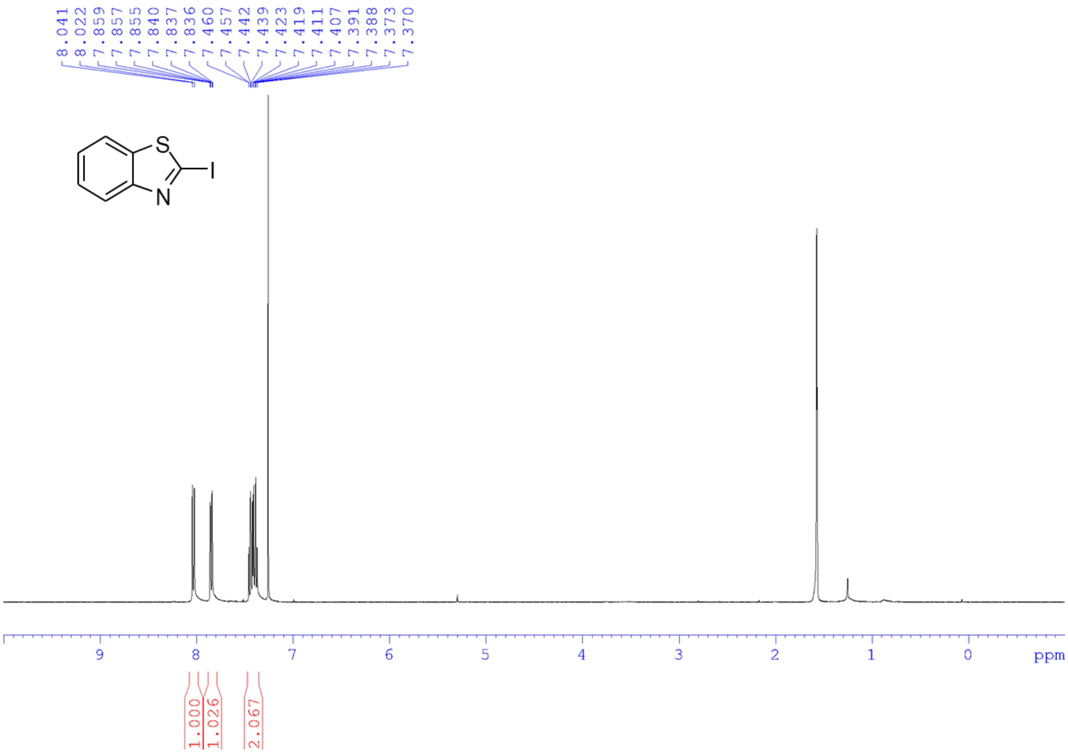


Fig. S6 ^{1}H-NMR spectrum of 2-iodobenzothiazole.

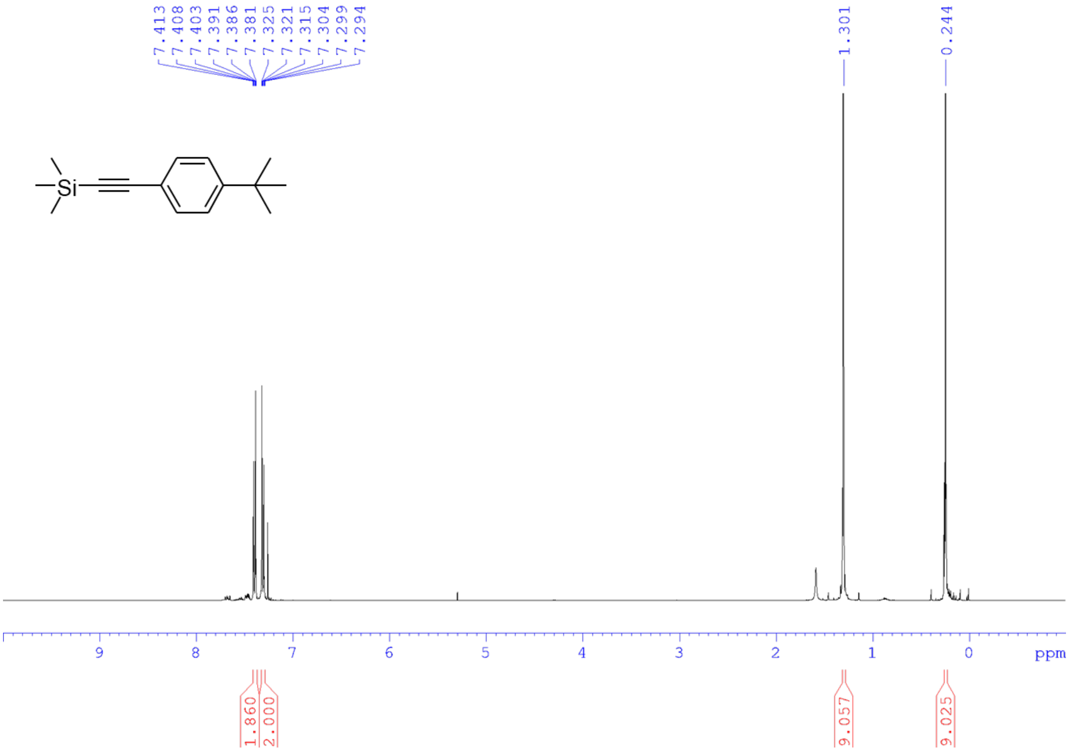


Fig. S7 ^{1}H-NMR spectrum of 1-(1,1-dimethylethyl)-4-[2-(trimethylsilyl)ethynyl]benzene.

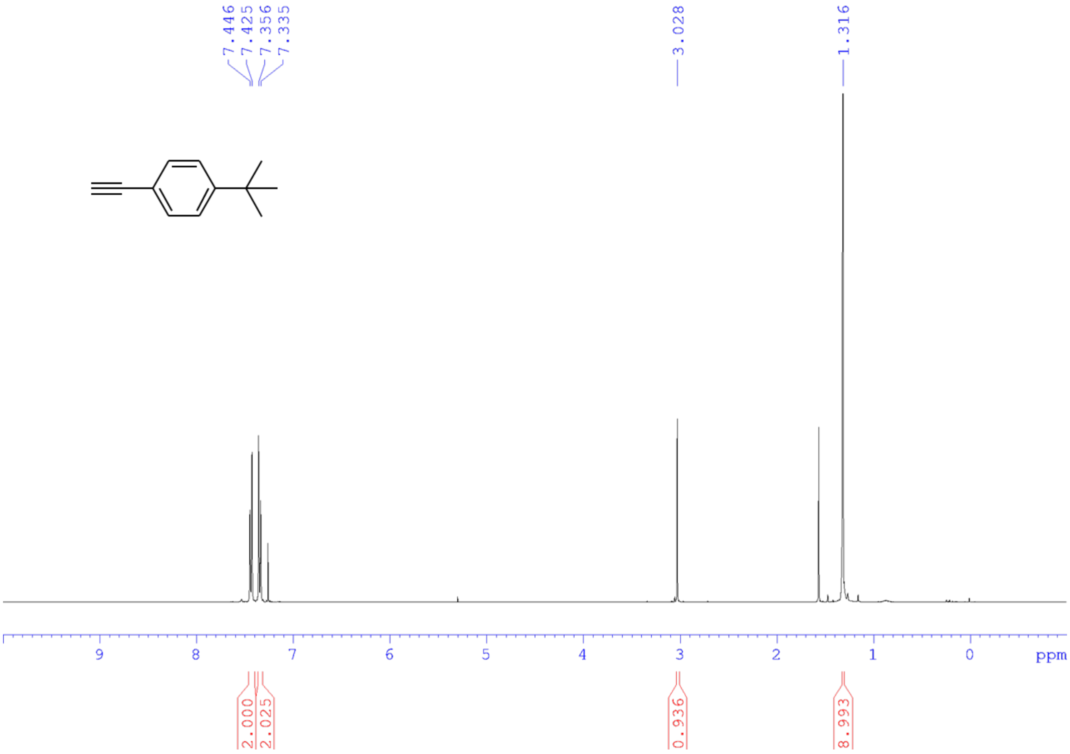


Fig. S8 ^{1}H NMR spectrum of 1-(1,1-dimethylethyl)-4-ethynylbenzene.

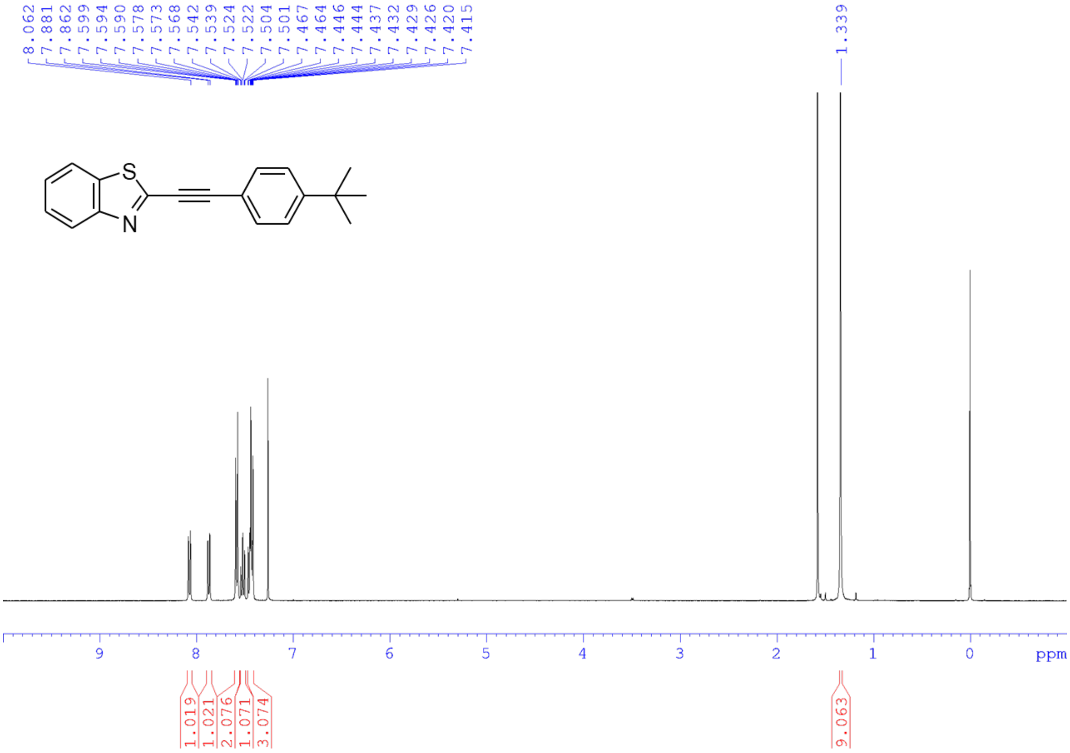


Fig. S9 ^{1}H NMR spectrum of **BPEB**.

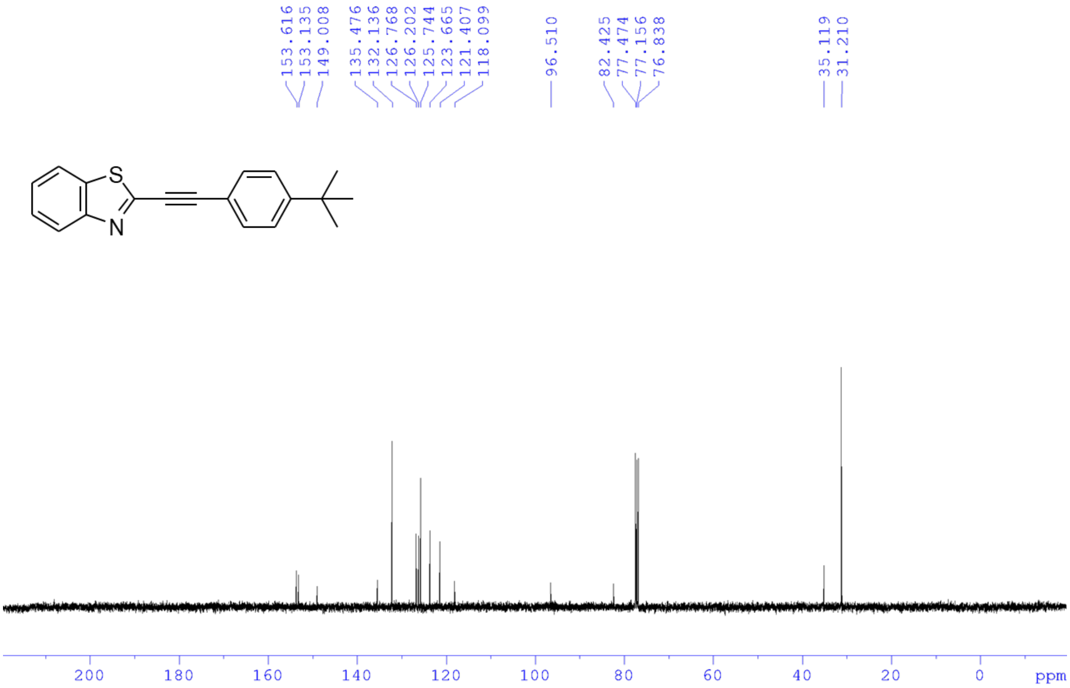


Fig. S10 ^{13}C NMR spectrum of **BPEB**.

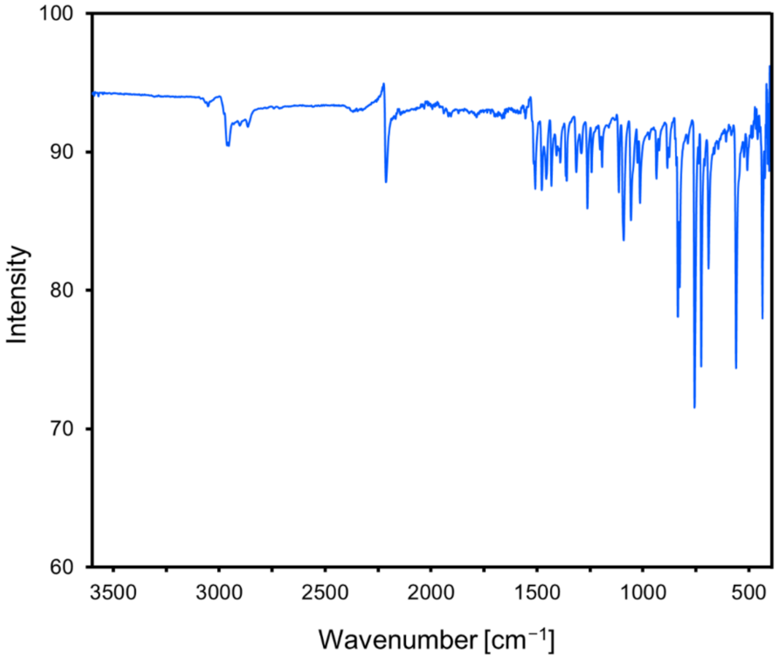


Fig. S11 IR spectrum of **BPEB** (after synthesis).

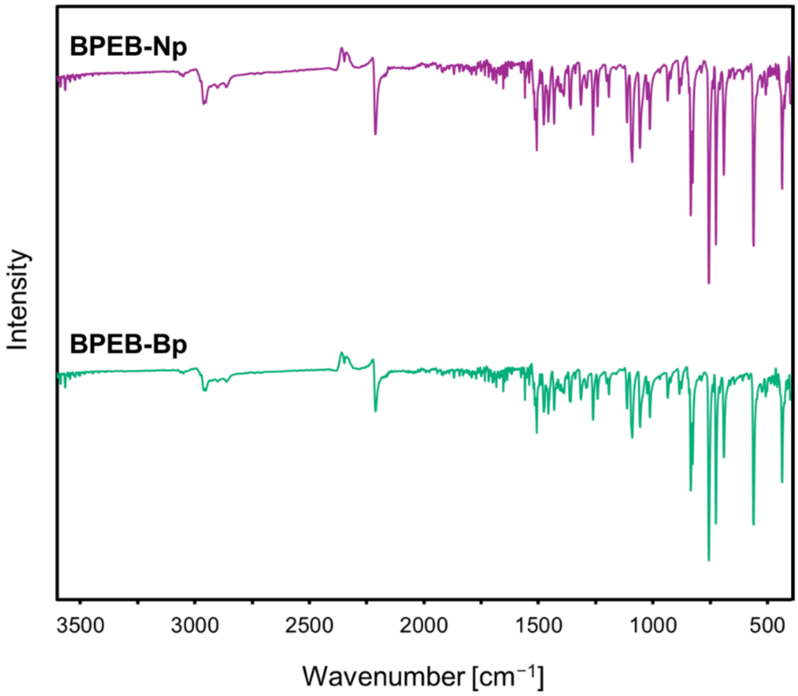


Fig. S12 IR spectra of **BPEB-Bp** and **BPEB-Np.**

BPEB-Bp

IR: ν 2956, 2859, 2210, 1507, 1474, 1431, 1358, 1312, 1261, 1193, 1113, 1092, 1056, 1014, 937 cm^{-1}.

BPEB-Np

IR: ν 2956, 2860, 2211, 1507, 1476, 1431, 1363, 1314, 1261, 1193, 1115, 1090, 1056, 1013, 937 cm^{-1}.

Table S3 Elemental analysis data for **BPEB-B** and **BPEB-N**

	H%	C%	N%
BPEB-B	5.96	78.20	4.75
BPEB-N	5.97	78.33	4.75
Calc.	5.88	78.31	4.81

7. Quantum chemical calculation

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Excited State   1:      Singlet-A      4.1531 eV  298.54 nm  f=1.2797
      77 -> 78          0.68201

Excited State   2:      Singlet-A      4.6755 eV  265.18 nm  f=0.1014
      75 -> 82         -0.10016
      76 -> 78          0.61573
      76 -> 83         -0.18490
      77 -> 79         -0.11647
      77 -> 82         -0.15380

Excited State   3:      Singlet-A      5.0553 eV  245.26 nm  f=0.0006
      74 -> 78          0.44620
      74 -> 79         -0.12599
      74 -> 83          0.19503
      75 -> 78         -0.10014
      75 -> 79         -0.14945
      75 -> 82          0.13516
      75 -> 83         -0.11185
      77 -> 79          0.30838
      77 -> 82         -0.24358
      77 -> 83          0.12379
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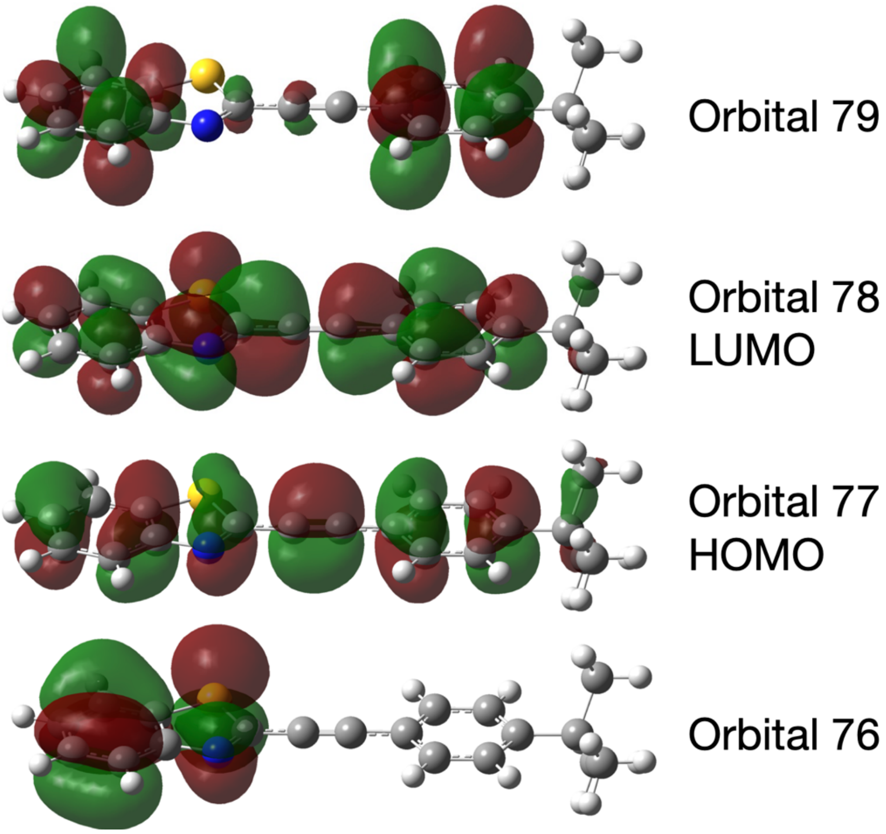

Fig. S13 Frontier orbitals of **BPEB**.

8. References

[1] X. Liu, X. Zhao, F. Liang and B. Ren, *Org. Biomol. Chem.*, 2018, **16**, 886–890.

[2] S. Zhang, J. F. Wunsch, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2024, **63**, e202406856.

[3] A. Grünwald, F.W. Heinemann and D. Munz, *Angew. Chem. Int. Ed.*, 2020, **59**, 21088–21095.