Electronic Supplementary Information

Diiodomethyl-sulfonyl moiety:

An unexplored halogen bond-donor motif

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1. Materials and methods

Diiodomethyl-*p*-tolylsulfone (DMTS) powder was kindly provided by Godo Shigen Co., Ltd. Solvents and compounds **1-3** were purchased from Sigma Aldrich at high purity grade.

Vibrational spectroscopy. IR spectra were collected using a Nicolet Nexus FT-IR spectrometer equipped with a Smart Endurance ATR device and analysed using the Omnic software version 7.3. Peak values are given in wavenumbers (cm^{-1}) upon automatic assignment.

Thermal analysis. Thermal analysis and melting points measurements were performed using a Mettler Toledo DSC 823e differential scanning calorimeter.

Nuclear Magnetic Resonance. ^{13}C NMR spectra were recorded at room temperature on a Bruker AV400 spectrometer. Chemical shifts are reported in parts per million (ppm) from TMS.

Ball milling experiments. Mechanochemical syntheses were performed using a Retsch MM400 ball mill with 1.5 mL vessels, operating at 30 Hz.

X-ray crystallography. Single crystal X-ray diffraction data were collected at Bruker APEX-II diffractometer equipped with sealed-tube and CCD detector, using Mo-Kα radiation (λ = 0.71073 Å). The crystals were cryo-cooled (103 K) for data collection using Bruker KRYOFLEX device. Structures were solved by SHELXS and refinements were carried out by full-matrix least-squares on F^2 using the SHELXL program.[S1] For powder X-ray diffraction (PXRD) measurements, a Bruker AXS D8 powder diffractometer was used, with experimental parameters as follows: Cu-Kα radiation (λ = 1.54056 Å), scanning interval 4-40° at 2θ, step size 0.016°, exposure time 1.5 s per step.

S1. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

2. ^{13}C NMR analysis in solution

Solutions of DMTS (50 mg) in 0.6 mL of deuterated solvent (0.2 M concentration) were prepared in acetone-d_6, dimethylsulfoxide-d_6 and pyridine-d_5. For each solvent, chemical shifts of all the carbon atoms of DMTS are reported in Table S1.

In a second series of experiments, ^{13}C NMR experiments were performed on a 0.07 M solution of DMTS in acetone-d_6 (30 mg/mL), upon addition of increasing amounts of ligand **3** (from 1:0 to 1:10 molar ratio). Results are listed in Table S1.

Table S1 ^{13}C NMR chemical shifts (in ppm) measured on 0.07 M DMTS solutions in acetone-d_6 upon addition of increasing amounts of 4,4'-bipydine (**3**). Signals from both XB-donor and XB-acceptor are reported.

	Chemical shifts (ppm)					
DMTS:3 molar ratio	**DMTS[a]**				**3**	
	Ar-CH	**Ar-C**	**CH_3**	**CHI_2**	**Ar-CH**	**Ar-C**
1:0	131.42 130.53	146.88 129.96	21.62	-19.17	/	/
1:1	131.41 (0.01) 130.52 (0.01)	146.86 (0.02) 129.97 (-0.01)	21.61 (0.01)	-19.10 (-0.07)	151.52 122.18	146.01
1:2	131.38 (0.04) 130.50 (0.03)	146.83 (0.05) 130.00 (-0.04)	21.61 (0.01)	-18.89 (-0.28)	151.52 122.16	145.98
1:5	131.35 (0.07) 130.48 (0.05)	146.79 (0.09) 130.00 8 (-0.04)	21.60 (0.02)	-18.78 (-0.39)	151.49 122.15	145.95
1:10	131.28 (0.14) 130.45 (0.08)	146.73 (0.15) 130.01 (-0.05)	21.58 (0.04)	-18.49 (-0.68)	151.42 122.14	145.90

[a] Chemical shifts changes (in ppm) with respect to pure DMTS (δ(pure DMTS) – δ (DMTS+**3**)) are given in parenthesis.

3. Crystallization experiments

Crystallization of DMTS powder. In a glass vial, 20 mg of DMTS (0.047 mmol) were dissolved in the minimum amount of dimethylsulfoxide (DMSO) or acetone, and the solutions were left to slowly evaporate at room temperature. In a separate experiment, a hot saturated solution of DMTS in DMSO was drop casted on a glass Petri dish, and let to evaporate under the fume hood. Both procedures gave colourless hexagonal crystals. M.p. 149 °C. FTIR (selected bands): 2971, 1591, 1325, 1318, 1305, 1291, 1144, 1110, 1075, 814, 735, 671, 625, 539, 508 cm^{-1}.

Synthesis of co-crystal $(DMTS)_2$·(1). In a glass vial, 20 mg of DMTS (0.047 mmol) and 8.6 mg of compound **1** (0.047 mmol) were dissolved in the minimum amount of DMSO by gentle heating. Slow cooling of the resulting solution afforded colourless crystals of $(DMTS)_2$·(**1**) in 7 days. M.p. 132 °C. FTIR (selected bands): 2980, 1595, 1417, 1321, 1302, 1209, 1142, 1080, 1070, 1001, 830, 809, 752, 666, 543, 526 cm^{-1}.

Synthesis of co-crystal $(DMTS)_2$·(2). A hot saturated solution of 20 mg of DMTS (0.047 mmol) and 8.5 mg of ligand **2** (0.047 mmol) in DMSO was drop casted on a glass Petri dish, and let to evaporate under the fume wood. Colourless needle-shaped crystals of $(DMTS)_2$·(**2**) were formed after one week. M.p. 124 °C. FTIR (selected bands): 2973, 1595, 1416, 1316, 1302, 1289, 1144, 1079, 987, 827, 815, 739, 664, 564, 545 cm^{-1}.

Synthesis of co-crystal (DMTS)·(3). Single crystals were obtained by slow evaporation of a solution of DMTS and compound **3** (1:1 molar ratio) in acetone, after seeding with the milled powder. Pale yellow crystals of (DMTS)·(**3**) were formed after 2 days. M.p. 118 °C. FTIR (selected bands): 2972, 2952, 1591, 1405, 1318, 1301, 1221, 1149, 1081, 1070, 989, 808, 735, 675, 671, 610, 548, 508 cm^{-1}.

Mechanochemical synthesis. For PXRD analysis, 100 mg of DMTS (0.24 mmol) and compounds **1-3** in 1:1 or 1:2 molar ratio (0.24 or 0.12 mmol, respectively) were milled at 30 Hz for 15 minutes (Fig. S7 and S8) and 25 Hz for 30 min (Fig. S9 and S10). The liquid-assisted grinding (LAG) approach was performed using the same amount and molar ratio XB donor and acceptor but adding in the milling jar 40 μL of acetone.

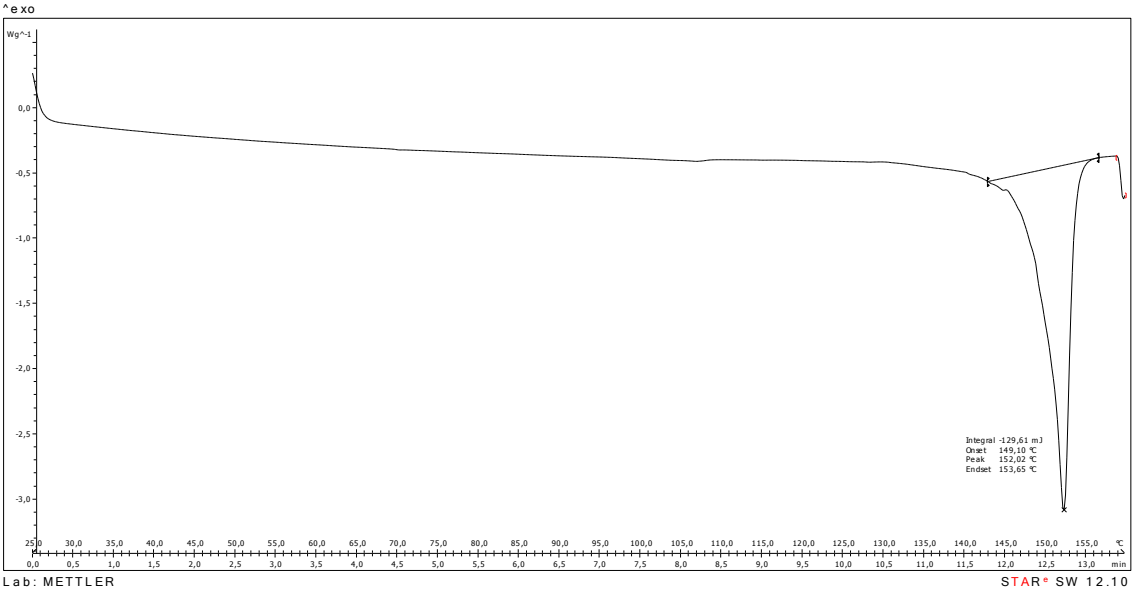

Figure S1. DSC thermogram of DMTS crystallized from acetone (first heating cycle at 10 °C/min heating rate).

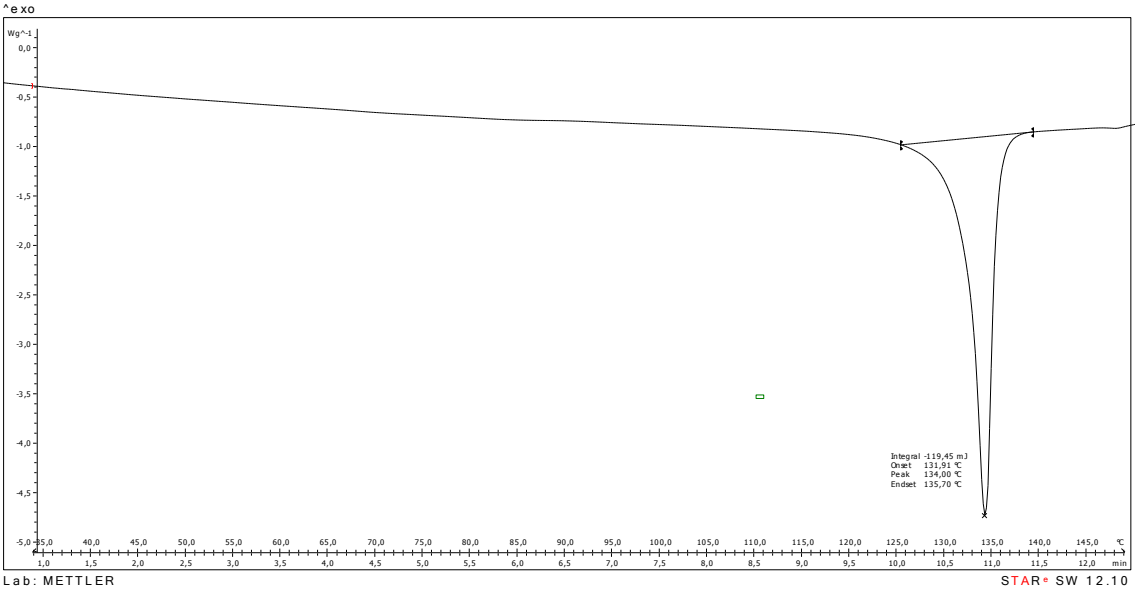

Figure S2. DSC thermogram of $(DMTS)_2$·(**1**) (first heating cycle at 10 °C/min heating rate).

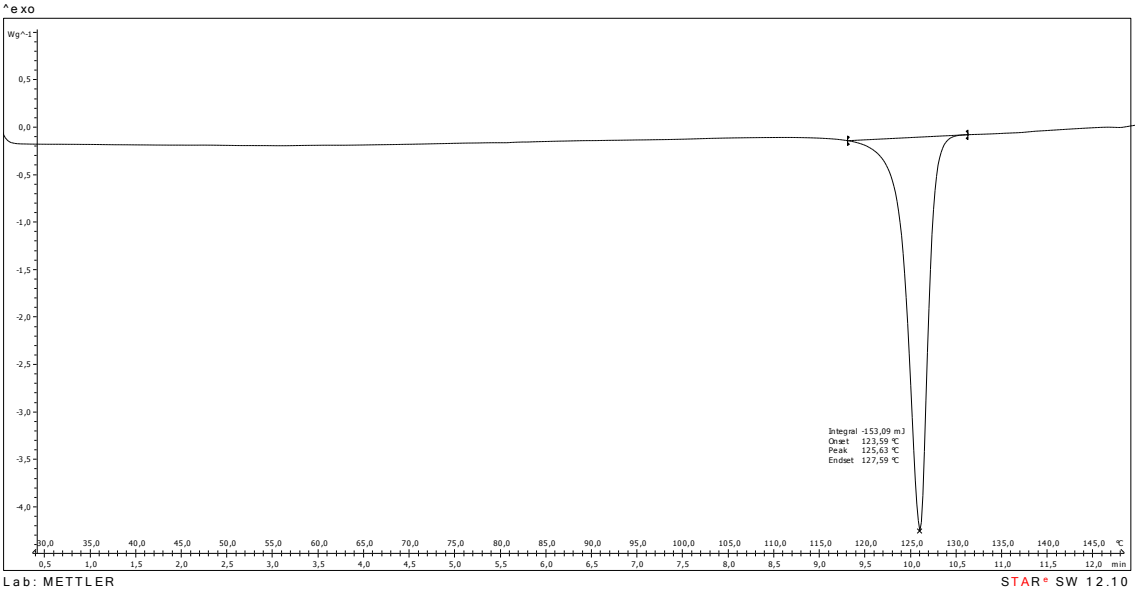

Figure S3. DSC thermogram of $(DMTS)_2$·(**2**) (first heating cycle at 10 °C/min heating rate).

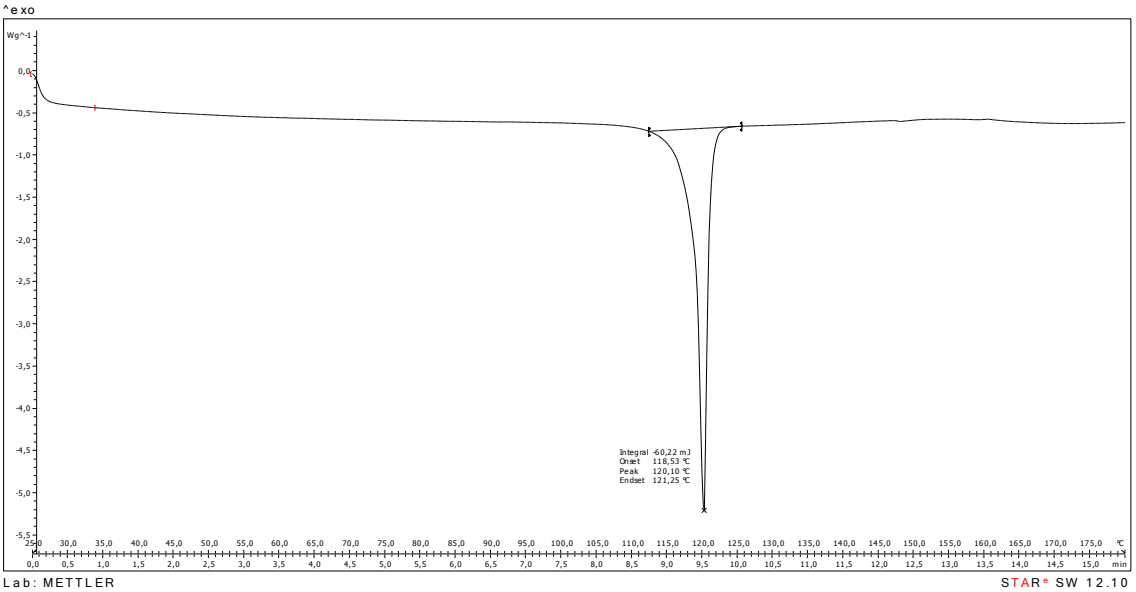

Figure S4. DSC thermogram of (DMTS)·(**3**) (first heating cycle at 10 °C/min heating rate).

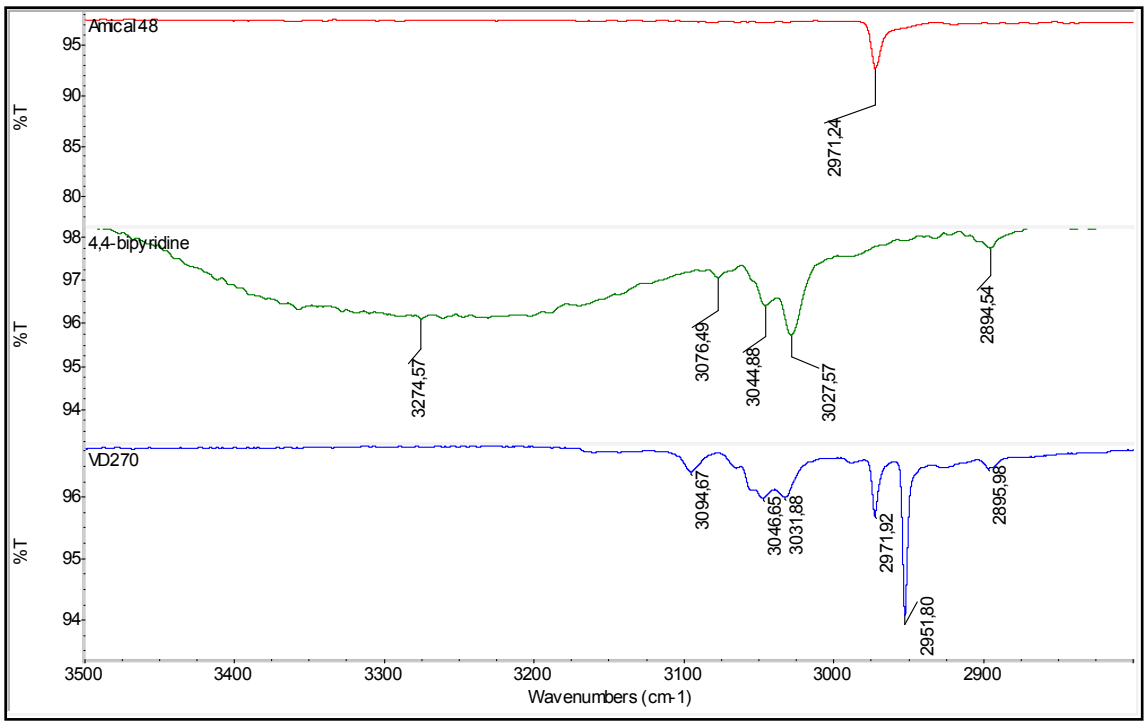

Fig. S5 FT-IR spectra (3500-2800 cm^{-1} region) of DMTS (red line), ligand **3** (green line), and (DMTS)·(**3**) XB adduct (blue line).

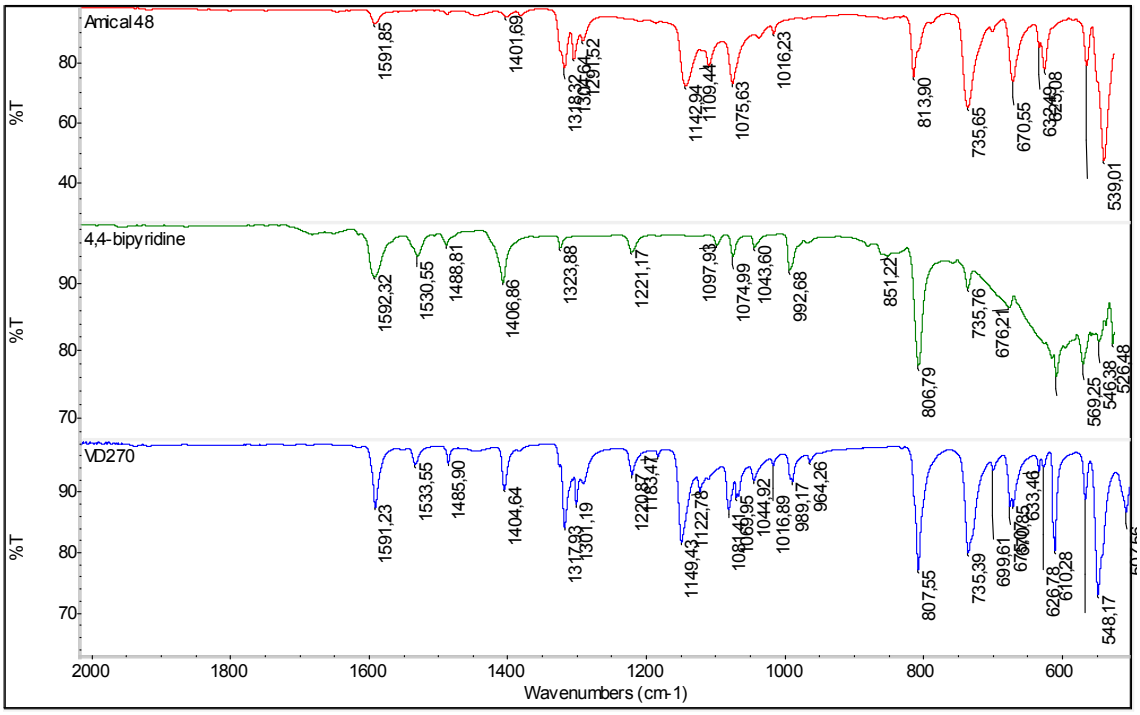

Fig. S6 FT-IR spectra (2000-550 cm^{-1} region) of DMTS (red line), ligand **3** (green line), and (DMTS)·(**3**) XB adduct (blue line).

4. Crystallographic data

Table S2 Single crystal X-ray data and structure refinement parameters for DMTS and its co-crystals.

	DMTS	**$(DMTS)_2$·(1)**	**$(DMTS)_2$·(2)**	**(DMTS)·(3)**
Chemical formula	$C_8H_8I_2O_2S$	$C_{12}H_{12}N_2.2C_8H_8I_2O_2S$	$C_{12}H_{10}N_2.2C_8H_8I_2O_2S$	$C_{10}H_8N_2.C_8H_8I_2O_2S$
Molecular weight	422.00	1028.24	1026.23	578.19
Crystal system, space group	Orthorhombic, $P2_12_12$	Monoclinic, $P2_1/c$	Triclinic P-1	Triclinic P-1
Temperature (K)	103(2)	103(2)	103(2)	103(2)
a (Å)	19.0268(7)	16.4024(9	11.1342(6)	8.6591(8)
b (Å)	7.8630(6)	5.6825(4)	17.3124(10)	9.7178(8)
c (Å)	8.0423(3)	19.6574(11)	19.0131(11)	13.0375(15)
α(°)	90	90	114.136(2)	93.590(5)
β (°)	90	113.993(2)	90.987(2)	96.031(5)
γ(°)	90	90	97.782(2)	114.648(5)
V ($Å^3$)	1126.01(7)	1673.89(18)	3303.1(3)	984.70(17)
Z	4	2	4	2
μ (mm^{-1})	5.739	3.882	3.935	3.313
Crystal size (mm^3)	0.31, 0.14, 0.11	0.36, 0.20, 0.08	0.26, 0.12, 0.10	0.26, 0.18, 0.06
F(000)	776	972	1936	552
Data collection				
Diffractometer	Bruker APEX-II CCD area detector diffractometer			
Absorption correction	Based on multi-scan			
Tmin,Tmax	0.269, 0.571	0.294, 0.398	0.353, 0.443	0.475, 0.530
No. of measured, independent and observed reflections	61066, 6641, 6532	18384, 3783, 2878	217267, 15974, 14207	15401, 6968, 5426
R_{int}	0.015	0.046	0.021	0.049
θ_{min} (°)	2.5	2.1	1.18	3.70

θ_{max} (°)	39.8	27.7	28.32	33.98
Refinement				
$R_{\_all}$, $R_{\_obs}$	0.015, 0.014	0.064, 0.043	0.037, 0.031	0.050, 0.032
$wR2_{\_all}$, $wR2_{\_obs}$	0.029, 0.029	0.082, 0.076	0.063, 0.061	0.065, 0.060
GOOF	1.19	1.05	1.10	1.02
CCDC number	1895418	1895419	1895420	1895421

Computer programs: Bruker APEX2, Bruker SAINT, SHELXS (G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122); SHELXL 2016/6 (G. M. Sheldrick, 2016); ORTEP-3 (L. J. Farrugia, *J. Appl. Cryst.* 1997, **30**, 565); Mercury (C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.* 2006, **39**, 453-457)..

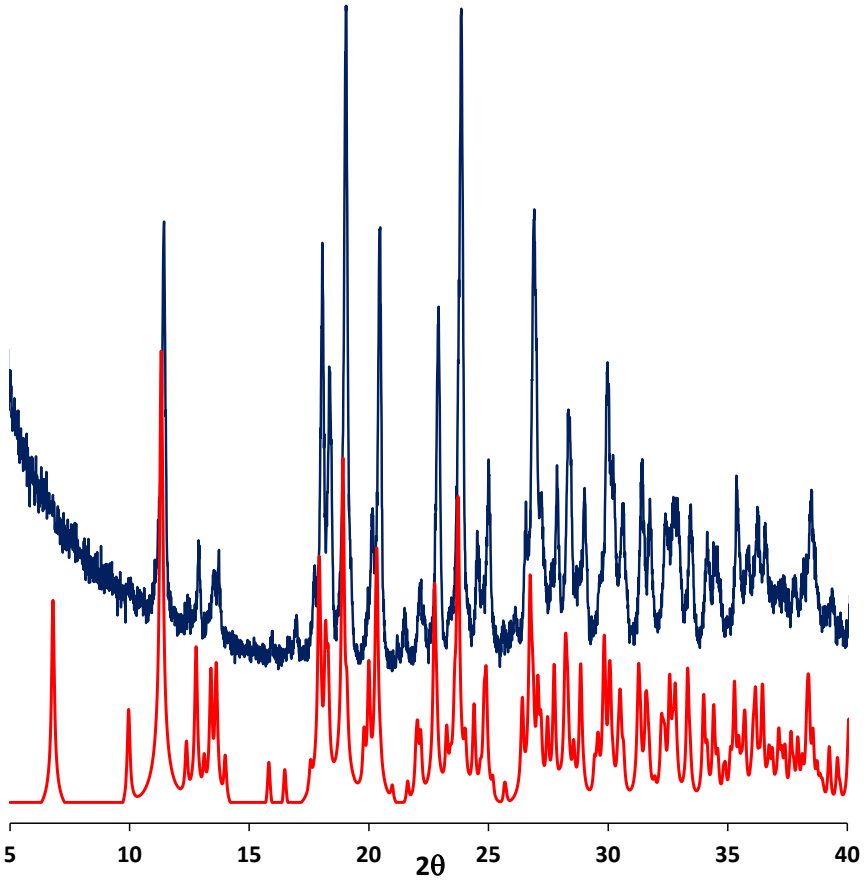

Fig. S7 Experimental PXRD pattern of (DMTS)·(**3**) powder obtained from ball milling (blue line), and simulated PXRD pattern of (DMTS)·(**3**) from single crystal (red line).

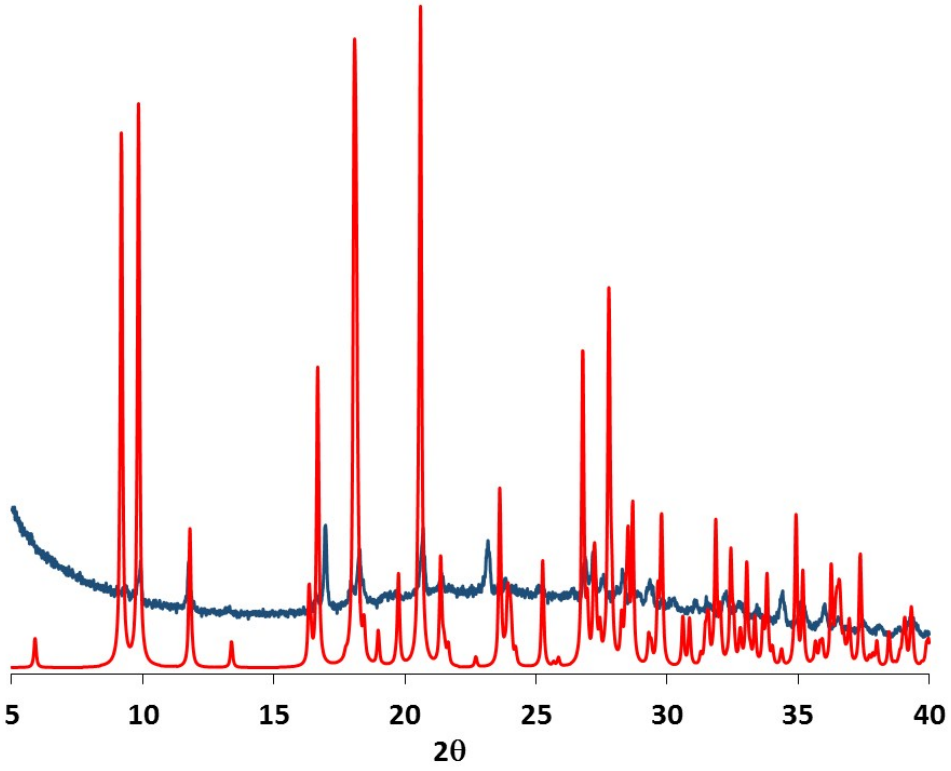

Fig. S8 Experimental PXRD pattern of $(DMTS)_2$·(**1**) powder obtained from evaporation under vacuum of a $(DMTS)_2$·(**1**) solution in acetone (blue line), and simulated PXRD pattern of $(DMTS)_2$·(**1**) from single crystal (red line).

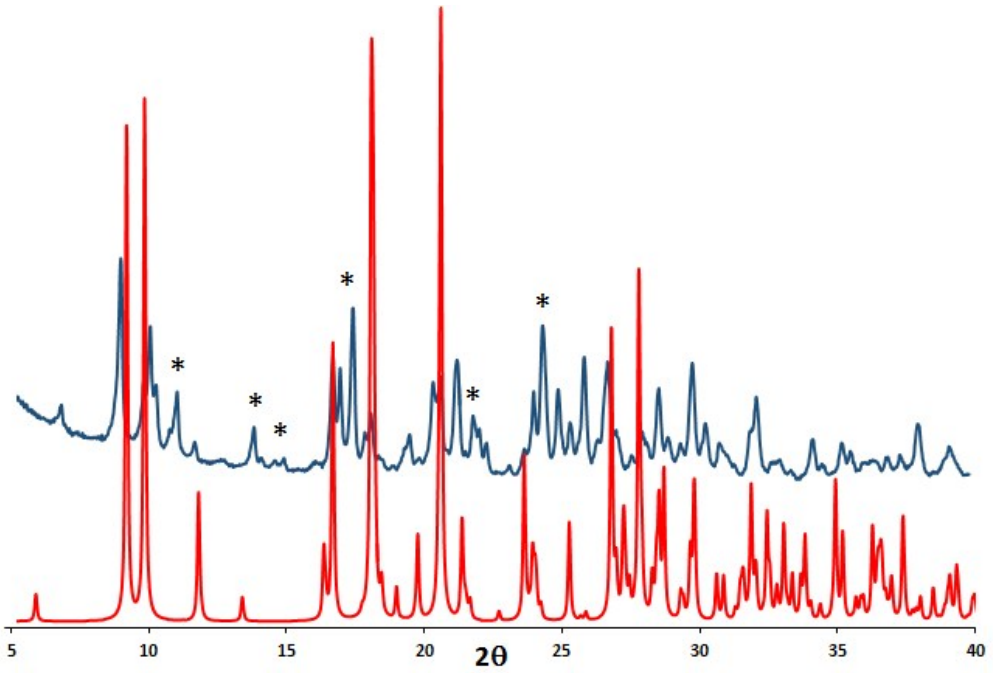

Fig. S9. Experimental PXRD pattern of (DMTS)·(**1**) powder obtained from ball milling (NO LAG) (blue line), and simulated PXRD pattern of (DMTS)·(**1**) from single crystal (red line). Some peaks from an unknown phase are present (*).

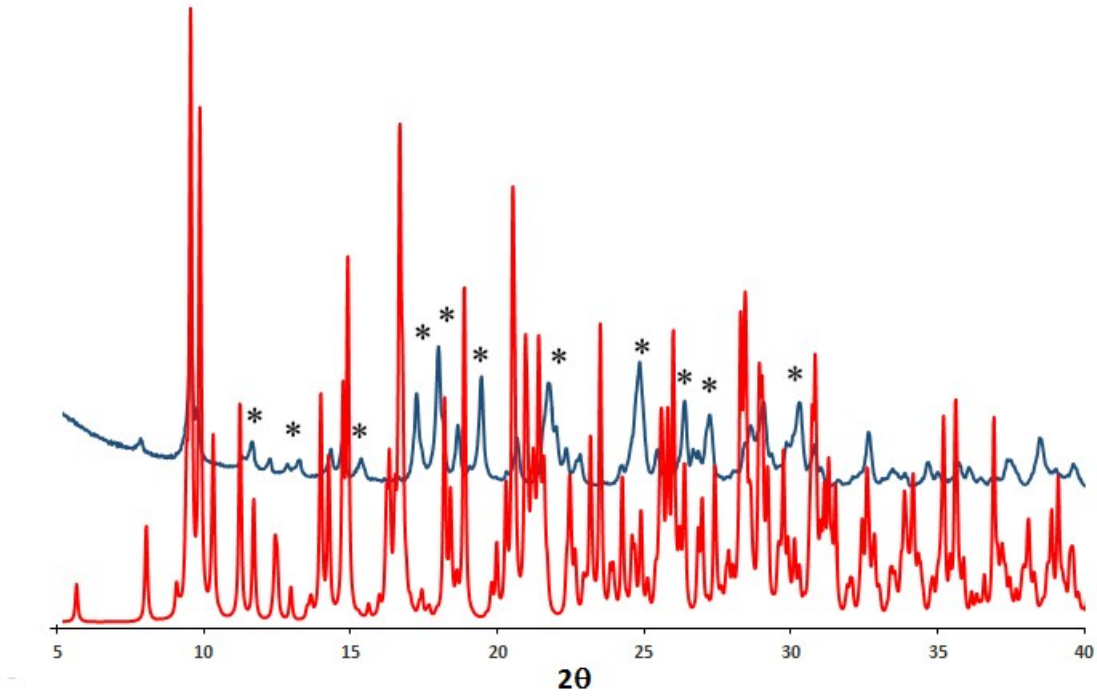

Fig. S10. Experimental PXRD pattern of (DMTS)·(**2**) powder obtained from ball milling (NO LAG) (blue line), and simulated PXRD pattern of (DMTS)·(**2**) from single crystal (red line). Some peaks from an unknown phase are present (*).

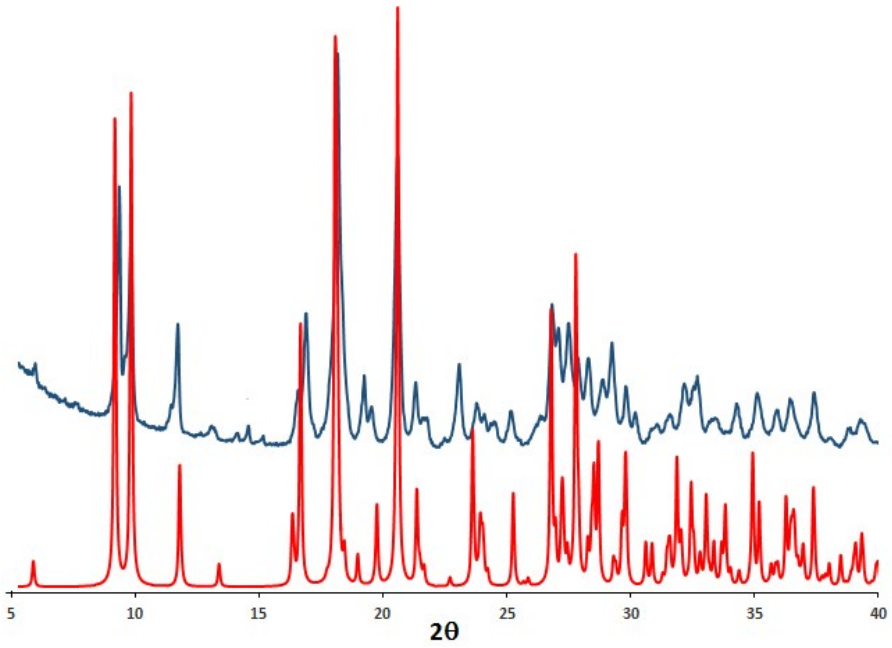

Fig. S11. Experimental PXRD pattern of (DMTS)·(**1**) powder obtained from ball milling (LAG) (blue line), and simulated PXRD pattern of (DMTS)·(**1**) from single crystal (red line).

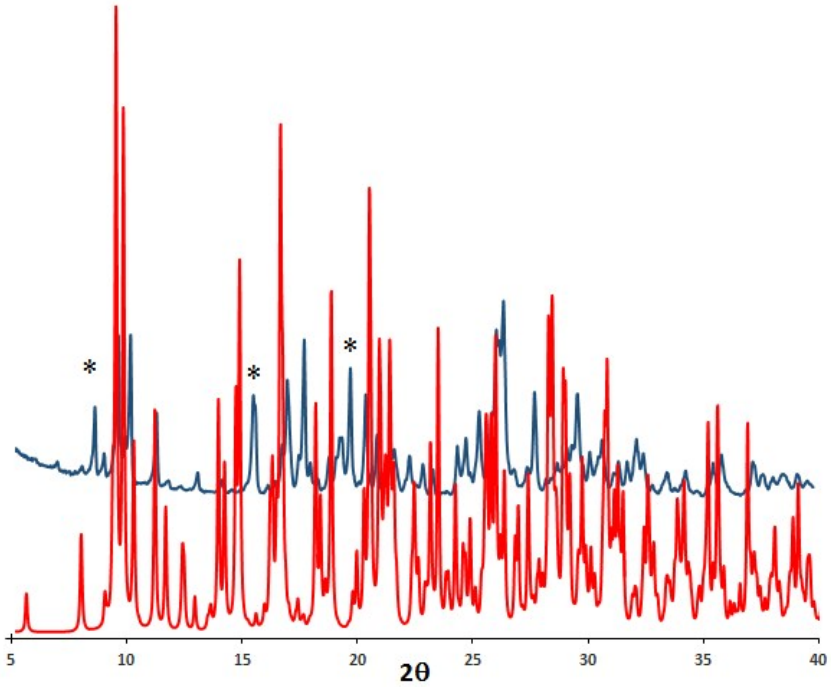

Fig. S12. Experimental PXRD pattern of (DMTS)·(**2**) powder obtained from ball milling (LAG) (blue line), and simulated PXRD pattern of (DMTS)·(**2**) from single crystal (red line). Some peaks from an unknown phase are present (*).