

**SUPPORTING INFORMATION for**  
**Crystal Engineering of Conjugated Oligomers and the Spectral Signature of  $\pi$ -Stacking in Conjugated Oligomers and Polymers.**

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## EXPERIMENTAL

The materials were synthesized by adaptations to reported procedures. The powder data were collected on Rigaku Rotaflex diffractometer at 40 kV and 100 mA with a Cu rotating anode target ( $\lambda=0.154$  nm) and a graphite monochromator. Samples were scanned from 3 to 35 degrees ( $2\theta$ ) at 0.01 degree intervals at a rate of 1 degree/min. Room temperature UV-vis absorption spectra were determined on a Shimadzu 3101PC with base-line correction; emission and excitation spectra were recorded on a Shimadzu 4121 interfaced with a Gateway computer. Low temperature absorption spectra were determined using a 120W full spectrum Sungun lamp. The spectrometer included a PAR 126 lock-in amplifier, Hamamatsu 375 photo-multiplier tube, and a Keithley model 575 interface. Low temperature spectra samples were cooled in a Janus 10DT cryostat.

The following two compounds were synthesized by a modification of the method reported by Chi and Chu, *Sci. Sinica (Engl. Ed.)* 1957, 6, 467. 471.

**Synthesis of 4,4'-chloromethyl-2,2'-bithiazole:** In a 50 mL, 3-neck flask equipped with stir bar, reflux condenser and nitrogen adapter, 5.0g (0.035 moles) of 1,3-dichloroacetone, 2.0g (0.016 moles) of dithiooxamide and 2.0g (0.024 moles) of calcium carbonate were combined. Under the flow of nitrogen, 20 mL of acetone was added. The mixture was refluxed for 22 hours. After this time, the solution fluoresced purple. The flask was cooled, and the product was filtered. The filtrate was washed with cold acetone. The precipitate extracted with boiling acetone. The solvent was removed to reveal a brown solid. This solid was sublimed at 125 C and 0.25 torr, resulting in a 23% yield of white solid. MP: 163-164 C.  $H^1$ NMR:  $\delta=7.43$  (s,1H); 4.73 (s,2H). MS:  $M^+=266,264$ . IR (cm $^{-1}$ ): 3100, 3016, 2966, 1658, 1553. Anal. Calc'd: C, 36.23; H, 2.28; N, 10.56. Found: C, 36.56; H, 2.42; N, 10.53.

**Synthesis of 4,4'-iodomethyl-2,2'-bithiazole:** In a 100 mL 3-neck flask equipped with stir bar, reflux condenser and nitrogen inlet, under the flow of nitrogen, 20.0 g (0.133 moles) of iodine was added to 2.0 g ( $7.52 \times 10^{-3}$  moles) 4,4'-chloromethyl-2,2'-bithiazole suspended in 30 mL of acetone. The mixture turned a yellow color. The reaction was refluxed for 3 hours. Afterward, the solvent was removed via vacuum. The sample was dissolved in boiling, dry chloroform, then filtered through a 3 cm plug of celite. The product was then recrystallized, from chloroform at 0 C, to yield a yellow solid. Product does not fluoresce in solution or on TLC. 74% yield.  $H^1$ NMR  $\delta=7.36$ (s, 1H); 4.55(s,2H). MS:  $M^+ = 448$ . Anal. Calc'd.: C, 21.64; H, 1.35; N, 6.31. Found: C, 21.85; H, 1.41; N, 5.98.

**Synthesis of 4,4'-(2-propenoxy)methyl-2,2'-bithiazole:** A lithium salt of allyl alcohol was formed by the addition of butyl lithium (2.1mL of 2.5M [5.35mmol]) to dry allyl alcohol (0.465g, 8mmol) dissolved in 10 mL THF at -78 C in a 50 mL 3-neck flask equipped with stir bar, reflux condenser and nitrogen inlet. The mixture was stirred at -78 C for one half hour. 4,4'-iodomethyl-2,2'-bithiazole (0.60g, 1.34 mmol) dissolved in 25 mL of THF was then added to the mixture via cannula. The solution was allowed to warm to room temperature at which point precipitate formed, and the solution fluoresced blue-purple. The mixture was then refluxed for 2 hours. The solvent was removed via vacuum. The product was purified by placing it on a silica gel column, then rinsing with chloroform. The desired compound was then washed off the column with ether. The light yellow solid was obtained in an 89% yield.  $H^1$  NMR:  $\delta=7.33$ (s, 1H), 5.96 (m, 1H); 5.33 (d, 1H); 5.23(d, 1H); 4.68(s,1H); 4.13(d, 2H).  $C^{13}$  NMR:  $\delta=161.3, 155.3, 134.3, 117.55, 117.51, 71.8, 67.9$ . MS (EI):  $M^+=308, 252, 194$ . Anal. Calc'd: C, 54.51; H, 5.23; N, 9.08. Found: C, 54.72; H, 5.48; N 8.91. MP: 53 C.

**4,4',4'',4'''-tetra-((S)-2-methylbutoxymethyl)-2,2',5',5'',2'',2'''-quaterthiazole** (dimer of 4,4'-((S)-2-methylbutoxymethyl)-2,2'-bithiazole): Butyl lithium (0.9 ml of 2.5M in hexanes [ 2.25 mmol]) was added via syringe to 0.748g (2.03 mmol) of 4,4'-((S)-2-methylbutoxy)methyl-2,2'-bithiazole dissolved in 10 mL of THF at -78 C in a 100mL schlenk flask equipped with stir bar. The solution turned a dark brown color as the butyl lithium was added. The mixture was stirred for 3 hours at -78 C. Then,  $Fe(acac)_3$  (0.838 g, 2.40 mmol)

dissolved in 20mL of THF was added via cannula. The reaction was stirred at -78 C for 15 minutes, then allowed to warm room temperature. The mixture was stirred for an additional 18 hours. The solvent was removed via vacuum. The product was then chromatographed on a silica gel column, using 90 hexanes/10 diethyl ether as the eluent. The second fluorescent fraction, fluorescing blue in dilute solution and yellow when concentrated was the product dimer, a yellow solid. 49% yield. MS (EI):  $M^+$ =735.  $^1\text{H}$  NMR:  $\delta$  = 7.35 (s,1H); 4.67 (s, 2H); 4.57 (s, 2H); 3.36 (m, 4H); 1.67 (m, 2H); 1.42 (m, 2H); 1.16 (m, 2H); 0.91 (m,12H). MP 58 C.

**4,4',4'',4'''-tetra-(2-propenoxymethyl)-2,2',5',5'',2'',2'''-quaterthiazole (4)** (Dimer of 4,4'-(2-propenoxymethyl)-2,2'-bithiazole): The procedure for the dimerization of 4,4'-((S)-2-methylbutoxymethyl)-2,2'-bithiazole was repeated with the exception that the product was purified on a silica gel column using 70 hexanes/30 ether as an eluent. 51% yield.  $^1\text{H}$  NMR:  $\delta$  = 7.40 (s, 1H); 5.92 (m, 2H); 5.26 (m, 4H); 4.70 (s, 2H); 4.59 (s, 2H); 4.15 (d, 2H); 4.08 (d, 2H). MS:  $M^+$ =614. Anal. Calc'd: C, 54.69; H, 4.92; N, 8.74. Found: C, 54.49; H, 5.27; N, 9.11. MP= 81 C.

**4,4',4'',4'''-tetra-(3-hydroxypropyloxymethyl)-2,2',5',5'',2'',2'''-quaterthiazole (5)** (Dimer of 4,4'-(3-hydroxypropanoxymethyl)-2,2'-bithiazole): 9-BBN (4.0 mL of 0.5 M in THF, 2.04 mmol) was added via syringe to 4,4'-(2-propenoxy)methyl-2,2'-bithiazole (0.250g, 0.407 mmol) dissolved in 30 mL THF in a 100 mL schlenk flask equipped with stir bar. The solution was stirred for seven hours. A solution of hydrogen peroxide (1.5g of a 50% solution) and sodium hydroxide (0.25g) was degassed, then added via cannula. The flask became warm; cloudiness was apparent. The reaction was stirred for 1 hour. The product was washed product with 3 x 30 mL water; then filtered to reveal a yellow solid which was then recrystallized from ethanol. 80% yield.  $^1\text{H}$  NMR:  $\delta$ =7.83 (s,1H); 4.57 (d, 4H); 4.41 (m,2H); 3.49 (m, 8H); 1.67 (t of t, 4H). MS (EI):  $M^+$ =686. Anal. Calc'd: C,48.96; H, 5.58; N, 8.16. Found: C, 48.89; H, 5.64; N, 8.03. MP= 146 C.

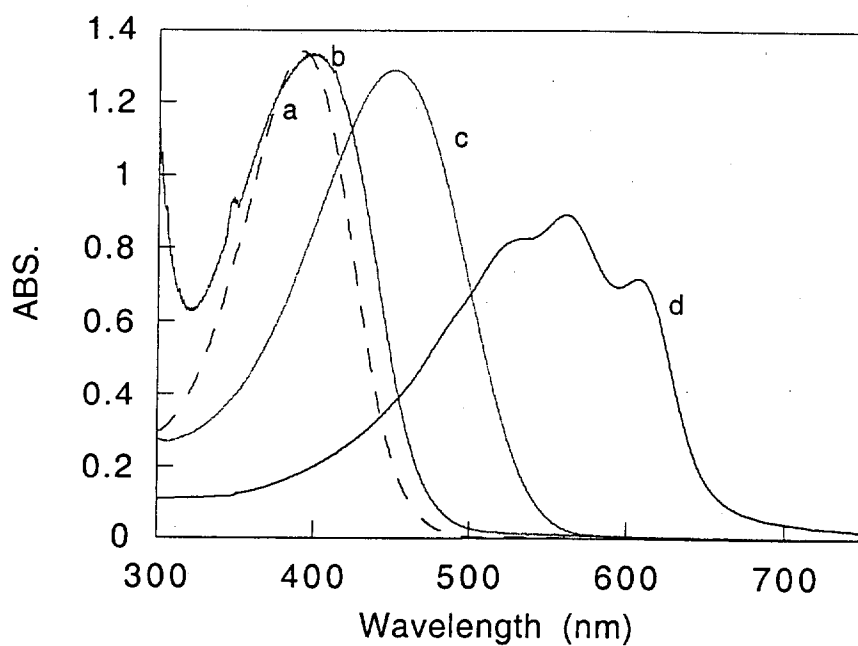


Figure S1. UV-vis spectra of regiorandom poly(3-butylthiophene) (solution (a) and film(b)) and HT-regioregular poly(3-octylthiophene) (solution and film, c and d, respectively).

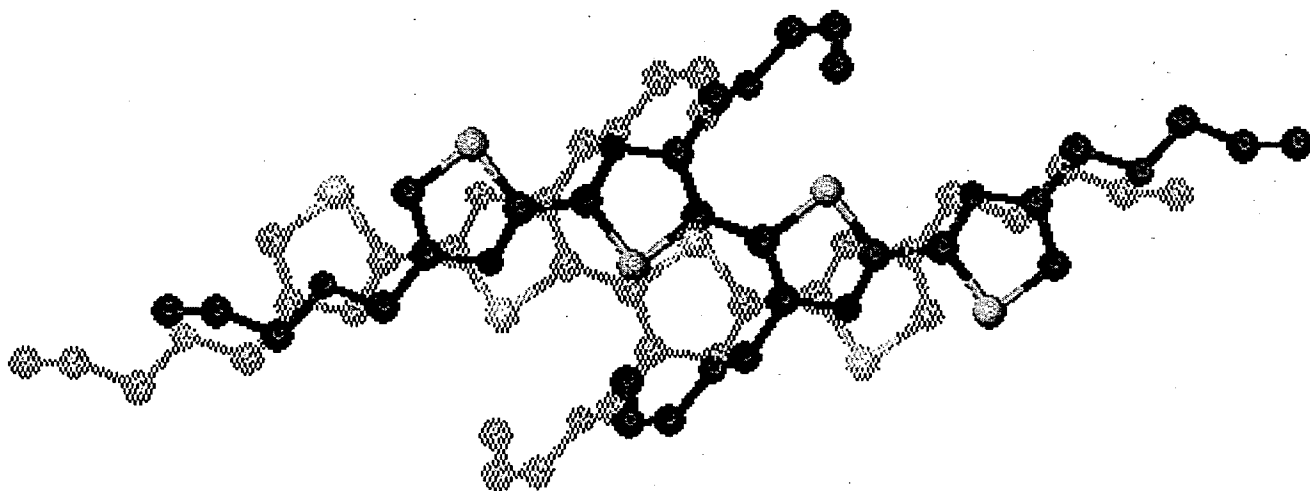


Figure S2. View of  $\pi$ -stack perpendicular to the plane of the rings showing minimal overlap of the  $\pi$ -systems on adjacent molecules. The shaded molecule lies ca. 3.46 Å below the unshaded one. This displacement pattern is repeated between each of the molecules in the  $\pi$ -stack (propenoxybithiazole dimer).

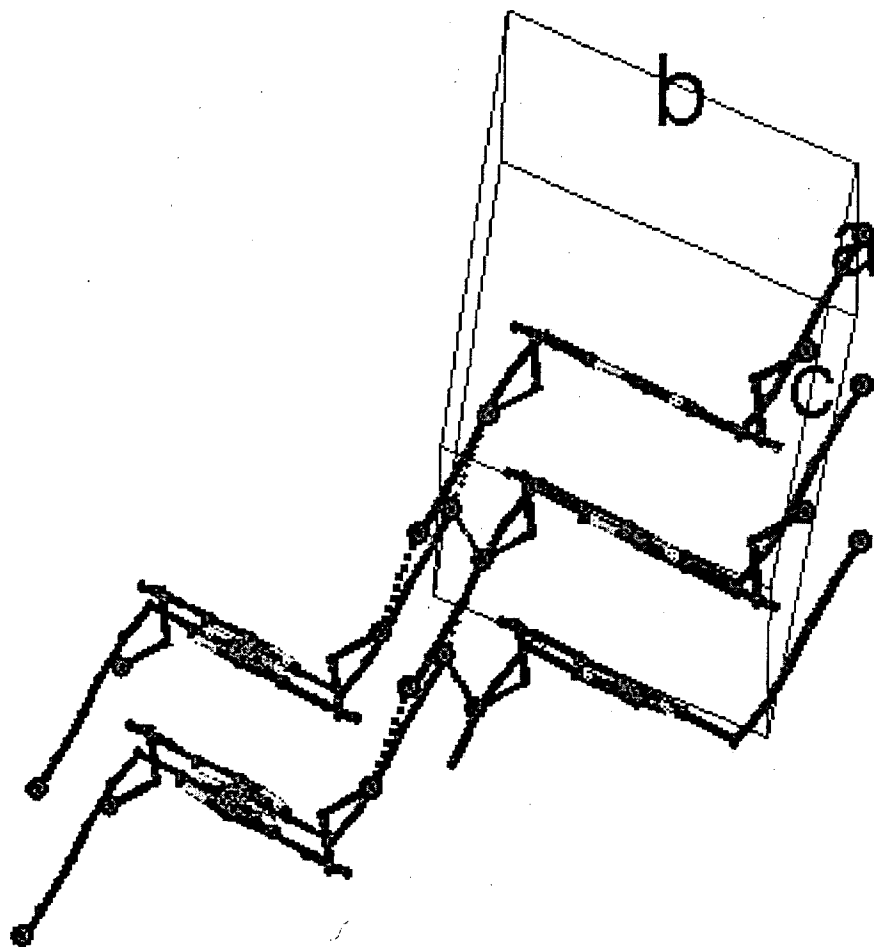


Figure S3. A view along the molecular axis of **2** showing the relative orientations of the  $\pi$ -stacks and the H-bonds between the terminal OH groups on the sidechains.

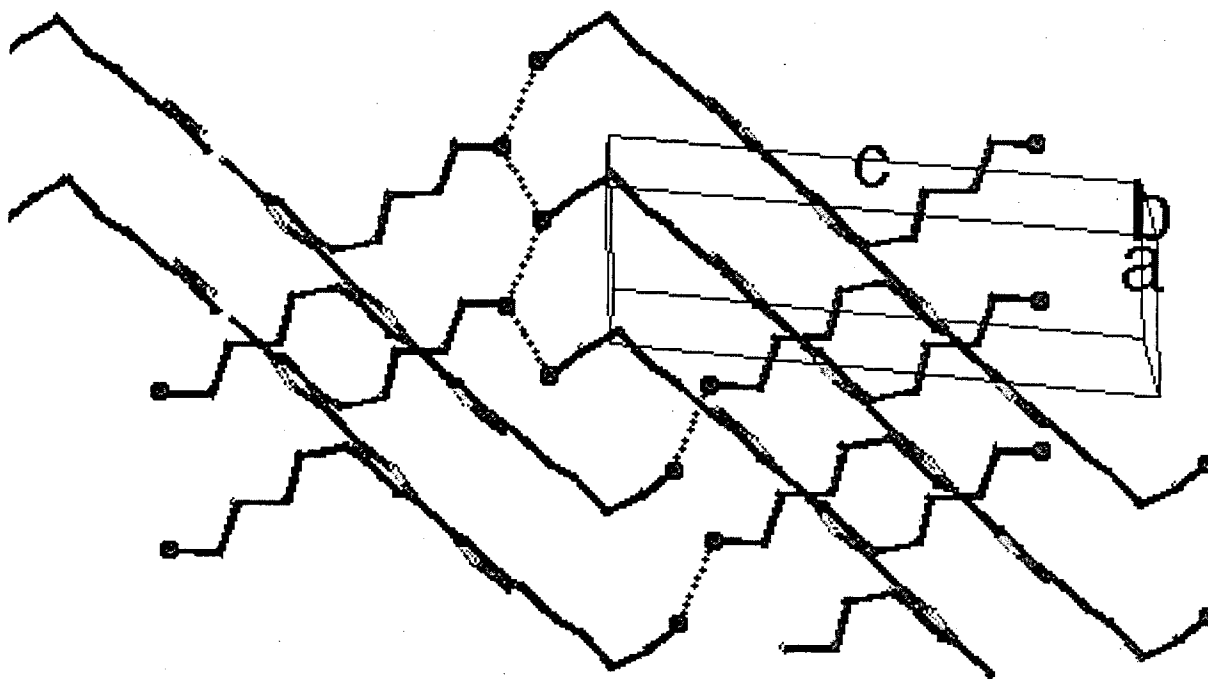


Figure S4. A view perpendicular to the long molecular axis of **2** showing the staircase molecular packing in the  $\pi$ -stacks and the H-bonds between the terminal OH groups on the sidechains. The stacking axis (crystallographic *a*-axis) is nearly vertical.

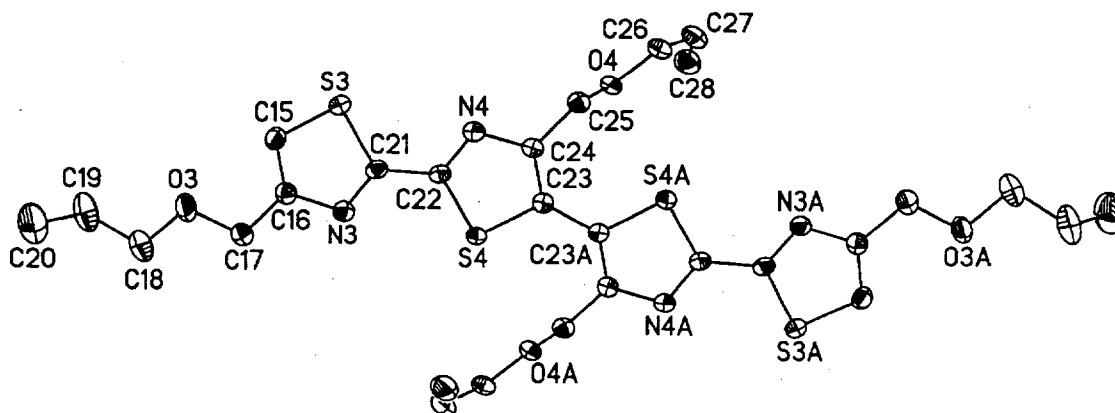


Figure S5. ORTEP drawing of one of the independent molecules of **2**. An inversion center is located between C23 and C23A.

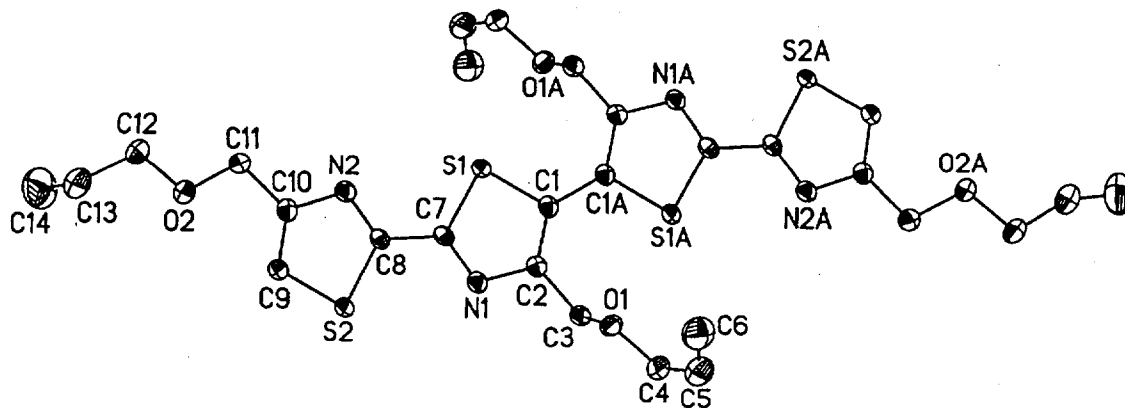


Figure S6. ORTEP drawing of the second independent molecules of **1**. An inversion center is located between C1 and C1A.

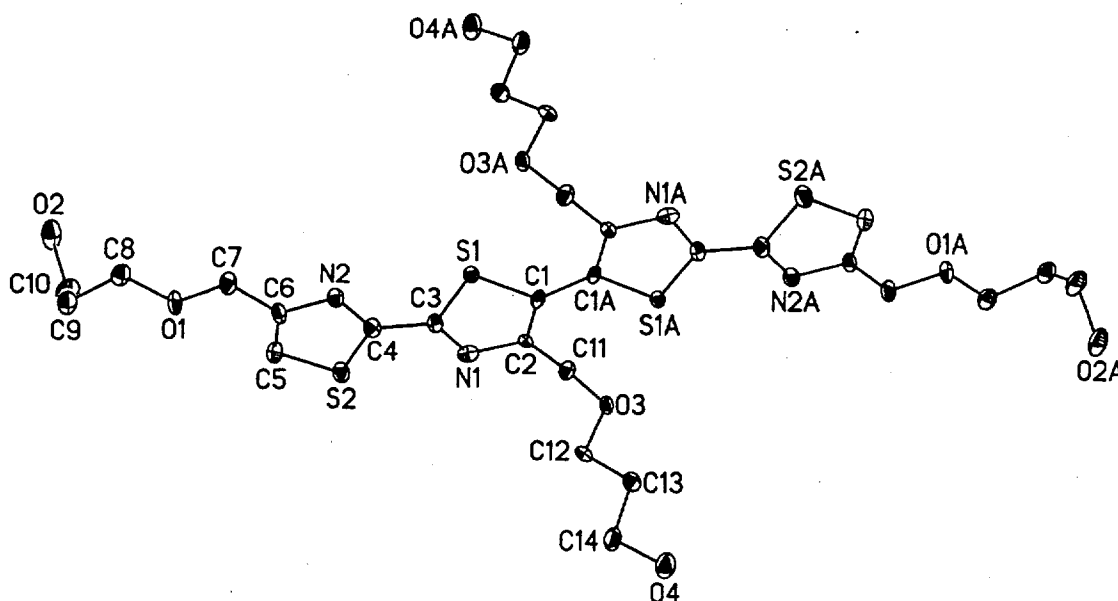


Figure S7. ORTEP drawing of the independent molecule of **2**. An inversion center is located between C1 and C1A.

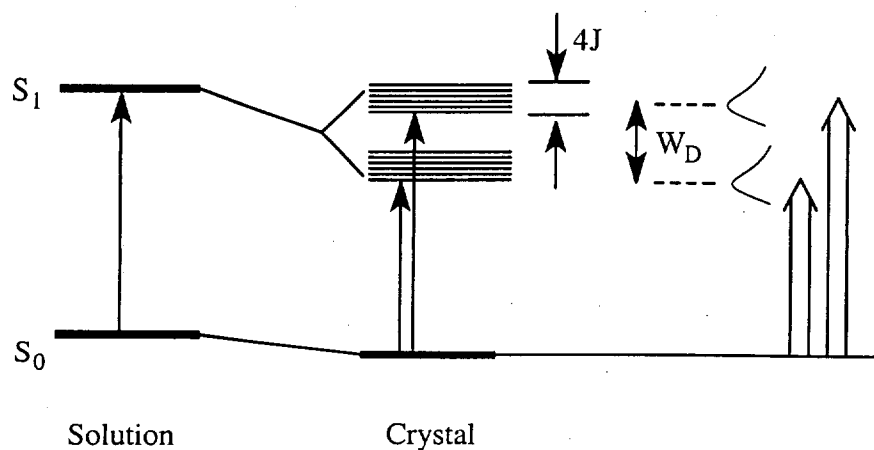


Figure 8S. Schematic illustration of the splitting of the  $2N$  degenerate ( $N$ = number of unit cells) energy levels in a molecular crystal with two molecules per unit cell. The Davydov splitting is  $W_D$ , and the width of the exciton bands is approximated as  $4J$ , where  $J$ =nearest neighbor interaction constant (adapted from ref. 21c).

Table S1. Crystal data and structure refinement for 1.

Empirical formula	C <sub>28</sub> H <sub>30</sub> N <sub>4</sub> O <sub>4</sub> S <sub>4</sub>	
Formula weight	614.80	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 4.71770(10) Å	$\alpha$ = 71.1000(10) deg.
	b = 16.96430(10) Å	$\beta$ = 88.3450(10) deg.
	c = 19.44940(10) Å	$\gamma$ = 89.7350(10) deg.
Volume, Z	1472.03(3) Å <sup>3</sup> , 2	
Density (calculated)	1.387 Mg/m <sup>3</sup>	
Absorption coefficient	0.364 mm <sup>-1</sup>	
F(000)	644	
Crystal size	0.04 x 0.24 x 0.41 mm	
Theta range for data collection	1.11 to 26.37 deg.	
Limiting indices	-5 ≤ h ≤ 5, -21 ≤ k ≤ 20, -24 ≤ l ≤ 24	
Reflections collected	19477	
Independent reflections	5810 [R(int) = 0.0642]	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5810 / 0 / 463	
Goodness-of-fit on F <sup>2</sup>	1.073	
Final R indices [I > 2σ(I)]	R1 = 0.0475, wR2 = 0.1157	
R indices (all data)	R1 = 0.0677, wR2 = 0.1254	
Extinction coefficient	0.0003(11)	
Largest diff. peak and hole	0.606 and -0.458 e.Å <sup>-3</sup>	

Table S2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 1.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U(\text{eq})$
S(1)	-1897(1)	979(1)	4986(1)	22(1)
S(2)	1320(1)	1214(1)	6999(1)	23(1)
O(1)	-5460(4)	-1574(1)	6483(1)	26(1)
O(2)	7188(4)	3364(1)	6083(1)	36(1)
N(1)	-2899(4)	295(1)	6358(1)	22(1)
N(2)	2147(4)	1997(1)	5629(1)	22(1)
C(1)	-4311(5)	155(1)	5262(1)	21(1)
C(2)	-4580(5)	-113(1)	6013(1)	20(1)
C(3)	-6505(6)	-786(2)	6484(1)	25(1)
C(4)	-7392(7)	-2226(2)	6855(2)	33(1)
C(5)	-6480(8)	-3021(2)	6737(2)	45(1)
C(6)	-4501(9)	-3094(2)	6279(2)	52(1)
C(7)	-1368(5)	873(1)	5883(1)	21(1)
C(8)	678(5)	1387(1)	6093(1)	20(1)
C(9)	3729(6)	2011(1)	6742(1)	24(1)
C(10)	3892(5)	2352(1)	6005(1)	23(1)
C(11)	5757(6)	3064(2)	5583(1)	26(1)
C(12)	8719(7)	4112(2)	5731(2)	36(1)
C(13)	10677(9)	4277(2)	6260(2)	55(1)
C(14)	10786(10)	4917(2)	6446(2)	77(1)
S(3)	-1111(1)	2716(1)	-2078(1)	26(1)
S(4)	1884(1)	990(1)	-30(1)	22(1)
O(3)	-7293(4)	4158(1)	-1187(1)	37(1)
O(4)	5563(4)	-589(1)	-1403(1)	23(1)
N(3)	-2165(4)	2461(1)	-713(1)	23(1)
N(4)	2937(4)	1259(1)	-1393(1)	21(1)
C(15)	-3590(6)	3325(2)	-1835(1)	26(1)
C(16)	-3873(5)	3107(1)	-1099(1)	25(1)
C(17)	-5788(6)	3507(2)	-685(2)	30(1)
C(18)	-8843(7)	4646(2)	-840(2)	45(1)
C(19)	-10788(7)	5212(2)	-1388(2)	55(1)
C(20)	-11141(10)	5981(2)	-1500(2)	74(1)
C(21)	-622(5)	2197(1)	-1166(1)	21(1)
C(22)	1399(5)	1520(1)	-936(1)	21(1)
C(23)	4307(5)	343(1)	-273(1)	20(1)
C(24)	4586(5)	594(1)	-1024(1)	20(1)
C(25)	6501(6)	230(1)	-1469(1)	23(1)
C(26)	7547(6)	-983(2)	-1750(2)	30(1)
C(27)	6671(7)	-1868(2)	-1611(2)	38(1)
C(28)	4664(7)	-2271(2)	-1161(2)	40(1)

Table S3. Crystal data and structure refinement for **2**.

Empirical formula	C <sub>28</sub> H <sub>38</sub> N <sub>4</sub> O <sub>8</sub> S <sub>4</sub>
Formula weight	686.86
Temperature	158(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 4.99020(10) Å    α = 105.9970(10) deg. b = 9.4924(2) Å    β = 91.4790(10) deg. c = 16.9038(3) Å    γ = 99.2800(10) deg.
Volume, Z	757.55(3) Å <sup>3</sup> , 1
Density (calculated)	1.506 Mg/m <sup>3</sup>
Absorption coefficient	0.371 mm <sup>-1</sup>
F(000)	362
Crystal size	0.02 x 0.06 x 0.34 mm
Theta range for data collection	2.51 to 26.43 deg.
Limiting indices	-6 ≤ h ≤ 6, -11 ≤ k ≤ 11, -21 ≤ l ≤ 21
Reflections collected	10353
Independent reflections	3097 [R(int) = 0.0604]
Absorption correction	None
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3097 / 0 / 203
Goodness-of-fit on F <sup>2</sup>	1.213
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.1354, wR <sub>2</sub> = 0.3732
R indices (all data)	R <sub>1</sub> = 0.1519, wR <sub>2</sub> = 0.3790
Extinction coefficient	0.017(5)
Largest diff. peak and hole	0.726 and -0.770 e.Å <sup>-3</sup>

Table S4. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U(\text{eq})$
S(1)	7748(5)	4015(3)	4086(2)	14(1)
S(2)	12217(6)	6548(3)	2589(2)	20(1)
N(1)	8262(19)	6669(10)	3936(6)	18(2)
N(2)	12037(19)	3928(10)	2762(6)	17(2)
O(1)	16813(17)	3162(9)	1172(5)	23(2)
O(2)	17045(18)	1584(12)	-1150(5)	33(2)
O(3)	5695(14)	8616(8)	5719(4)	15(2)
O(4)	11664(17)	10719(11)	8135(5)	29(2)
C(1)	5900(20)	5233(12)	4710(6)	15(2)
C(2)	6410(20)	6592(12)	4517(7)	15(2)
C(3)	9100(20)	5392(12)	3661(6)	15(2)
C(4)	11030(20)	5157(12)	3029(6)	16(2)
C(5)	14210(20)	5401(13)	2009(7)	20(2)
C(6)	13840(20)	4083(13)	2174(7)	17(2)
C(7)	15190(20)	2790(13)	1791(7)	21(2)
C(8)	18080(20)	1965(13)	731(7)	22(2)
C(9)	19920(20)	2539(14)	151(7)	24(3)
C(10)	18380(30)	2894(15)	-538(7)	30(3)
C(11)	5140(20)	7958(12)	4868(7)	18(2)
C(12)	8450(20)	9268(12)	5963(7)	19(2)
C(13)	8800(20)	9619(12)	6897(7)	17(2)
C(14)	11700(20)	10333(14)	7250(7)	23(3)