Supporting Information

A 2D covalent organic framework involving strong intramolecular hydrogen bonds for advanced supercapacitor

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Section A. Supplementary Methods

Experimental section

Synthesis of 1,3,5-triformylphloroglucinol (TFP)



TFP was synthesized according to the reported procedure with slight modification.^{1,2} Hexamethyllenetetramine (15.098 g, 108 mmol), m-trihydroxybenzene (6.014 g, 49 mmol) and trifluoroacetic acid (90 mL) were added into a 500 mL flask under N₂ atmosphere. The reaction mixture was heated to reflux at 95 °C for 2 h. Then 160 mL of 3 M HCl was added slowly to the reaction mixture and reacted for another 2 h. After cooling to room temperature, the solution was filtered through filter paper, extracted with CH₂Cl₂ (400 mL) and dried over MgSO₄. The filtrate was evaporated under reduced pressure to give the TFP as yellow solid, then the crude product was recrystallized to obtain yellow crystals 1.51 g (13.1% yield). Anal. Calcd. for (C₉H₆O₆): C, 51.44; H, 2.88; O, 45.68. Found C, 51.25; H, 3.29; O, 45.46. FT-IR (power, cm⁻¹): 2898, 1642, 1584, 1428, 1241, 1179, 969, 874, 791, 602. ¹H NMR (400 MHz, CDCl₃): δ 14.14 (s, 3H), 10.18 (s, 3H).

Synthesis of model compound o-hydroxy diphenylbenzobisthiazole (HDB)



Salicylaldehyde (20 mg, 0.2 mmol), 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABT) (20 mg, 0.1 mmol) were weighed into a glass bottle (volume of ca. 10 mL). To the mixture was added mesitylene (M) (0.286 mL) and 1,4-dioxane (D) (1.714 mL). The mixture was sonicated to afford a homogenous dispersion, and then added 0.2 mL of 3 M aqueous acetic acid (AcOH). The glass bottle was transferred into a 25 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 120 °C for 3 days and cooled to room temperature. The resulting grey crystal solid was collected with 81% yield. Anal. Calcd. for ($C_{20}H_{12}N_2O_2S_2$): C, 63.81; H, 3.21; N, 7.44; O, 8.50; S, 17.04. Found C, 63.76; H, 3.40; N, 7.40; O, 8.46; S, 16.98. FT-IR (power, cm⁻¹): 3450, 2927, 1633, 1478, 1404, 1222, 1012, 839, 748, 702.

Synthesis of PG-BBT



A glass bottle was charged with TFP (21 mg, 0.1 mmol), DABT (36.75 mg, 0.15 mmol), 0.286 mL of M and 1.714 mL of D. The resulting solution was sonicated for 2 minutes to afford a homogenous dispersion, and then added 0.2 mL of 3 M aqueous acetic acid. The glass bottle was transferred into a 25 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 120 °C for 3 days and cooled to room temperature. The resulting black precipitate was collected by filtration and washed with THF (5 × 20 mL), DMF (5 × 20 mL) and MeOH (5 × 20 mL), Soxhlet extracted by THF 24 h, then dried at 100 °C under vacuum for 24 h to give a black powder with 78% yield. Anal. Calcd. for ($C_{15}H_8N_2O_3S_2$)_n: C, 54.87; H, 2.46; N, 8.53; O, 14.62; S, 19.52. Found C, 54.76; H, 2.60; N, 8.47; O, 14.72; S, 19.45. FT-IR (power, cm⁻¹): 3428, 2931, 2861, 1628, 1548, 1477, 1394, 1335, 1170, 1110, 862, 673, 626.



A glass bottle was charged with 1,3,5-benzenetricarboxaldehyde (BTC) (16.2 mg, 0.1 mmol), DABT (36.75 mg, 0.15 mmol), 0.286 mL of M and 1.714 mL of D. The resulting solution was sonicated for 2 minutes to afford a homogenous dispersion, and then added 0.2 mL of 3 M aqueous acetic acid. The glass bottle was transferred into a 25 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 120 °C for 3 days and cooled to room temperature. The resulting black precipitate was collected by filtration and washed with THF (5 × 20 mL), DMF (5 × 20 mL) and MeOH (5 × 20 mL), Soxhlet extracted by methanol 24 h, then dried at 100 °C under vacuum for 24 h to give a yellow powder with 75% yield. Anal. Calcd. for (C₁₅H₈N₂S₂)_n: C, 64.26; H, 2.88; N, 9.99; S, 22.87. Found C, 64.14; H, 3.23; N, 9.87; S, 22.76. FT-IR (power, cm⁻¹): 3417, 2920, 2846, 1627, 1578, 1531, 1484, 1382, 1315, 1274, 1099, 1058, 869, 801, 686, 605.

Synthesis of partially functionalized PG_xBZ_{1-x}BBT



A glass bottle was charged with DABT (36.75 mg, 0.15 mmol) and TFP/BTC (total 0.1 mmol) at different molar ratios (25%, 50% and 75%), 0.286 mL of M and 1.714 mL of D. The resulting solution was sonicated for 2 minutes to afford a homogenous dispersion, and then added 0.2 mL of 3 M aqueous acetic acid. The glass bottle was transferred into a 25 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 120 °C for 3 days and cooled to room temperature. The resulting black precipitate was collected by filtration and washed with THF (5 \times 20 mL), DMF (5 \times 20 mL) and MeOH (5 \times 20 mL), Soxhlet extracted by methanol 24 h, then dried at 100 °C under vacuum for 24 h to give solid powder. For PG0.25BZ0.75BBT, a brown powder with 72% yield. Anal. Calcd. for (C₃₀H₁₁N₄OS₄)_n: C, 63.03; H, 1.94; N, 9.80; O, 2.79; S, 22.44. Found C, 62.94; H, 2.26; N, 9.65; O, 2.83; S, 22.32. FT-IR (power, cm⁻¹): 3390, 2975, 1628, 1506, 1434, 1380, 1316, 1190, 1098, 1054, 863, 728, 682, 574. For PG_{0.5}BZ_{0.5}BBT, a brown powder with 71% yield. Anal. Calcd. for (C₁₅H₆N₂OS₂)_n: C, 61.21; H, 2.05; N, 9.52; O, 5.44; S, 21.78. Found C, 61.02; H, 2.61; N, 9.35; O, 5.56; S, 21.46. FT-IR (power, cm⁻¹): 3373, 2927, 1618, 1497, 1435, 1398, 1307, 1208, 1108, 1054, 855, 728, 682, 538. For **PG**_{0.75}**BZ**_{0.25}**BBT**, a brown powder with 74% yield. Anal. Calcd. for $(C_{30}H_{13}N_4O_3S_4)_n$: C, 59.49; H, 2.16; N, 9.25; O, 7.92; S, 21.18. Found C, 59.23; H, 2.6; N, 9.12; O, 8.02; S, 21.03. FT-IR (power, cm⁻¹): 3381, 3061, 1621, 1513, 1418, 1407, 1300, 1193, 1052, 839, 721, 685, 579.

Materials Characterization: Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet iS10 spectrometer in the spectral range of 500-4000 cm⁻¹. ¹H NMR spectra were performed on a MERCURY plus 400 spectrometer. ¹³C cross-polarization with magic anglespinning (CP-MAS) solid-state nuclear magnetic resonance (NMR) spectra were taken on a Bruker ARX 300 MHz spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was measured by a Thermo Scientific ESCALAB 250 XI. Thermogravimetric analyses (TGA) were observed using a Mettler Toledo TGA/DSC1/1100SF analyser in the temperature range of 50 to 800 °C under flowing N2. Powder X-ray diffraction (PXRD) patterns were obtained from a Bruker D8 diffractometer using Cu Ka radiation. The Brunauer-Emmett-Teller (BET) surface areas were collected on N2 sorption isotherms at 77 K using a Micromeritics ASAP2020 surface area and pore size analyser. Pore size distribution was determined by nonlocal density functional theory mode in the instrument software package. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800. Transmission electron microscopy (TEM) images were observed on a JEOL JEM-2100. Scanning transmission electron microscopy (STEM) images, HRTEM images and EDS mapping were carried out on a Tecnai G2 F30 transmission electron microscopy at an acceleration voltage of 300 kV. The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo Ka radiation ($\lambda =$ 0.71073 Å). Raman spectra were tested by Raman spectroscopy (Renishaw InVia). Cell parameters were retrieved using SMART software and refined using SAINT³ on all observed reflections. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by Bruker.⁴ Structures were solved by direct methods using the program SHELXL-97.⁵ All of the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients.

Electrochemical performance experiments: The electrochemical performances of the samples were studied in an electrochemical station (CHI760E). Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and Electrochemical impedance spectroscopy (EIS) tests were conducted on in a three-electrode setup, including a Pt plate (1 cm²) as the counter electrode and Hg/HgO electrode as the reference electrode. The working electrode was prepared by mixing active material, acetylene black and poly(tetrafluoethylene) in a mass ratio of 8:1:1, and then dispersed in ethanol by ultrasonication to obtain homogeneous slurry. The slurry was coated on a Ni foam substrate (1 cm²). The mass loading of active materials on Ni foam was 2.1 mg cm⁻². Moreover, the asymmetric supercapacitor devices were assembled to test the electrochemical performance, with activated materials acting as the positive, activated carbon (AC) as the negative electrode. All the electrochemical measurements were performed by using 3 M KOH aqueous electrolyte. EIS measurements were performed by in the frequency range from 0.01 to 10⁵ Hz at open circuit potential with a potential amplitude of 5 mV.

Calculation Section

The specific capacitance of electrode materials was calculated by the following equation (1) and equation (2):⁶

$$E_{\text{int/D}} = I \int_{t(U_{\text{max}})}^{t(U_{\text{min}})} U(t) dt$$
(1)

$$C_{\rm int/D} = \frac{2E_{\rm int/D}}{U_{\rm max}^2}$$
(2)

Where $E_{int/D}$ is the energy density (Wh kg⁻¹), *I* is the discharge current, *U* is the potential range (V), *t* is the discharge time (s), $C_{int/D}$ is the specific capacitance (F g⁻¹).

Energy density and power density of the **PG-BBT** are evaluated according to equation (3) and equation (4), respectively:

$$E = \frac{1}{2}C_{sp}V^2 \tag{3}$$

$$P = \frac{E}{\Delta t} \tag{4}$$

where *E* stands for the energy density (Wh kg⁻¹), C_{sp} represents the specific capacitance (F g⁻¹), *V* refers to the potential window (V), *P* is the power density (W kg⁻¹) and Δt is the discharge time (S).

Section B. Supplementary data



Fig. S1 PXRD patterns of PG-BBT synthesized in different ration solvents. Note that the optimized condition $(V_M/V_D = 1/6)$.



Fig. S2 PXRD patterns of BZ-BBT synthesized in different ration solvents. Note that the optimized condition $(V_M/V_D = 1/6)$.



Fig. S3 Chemical stability tests of PG-BBT. The FT-IR patterns of PG-BBT treated for 7 days in different solvents.



Fig. S4 Chemical stability tests of PG-BBT. The PXRD patterns of BBT-COF treated for 7 days in different solvents.



Fig. S5 Chemical stability tests of BZ-BBT. The FT-IR patterns of BZ-BBT treated for 7 days in different solvents.



Fig. S6 Chemical stability tests of **BZ-BBT**. The PXRD patterns of **BZ-BBT** treated for 7 days in different solvents.



Fig. S7 Thermogravimetric analysis (TGA) curves of PG-BBT.

The weight of the **PG-BBT** decreased slightly below 130 °C, which could be attributed to the weight loss of solvent. **PG-BBT** exhibited no discernible weight loss from 130 to 300 °C, and then **PG-BBT** started to decompose. Further heated to 800 °C, there was still 64% of weight residual for **PG-BBT**, indicating its excellent thermal stability.



Fig. S8 Thermogravimetric analysis (TGA) curves of BZ-BBT.

The weight of the **BZ-BBT** decreased slightly below 120 °C, which could be attributed to the weight loss of solvent and water. **BZ-BBT** exhibited no discernible weight loss from 120 to 220 °C, and then **BZ-BBT** started to decompose. Further heated to 800 °C, there was still 53% of weight residual for **BZ-BBT**, indicating its good thermal stability.



Fig. S9 PXRD patterns of **PG-BBT** observed (black) and calculated with the eclipsed (red) and staggered (blue) stacking models. Comparison of the observed and the simulated PXRD profiles indicated that the preferable structure of **PG-BBT** is the eclipsed arrangement.



Fig. S10 Simulation of the PG-BBT unit cell.

Simulation of the **PG-BBT** unit cell content calculated in a slip-AA arrangement (along the y-axis): top view onto the ab-plane and view perpendicular to the c-axis. The simulation obviously elucidates the 2D structure with hexagonal P6/m space group and eclipsed stacking model. **PG-BBT** connected by benzobisthiazole units with hexagonal pores, and the layer-by-layer stacking was also observed.



Fig. S11 Experimental powder pattern (black) and Pawley refined pattern (red) of **PG-BBT** with an eclipsed arrangement; different plot is given in (blue).

The experimental PXRD patterns agree well with the simulated PXRD profiles, and the structural simulations shows AA eclipsed stacking mode with hexagonal P6/m space group. To obtain the unit cell parameters, Pawley refinement was studied, which offered the value a = b = 23.0063 Å and c = 3.5017 Å along with *Rwp* = 4.76% and *Rp* = 3.56%.



Fig. S12 PXRD patterns of **BZ-BBT** observed (black) and calculated with the eclipsed (red) and staggered (blue) stacking models. Comparison of the observed and the simulated PXRD profiles indicated that the preferable structure of **BZ-BBT** is the eclipsed arrangement.



Fig. S13 Simulation of the BZ-BBT unit cell.

Simulation of the **BZ-BBT** unit cell content calculated in a slip-AA arrangement (along the y-axis): top view onto the ab-plane and view perpendicular to the c-axis. The simulation obviously elucidates the 2D structure with hexagonal P6/m space group and eclipsed stacking model. **BZ-BBT** connected by benzobisthiazole units with hexagonal pores, and the layer-by-layer stacking was also observed.



Fig. S14 Experimental powder pattern (black) and Pawley refined pattern (red) of **BZ-BBT** with an eclipsed arrangement; different plot is given in (blue).

The experimental PXRD patterns agree well with the simulated PXRD profiles, and the structural simulations shows AA eclipsed stacking mode with hexagonal P6/m space group. To obtain the unit cell parameters, Pawley refinement was studied, which offered the value a = b = 21.8778 Å and c = 3.5331 Å along with *Rwp* = 4.83% and *Rp* = 3.68%.



Fig. S15 Intramolecular hydrogen bonding in **PG-BBT** (indicated by purple lines; C, grey; N, blue; O, red; S, yellow; H, green).

Intense intramolecular hydrogen bonding was generated between hydroxy group and adjacent nitrogen atom with N-H···O bond length of 2.16 Å and \angle N-H···O angle of 125.46°.



Fig. S16 XPS measurements of PG-BBT. (a) C 1s, (b) N 1s, (c) O 1s and (d) S 2p spectrum.

The N 1s peak at 399 eV, S 2p peak at 164 eV and O 1s peak at 532.8 eV is attributed to the C=N, C-S and C-OH bonds, respectively.



Fig. S17 FT-IR spectrum of BZ-BBT.

The disappearance of the characteristic C=O vibration band (1680 cm⁻¹), N-H vibration band (3068-3351 cm⁻¹) and S-H vibration band (2533 cm⁻¹), and the appearance of C=N bonding (1623 cm⁻¹), indicates the formation of **BZ-BBT.**



Fig. S18 ¹³C-CP-MAS solid-state NMR spectroscopy analyses of BZ-BBT.

The characteristic resonance signal at 163 ppm is derived from the C=N group, which clearly reveals the conversion of monomer to polymer **BZ-BBT**.



Fig. S19 XPS measurements of BZ-BBT. (a) C1s, (b) N1s and (c) S2p spectrum.

The N 1s peak at 399 eV and S 2p peak at 164 eV is attributed to the C=N and C-S bond, respectively.



Fig. S20 (a) N_2 sorption and desorption isotherms of BZ-BBT. (b) The pore size distribution of BZ-BBT calculated by NLDFT.

The curve displays a typical type-I shape with a sharp uptake under low relative pressure ($P/P_0 < 0.01$), suggesting a microporous structure. The BET surface area of **BZ-BBT** is estimated to be 440 m² g⁻¹. The average pore size of **BZ-BBT** is 1.57 nm.



Fig. S21 SEM images of BZ-BBT.

The SEM images show a homogeneous morphology, which was consisted of a large number of rods that form highly interconnected network structure. These rods are available in sizes from 200 to 400 nm.



Fig. S22 TEM images of BZ-BBT.

The TEM images clearly clarify that **BZ-BBT** exhibits orderly layer-by-layer structure.



Fig. S23 Peak currents vs. scan rate of PG-BBT.

Peak current is proportional to the square root of the scan rate (i $\propto v^{1/2}$, where i is the peak current, v is the scan rate), indicating diffusion-controlled reaction kinetics processes.



Fig. S24 Cyclic stability measurement of PG-BBT at a current density of 1 A g⁻¹.

The capacitance was 96% of the initial value after 10000 cycles, which is indicative of outstanding cycling performance.



Fig. S25 The Nyquist plot of PG-BBT.

 R_s shows the total resistance including electrolyte, electrode and separator. CPE exhibits pseudocapacitor. R_{ct} represents the charge transfer resistance and Z_w is the Warburg impedance which is attributed to the ion diffusion and electrolyte penetration. Each EIS plot includes a semi-circle in the high frequency region and a straight part in the low frequency region. The semi-circular arc is attributed to charge transfer resistance through the electrode-electrolyte interface, and the straight line represents the diffusion properties of the electrolyte through the electrode surface. The charge transfer resistance R_{ct} of **PG-BBT** was evaluated to be 1.1 Ω .



Fig. S26 Imaginary capacitance vs frequency for PG-BBT (a) after 2000 cycles and (b) 10000 cycles.

Complex capacitance studies determined the dielectric relaxation time constant (τ_0), which represents the supercapacitor factor of merit. The τ_0 values are 3.3 and 0.4 s after 2000 cycles and 10000 cycles, respectively.



Fig. S27 The Nyquist plot of PG-BBT after 2000 cycles and after 10000 cycles.

Each EIS plot includes a semi-circle in the high frequency region and a straight part in the low frequency region. The semi-circular arc is attributed to charge transfer resistance through the electrode-electrolyte interface, and the straight line represents the diffusion properties of the electrolyte through the electrode surface. The charge transfer resistance R_{ct} of **PG-BBT** was evaluated to be 1.0 and 0.6 Ω after 2000 cycles and 10000 cycles, respectively. After 10000 cycles, **PG-BBT** displayed a slope that is larger than 2000 cycles, indicating faster ion diffusion properties.



Fig. S28 FT-IR spectrum of PG_xBZ_{1-x}BBT.



Fig. S29 ¹³C-CP-MAS solid-state NMR spectroscopy analyses of PG_xBZ_{1-x}BBT.



Fig. S30 PXRD patterns of PG_xBZ_{1-x}BBT.



Fig. S31 SEM and TEM images of $PG_xBZ_{1-x}BBT$. SEM images and their corresponding to TEM images (a) $PG_{0.25}BZ_{0.75}BBT$, (b) $PG_{0.5}BZ_{0.5}BBT$ and (c) $PG_{0.75}BZ_{0.25}BBT$.



Fig. S32 (a) CV curves of **BZ-BBT** at different scan rate. (b) GCD profiles of **BZ-BBT** at different current densities. (c) The specific capacitance of **BZ-BBT** at different current densities. (d) Nyquist plot of **BZ-BBT**.

The CV curves present different scan rates from 5 to 30 mV s⁻¹ and display a pair of redox peaks, indicating the pseudocapacitive behaviour. The GCD profiles show different current densities from 1 to 10 A g⁻¹. The GCD curves exhibit a severely distorted triangular shape, which is resulted from the typical pseudocapacitive behaviour, in agreement with the CV analyses. The discharging capacitances of **BZ-BBT** are calculated to be 166, 139, 130, 120 and 104 F g⁻¹ at 1, 2, 3, 5 and 10 A g⁻¹, respectively. The specific capacitance at 10 A g⁻¹ retains 62% of that at 1 A g⁻¹, indicating its good rate capability. EIS test indicates low charge transfer resistance, which is favourable for good rate performance.



Fig. S33 (a) CV curves of different functionalized $PG_xBZ_{1-x}BBT$ (the ratio of [TFP]/[BTC] is 25%, 50% and 75%, respectively.) at scan rate of 10 mV s⁻¹. (b) GCD profiles of different functionalized COFs at current density of 1 A g⁻¹. (c) The specific capacitance of different functionalized COFs at different current densities. (d) Nyquist plot of different functionalized COFs.

The capacitive properties of partial-hydroxyl functionalized $PG_xBZ_{1-x}BBT$ (the molar ratio of [TFP]/[BTC] is controlled at 0.25, 0.5 or 0.75.) were studied. The CV curves display similar pair of redox peaks, indicating the pseudocapacitive behaviour. The specific capacitances of $PG_{0.25}BZ_{0.75}BBT$, $PG_{0.50}BZ_{0.50}BBT$ and $PG_{0.75}BZ_{0.25}BBT$ are 197, 248 and 366 F g⁻¹ at 1 A g⁻¹ in the three-electrode system, respectively. The results indicate that electrochemical performance increases as the hydroxy group increasing, and are further confirmed by EIS test.



Fig. S34 Raman spectra of PG-BBT in the (i) charge and (ii) discharge process.

The two typical bands at 1329 and 1645 cm⁻¹ is ascribed to radical semiquinone and -C=N- stretching vibration in the discharge process, respectively. After charging, the -C=N- stretching vibration signal at 1616 cm⁻¹ weakened and the increased delocalization signal at 1522 cm⁻¹ appeared, indicating the oxidation process.

Electrode	Electrolyte	Current	Specific	References
type		density/scan rate	capacitance (F g ⁻¹)	
TpPa-(OH) ₂	1 M Phosphate	0.5 A g ⁻¹	416	Chem. Mater., 2017, 29, 2074-
	buffer			2080.
TpOMe-	3 M H ₂ SO ₄	3.3 mA cm ⁻²	169	J. Am. Chem. Soc., 2018, 140 ,
DAQ				10941-10945.
DqTp-COF	1 M H ₂ SO ₄	1.56 mA cm ⁻²	154	ACS Appl. Mater. Interfaces,
				2018, 10 , 28139-28146.
WO ₃	1 M H ₂ SO ₄	10 mV s ⁻¹	639.8	Angew. Chem., Int. Ed., 2014,
				53 , 11935-11939.
h-	0.2 M H ₂ SO ₄	5 mV s ⁻¹	498	Nano Lett., 2015, 15, 6802-
WO ₃ ·nH ₂ O				6808.
r-LaMnO _{2.91}	1 M KOH	2 mV s ⁻¹	609.8	Nature materials, 2014, 13,
				726-732.
MnCo ₂ O ₄	2 M KOH	5 A g ⁻¹	474	Adv. Funct. Mater., 2016, 26,
				4085-4093.
np-	1 M Na ₂ SO ₄	10 A g ⁻¹	608	ACS Appl. Mater. Interfaces,
Ag@Fe ₃ O ₄				2018, 10 , 17223-17231.
PG-BBT	3 M KOH	1 A g ⁻¹	724	this work

 Table S1 Comparison of specific capacitance with COFs and metal oxide electrode materials.

PG-BBT				
Hexagonal P6/m (175)				
a = b = 23.0063 Å, $c = 3.5017$ Å				
01	0.73887	0.26445	0	
N2	0.52778	0.13839	0	
C3	0.70513	0.30075	0	
C4	0.63371	0.26080	0	
C5	0.60098	0.18197	0	
C6	0.51112	0.06877	0	
C7	0.56952	0.05781	0	
C8	0.43850	0.01198	0	
S9	0.64725	0.13472	0	

Table S2 Fractional atomic coordinates for the hexagonal (P6/m) unit cell of **PG-BBT** calculated using the Materials Studio 7.0.

PG-BBT				
Hexagonal P63/m (176)				
<i>a</i> = <i>b</i> = 24.1505 Å, <i>c</i> = 6.4288 Å				
01	0.37909	0.79604	1/4	
C2	0.05934	-0.00807	1/4	
C3	0.06562	0.05768	1/4	
C4	0.38153	0.64247	1/4	
C5	0.40770	0.71695	1/4	
C6	0.71154	0.48150	3/4	
S7	0.65514	0.51234	3/4	
C8	0.72170	0.59197	3/4	
С9	0.78435	0.59334	3/4	
C10	0.84991	0.65372	3/4	
C11	0.84283	0.71293	3/4	
C12	0.71494	0.65149	3/4	
C13	0.78054	0.71174	3/4	
S14	0.90797	0.79286	3/4	
C15	0.86482	0.88714	3/4	
N16	0.85203	0.82099	3/4	
N17	0.75147	1.22044	3/4	
N18	0.78624	0.77453	3/4	

Table S3 Fractional atomic coordinates for the hexagonal (P63/m) unit cell of **PG-BBT** calculated using the Materials Studio 7.0.

BZ-BBT					
Hexagonal P6/m (175)					
	<i>a</i> = <i>b</i> = 21.8778 Å, <i>c</i> = 3.5331 Å				
N1	0.53035	0.14014	0		
C2	0.70831	0.30159	0		
C3	0.63472	0.25944	0		
C4	0.60127	0.18207	0		
C5	0.51151	0.06813	0		
C6	0.56828	0.05660	0		
C7	0.44193	0.01185	0		
S8	0.65209	0.13673	0		

Table S4 Fractional atomic coordinates for the hexagonal (P6/m) unit cell of **BZ-BBT** calculated using the Materials Studio 7.0.

BZ-BBT				
Hexagonal <i>P</i> 63/m (176)				
a = b = 24.1447 Å, $c = 7.2647$ Å				
C1	0.05889	-0.00877	1/4	
C2	0.06589	0.05724	1/4	
C3	0.38275	0.64421	1/4	
C4	0.40726	0.71802	1/4	
C5	0.70899	0.48049	3/4	
S6	0.65286	0.51146	3/4	
C7	0.71929	0.59124	3/4	
C8	0.78180	0.59243	3/4	
C9	0.84829	0.65335	3/4	
C10	0.84140	0.71345	3/4	
C11	0.71268	0.65167	3/4	
C12	0.77922	0.71255	3/4	
S13	0.90677	0.79327	3/4	
C14	0.86432	0.88803	3/4	
N15	0.85111	0.82174	3/4	
N16	0.75327	1.22327	3/4	
N17	0.78525	0.77551	3/4	

Table S5 Fractional atomic coordinates for the hexagonal (P63/m) unit cell of **BZ-BBT** calculated using the Materials Studio 7.0.

	HDB
Formula	$C_{20}H_{12}N_2O_2S_2$
Fw	376.44
<i>T</i> (K)	173
λ (Å)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> _{21/c}
<i>a</i> (Å)	11.2568(12)
<i>b</i> (Å)	5.8241(7)
<i>c</i> (Å)	12.8702(17)
α (⁰)	90
β (⁰)	112.433(4)
γ (⁰)	90
$V(Å^3)$	779.93(16)
Ζ	2
Dcalc (g/cm ³)	1.603
$\mu \text{ (mm}^{-1}\text{)}$	0.360
F(000)	388
$ heta\left(^{0} ight)$	3.4, 25.3
	-13<=h<=12
Index ranges	-7<=k<=6
	-15<= <i>l</i> <=15
Reflections collected	4365
GOF (F ²)	1.053
$R_1^a, w R_2^b$ (I>2 σ (I))	0.0413, 0.0697
R_1^a, wR_2^b (all data)	0.0709, 0.0774

Table S6 Summary of crystallographic data for HDB.

 $R_{1^{a}} = \Sigma \overline{||F_{o}| - |F_{c}|| / \Sigma F_{o}|} \cdot wR_{2^{b}} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})]^{1/2}$

		HDB	
S1-C9	1.6950(5)	C9-S1-C12	90.37(1)
S1-C12	1.6817(5)	C20-S2-C23	90.92(1)
S2-C20	1.6969(5)	C5-N1-C8	119.58(1)
S2-C23	1.6756(5)	C16-N2-C19	118.27(1)
N1-C5	1.3927(4)	C2 -C1-C13	111.95(1)
N1-C8	1.2556(4)	C2 -C1-C2_a	104.48(1)
N2-C16	1.3911(4)	C2_a-C1-C13_a	111.93(1)
N2-C19	1.2601(4)	C2_a-C1-C13	111.93(1)
S2-C23	1.6756(5)	N1-C5-C4	124.12(1)
C1-C2	1.5127(4)	N1-C5-C6	117.38(1)
C1-C13	1.5187(4)	N2-C19-C20	121.84(1)
C2-C3	1.3723(4)	S2-C20-C21	110.26(1)
C2-C7	1.3621(4)	S2-C23-C22	113.20(1)

Table S7 Selected bond lengths $[{\rm \AA}]$ and angles $[^\circ]$ for HDB.

Symmetry transformations used to generate equivalent atoms for HDB: a = -x, 1- y, -z

Section C. Supplementary References

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