polymers

MDPI

Supplementary Materials: Highly Productive Synthesis, Characterization, and Fluorescence and Heavy Metal Ion Adsorption Properties of Poly(2,5-dimercapto-1,3,4-thiadiazole) Nanosheets

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Table S1. Solubility and solution color of BT monomer and PBT polymers prepared with (a) an I_2/BT molar ratio of 1.5 and an initial BT concentration of 50 mmol L^{-1}, and (b) an H_2O_2/BT molar ratio of 3.53 and an initial BT concentration of 58.25 mmol L^{-1} in ethanol at 25 °C for 24 h.

Solvent	Solubility and solution color of PBT polymers and BT monomer		
	PSA polymers prepared by two oxidants		BT monomer
	(a) I_2	(b) H_2O_2	
1 mol L^{-1} HCl	insoluble	insoluble	slightly soluble, pale yellow
0.1 mol L^{-1} $NH_3 \cdot H_2O$	soluble, colorless	soluble, colorless	soluble, colorless
THF	insoluble	slightly soluble, colorless	soluble, yellow
DMF	slightly soluble, pale yellow	slightly soluble, pale yellow	soluble, dark yellow
NMP	slightly soluble, pale yellow	mainly soluble, colorless	soluble, yellowish-brown
DMSO	slightly soluble, pale yellow	partially soluble, pale yellow	soluble, pale yellow
C_2H_5OH	insoluble	slightly soluble, colorless	soluble, pale yellow
CH_3OH	insoluble	slightly soluble, colorless	soluble, pale yellow
CH_3COCH_3	insoluble	slightly soluble, colorless	soluble, colorless
CH_3NO_2	insoluble	slightly soluble, colorless	partially soluble, pale yellow

Table S2. Main composition and proportion (%) of frontier orbitals in BT.

Atom	HOMO–1	HOMO	LUMO	LUMO+1
S(1)	28.62	0.07	19.76	8.18
C(2)	0.10	8.81	28.41	39.52
S(2)	35.55	30.45	5.16	5.55
N(3)	0.04	10.71	6.54	0.48
N(4)	0.04	10.71	6.54	0.48
C(5)	0.10	8.81	28.41	39.52
S(5)	35.55	30.45	5.16	5.55

Table S3. Main atomic electron spin densities for BT.

Atom	Electron spin density	Atom	Electron spin density
S(1)	-0.041207	N(4)	0.145016
C(2)	0.055810	C(5)	0.055811
S(2)	0.330757	S(5)	0.330757
N(3)	0.145017		

Table S4. FT-IR spectra data of solid BT and PBT and their assignments [1–6].

IR data/cm^{-1} of solid BT	IR data/cm^{-1} of solid PBT synthesized with		Assignment
	(a) I_2	(b) H_2O_2	
3404 (w)	3438 (s)	3437 (s)	υ (adventitious H_2O)
3056 (w)	2977(w), 2913 (w)	2976 (w), 2915 (w)	υ (N_{ring}–H)
2476 (w)	-	-	$\upsilon_{s.}$ (S–H)
1637 (w)	1635 (s)	1635 (s)	$\upsilon_{s.}$ (C=N)
1501 (vs)	-	-	δ (N–H)$_{ip.}$
1447 (s)	-	-	δ (N–H)$_{rock}$
1387 (m)	1381 (vs)	1380 (vs)	υ (thiadiazole ring skeleton)
1262 (vs)	1245 (w)	1251 (w)	thioamide II mode
1119 (s)	1122 (w)	1119 (w)	υ (thiadiazole ring skeleton)
1049 (vs)	1038 (vs)	1041 (vs)	υ (N–N)
938 (m)	-	-	υ (C=S)
749 (m)	744 (w)	744 (w)	δ (N–H)$_{tor.}$
712 (vs)	713 (w)	715 (w)	$\upsilon_{as.}$ (C–S–C endocyclic)
653 (m)	646 (w)	645 (w)	$\upsilon_{s.}$ (C–S–C endocyclic)
533 (w)	529 (w)	531 (w)	υ (S–C–S)
-	492 (w)	492 (w)	υ (S–S)

w: weak, m: medium, s: strong, vs: very strong, υ: stretch, δ: deformation, as.: asymmetric, s.: symmetric, ip.: in-plane, tor.: torsion

Table S5. WAXD data of solid BT and PBTs synthesized with I_2 and H_2O_2.

Analyte	Bragg angle 2θ
BT monomer	13.3, 15.5, 17.0, 17.6, 18.1, 19.3, 19.8, 20.9, 22.1, 22.5, 22.9, 23.5, 25.5, 25.8, 26.5, 26.9, 27.8, 29.4, 29.8, 30.2, 30.9, 31.3, 32.1, 32.7, 33.0, 33.4, 33.7, 35.5, 37.2, 37.5, 38.1, 38.6, 39.8, 40.3, 40.9, 41.5, 42.4, 43.5, 45.2, 46.1, 48.7, 51.1, 52.5, 53.1
PBT synthesized with I_2	17.7, 17.9, 18.6, 20.6, 20.8, 26.2, 27.8, 31.9, 32.6, 33.0, 33.9, 35.8, 36.3, 36.9, 37.5, 37.9, 38.8, 41.1, 42.9, 43.2, 45.3, 48.9, 49.8, 51.9, 53.3, 57.4
PBT synthesized with H_2O_2	17.8, 18.0, 18.7, 20.7, 20.9, 26.3, 27.9, 32.0, 32.7, 33.1, 34.0, 35.9, 36.4, 37.0, 37.6, 38.0, 38.9, 41.1, 43.0, 43.4, 45.4, 49.0, 49.9, 52.0, 53.4, 57.5

Table S6. Proposed composition and corresponding theoretical mass-to-charge ratio of PBT molecules synthesized with I_2 and H_2O_2.

PBT synthesized with I_2			PBT synthesized with H_2O_2		
Experimental value of *m*/*z*	**Proposed composition**	**Calculated value of *m*/*z***	**Experimental value of *m*/*z***	**Proposed composition**	**Calculated value of *m*/*z***
859.1	$[H(C_2N_2S_3)_6H–S]^+$	859.2	863.1	$[H(C_2N_2S_3)_6H–S+4H]^+$	863.2
968.1	$[H(C_2N_2S_3)_6H–S+Ag+H]^+$	968.1	897.0	$[H(C_2N_2S_3)_6H–S+K]^+$	898.3
1001.6	$[H(C_2N_2S_3)_6H +Ag+2H]^+$	1001.2	971.0	$[H(C_2N_2S_3)_6H +2K+H]^+$	970.5
1085.1	$[H(C_2N_2S_3)_7H +2Na+2H]^+$	1085.5	1004.7	$[H(C_2N_2S_3)_6H +Ag+5H]^+$	1004.2
1185.8	$[H(C_2N_2S_3)_8H]^+$	1187.7	1085.9	$[H(C_2N_2S_3)_7H +2Na+2H]^+$	1085.5
1300.7	$[H(C_2N_2S_3)_8H+Ag+5H]^+$	1300.6	1120.0	$[H(C_2N_2S_3)_8H–2S]^+$	1123.7
1401.2	$[H(C_2N_2S_3)_8H+2Ag]^+$	1403.5	1186.4	$[H(C_2N_2S_3)_8H]^+$	1187.7
1514.4	$[H(C_2N_2S_3)_8H+3Ag+3H]^+$	1514.4	1228.5	$[H(C_2N_2S_3)_8H+K+2H]^+$	1228.8
1618.1	$[H(C_2N_2S_3)_8H+4Ag]^+$	1619.3	1301.8	$[H(C_2N_2S_3)_9H–S]^+$	1303.8
1728.7	$[H(C_2N_2S_3)_8H+5Ag+H]^+$	1728.2	1343.9	$[H(C_2N_2S_3)_9H–S+K+H]^+$	1343.9
1834.0	$[H(C_2N_2S_3)_8H+6Ag]^+$	1835.1	1402.9	$[H(C_2N_2S_3)_8H+ 2Ag]^+$	1403.5
1942.0	$[H(C_2N_2S_3)_8H+7Ag]^+$	1943.0	1452.4	$[H(C_2N_2S_3)_{10}H– S]^+$	1452.1
2050.2	$[H(C_2N_2S_3)_8H+8Ag]^+$	2050.9	1524.8	$[H(C_2N_2S_3)_{10}H+ K+H]^+$	1524.1
2265.5	$[H(C_2N_2S_3)_{15}H+K+H]^+$	2265.3	1567.6	$[H(C_2N_2S_3)_{10}H+ +K+2Na]^+$	1569.2
2377.2	$[H(C_2N_2S_3)_{16}H +3H]^+$	2376.4	1619.5	$[H(C_2N_2S_3)_8H+ 4Ag]^+$	1619.3
2481.1	$[H(C_2N_2S_3)_{16}H +Ag]^+$	2481.3	1676.3	$[H(C_2N_2S_3)_{11}H+ 2Na]^+$	1678.3
2591.5	$[H(C_2N_2S_3)_{16}H +2Ag+2H]^+$	2591.2	1728.6	$[H(C_2N_2S_3)_8H+ 5Ag+H]^+$	1728.2
2696.5	$[H(C_2N_2S_3)_{16}H +3Ag]^+$	2697.1	1834.2	$[H(C_2N_2S_3)_8H+ 6Ag]^+$	1835.1
2805.1	$[H(C_2N_2S_3)_{16}H +4Ag]^+$	2805.0	1944.7	$[H(C_2N_2S_3)_8H+ 7Ag+H]^+$	1944.0
2910.4	$[H(C_2N_2S_3)_{16}H +5Ag]^+$	2912.9	2049.6	$[H(C_2N_2S_3)_8H+ 8Ag]^+$	2050.9
			2159.3	$[H(C_2N_2S_3)_{14}H+K+2Na]^+$	2162.1
			2265.0	$[H(C_2N_2S_3)_{15}H+K]^+$	2264.3
			2379.8	$[H(C_2N_2S_3)_{16}H+6H]^+$	2379.4
			2485.2	$[H(C_2N_2S_3)_{16}H+Ag+4H]^+$	2485.3
			2596.2	$[H(C_2N_2S_3)_{16}H+2Ag+7H]^+$	2596.2
			2703.3	$[H(C_2N_2S_3)_{16}H+3Ag+6H]^+$	2703.1
			2811.3	$[H(C_2N_2S_3)_{16}H+4Ag+6H]^+$	2811.0
			2923.6	$[H(C_2N_2S_3)_{19}H+Ag]^+$	2925.9
			3022.8	$[H(C_2N_2S_3)_{16}H+6Ag+2H]^+$	3022.8
			3132.8	$[H(C_2N_2S_3)_{16}H+7Ag+4H]^+$	3132.7
			3245.6	$[H(C_2N_2S_3)_{21}H+Ag+Na]^+$	3245.3
			3351.7	$[H(C_2N_2S_3)_{21}H+2Ag+Na]^+$	3353.2
			3457.6	$[H(C_2N_2S_3)_{23}H+2Na]^+$	3456.8
			3564.0	$[H(C_2N_2S_3)_{23}H+Ag+2Na]^+$	3564.7
			3670.7	$[H(C_2N_2S_3)_{24}H+Ag+3H]^+$	3670.0
			3780.6	$[H(C_2N_2S_3)_{24}H+2Ag+6H]^+$	3780.9

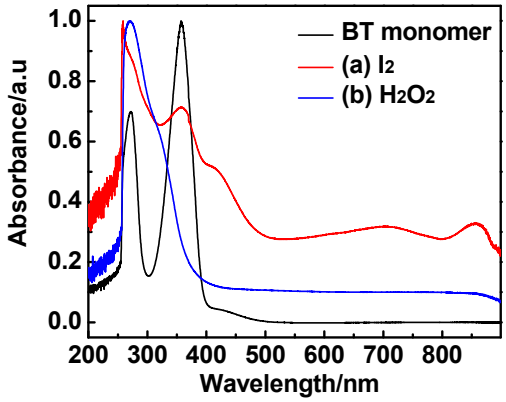

Figure S1. UV-Vis spectra of BT monomer and PBT polymers prepared with (a) an I_2/BT molar ratio of 1.5 and an initial BT concentration of 50 mmol L^{-1}, and (b) an H_2O_2/BT molar ratio of 3.53 and an initial BT concentration of 58.25 mmol L^{-1} in ethanol at 25 °C for 24 h.

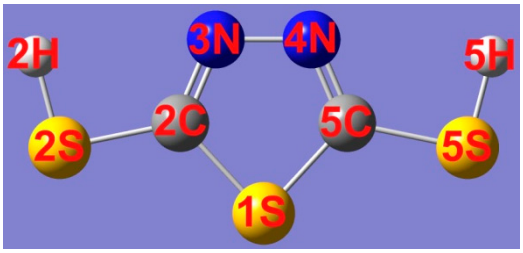

Figure S2. Molecular model of BT monomer with minimized energy.

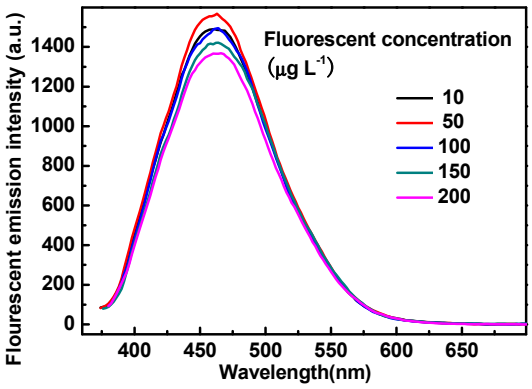

Figure S3. Fluorescent emission spectra of PBT solutions in NMP at different concentrations. The PBT was synthesized with I_2 as the oxidant.

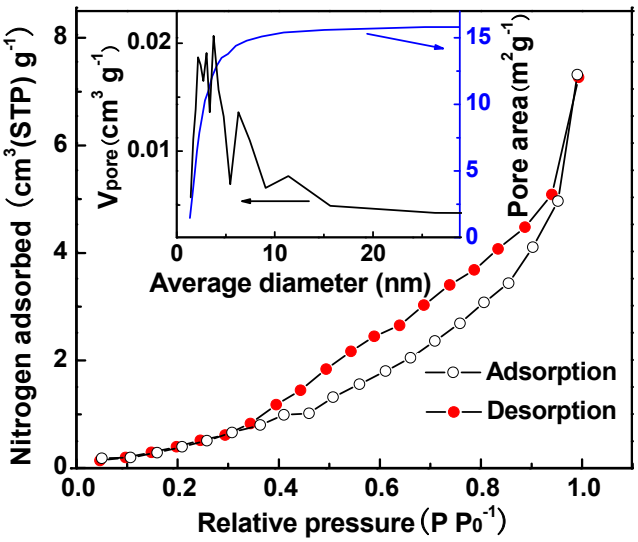

Figure S4. Nitrogen adsorption-desorption isotherms and pore size distribution curves (inset) of fine PBT powders synthesized with I_2 as oxidant.

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