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Electronic Supplementary Information

The C–C to C=C conversion within a supramolecular framework of tetrathiafulvalene: a confinement effect and a radical catalyzed dehydrogenation

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1. Experimental section

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1. Experimental section

General Remarks. The compound, dimethylthio-tetrathiafulvalene-bicarboxylate sodium salt (Na_2L), was prepared using a method reported previously.[1] Compounds $MeBpeI_2$ and $MeBpaI_2$ were synthesized from their bipyridine derivatives according to a modified method in the literature.[2] All other reagents were purchased from commercial suppliers (Alfa Aesar). Infrared (IR) spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Elemental analyses of C, H, and N were performed using an EA1110 elemental analyzer. Electronic absorption spectra were measured on a Shimadzu UV-3150 spectrometer. Powder X-ray diffraction (PXRD) of the compounds were carried out on a D/MAX-3C X-ray diffraction meter with Cu$K\alpha$ (λ = 1.5406 Å) radiation. Cyclic voltammetry (CV) experiments of the solid state compounds were performed in acetonitrile with 0.10 $mol \cdot L^{-1}$ tetrabutylamonium perchloride under an argon atmosphere on a CHI600 electrochemistry workstation in a three-electrode system, a surface-modified Pt-plate working electrode, a Pt wire auxiliary electrode, and a saturated calomel electrode (SCE) as reference. ^1H NMR spectra were recorded in *d*6-DMSO using tetramethylsilane, $Si(CH_3)_4$, as an internal standard on a UNITYNOVA-400 spectrophotometer.

Preparation of Compounds

$(MeBpe)[ZnL_2(H_2O)_4]\cdot 2H_2O$ (**1** and **1'**). The mixed solution of Na_2L (4.4 mg, 0.01 mmol) in water (5 mL) and $MeBpaI_2$ (4.7 mg, 0.01 mmol) in DMF (2 mL) was stirred for 10 min. Then, an aqueous solution (2 mL) of $ZnCl_2$ (2.7 mg, 0.02 mmol) was added. The final mixture was placed in thick Pyrex tubes (0.7 cm dia., 15 cm length) at room temperature. Black crystals of **1** were obtained for 5 days and were used for all measurements (1.4 mg, yield: 24.3% based on Na_2L). Anal. Calcd. for $C_{34}H_{40}N_2O_{14}S_{12}Zn$ (MW 1150.9): C, 35.48; H, 3.50; N, 2.43 %. Found: C, 35.61; H, 3.42; N, 2.49 %. IR data (cm^{-1}): 1633(s), 1580(s, b), 1520(w), 1473(w), 1429(w), 1353(s, b), 1195(w), 1097(w), 986(m), 892(w), 859(w), 792(m), 745(vs), 698(w), 657(w).

Crystals of **1'** were obtained by following a similar procedure to that of **1**, but

$MeBpeI_2$ (4.7 mg, 0.01 mmol) was used instead of $MeBpaI_2$. Black crystals of **1'** appeared for 4 days and were used for all measurements (1.9 mg, yield: 33.3% based on Na_2L). Anal. Calcd. for $C_{34}H_{40}N_2O_{14}S_{12}Zn$ (MW 1150.9): C, 35.48; H, 3.50; N, 2.43 %. Found: C, 35.62; H, 3.42; N, 2.47 %. IR spectra are the same as those of the crystals **1** (Fig. S2).

(MeBpa)[$ZnL_2(H_2O)_4$]·$2H_2O$ (**2**). Compound **2** was obtained by following a similar procedure to that of **1** including the same reactants and solvents, except that the final mixture was degassed by argon before sealed. Single crystals of **2** as yellow blocks were obtained for 6 days at room temperature and were used for all measurements (1.2 mg, yield: 21.1% based on Na_2L). Anal. Calcd. for $C_{34}H_{42}N_2O_{14}S_{12}Zn$ (MW 1152.9): C, 35.42; H, 3.67; N, 2.43 %. Found: C, 35.36; H, 3.71; N, 2.45 %. IR data (cm^{-1}): 1642(s), 1572(vs, b), 1519(w), 1472(w), 1429(w), 1342(vs, b), 1180(w), 1097(w), 1093(w), 977(m), 887(w), 851(w), 792(m), 742(vs), 691(m), 657(w).

(MeBpe)[$MnL_2(H_2O)_4$]·$2H_2O$ (**3** and **3'**). Crystals of **3** were obtained by following a similar procedure to that of **1**, but $MnCl_2·4H_2O$ (3.9 mg, 0.02 mmol) or $Mn(ClO_4)_2·6H_2O$ (7.2 mg, 0.02 mmol) was used instead of Zn(II) salt. Black crystals of **3** appeared for 4 days and were used for all measurements (1.6 mg, yield: 28.1% based on Na_2L). Anal. Calcd. for $C_{34}H_{40}MnN_2O_{14}S_{12}$ (MW 1140.4): C, 35.81; H, 3.54; N, 2.46 %. Found: C, 35.99; H, 3.46; N, 2.49 %. IR data (cm^{-1}): 1633(s), 1582(s, b), 1519(w), 1471(w), 1426(w), 1353(s, b), 1192(m), 1095(m), 980(m), 892(w), 845(w), 792(m), 759(w), 739(s), 689(m).

Crystals of **3'** were obtained by following a similar procedure to that of **3**, but $MeBpeI_2$ (4.7 mg, 0.01 mmol) was used instead of $MeBpaI_2$. Black crystals of **3'** appeared for 3 days and were used for all measurements (1.7 mg, yield: 29.8% based on Na_2L). Anal. Calcd. for $C_{34}H_{40}MnN_2O_{14}S_{12}$ (MW 1140.4): C, 35.81; H, 3.54; N, 2.46 %. Found: C, 35.91; H, 3.49; N, 2.41 %. IR spectra are the same as those of the crystal **3** (Fig. S2).

(MeBpa)[$MnL_2(H_2O)_4$]·$2H_2O$ (**4**) Compound **4** was obtained by following a similar procedure to that of **2**, but $MnCl_2·4H_2O$ (3.9 mg, 0.02 mmol) or $Mn(ClO_4)_2·6H_2O$ (7.2 mg, 0.02 mmol) was used instead of Zn(II) salt. Single crystals of **4** as yellow blocks for 5 days and were used for all measurements (1.3 mg, yield: 22.8% based on Na_2L). Anal. Calcd. for $C_{34}H_{42}MnN_2O_{14}S_{12}$ (MW 1142.4): C, 35.75; H, 3.71; N, 2.45 %. Found: C, 35.72 H, 3.75; N, 2.42 %. IR data (cm^{-1}): 1644(s), 1575(s, b), 1527(w), 1468(w), 1426(w), 1345(s, b), 1181(m), 1092(m), 980(m), 890(w), 845(w), 792(m), 759(w), 737(s), 689(m).

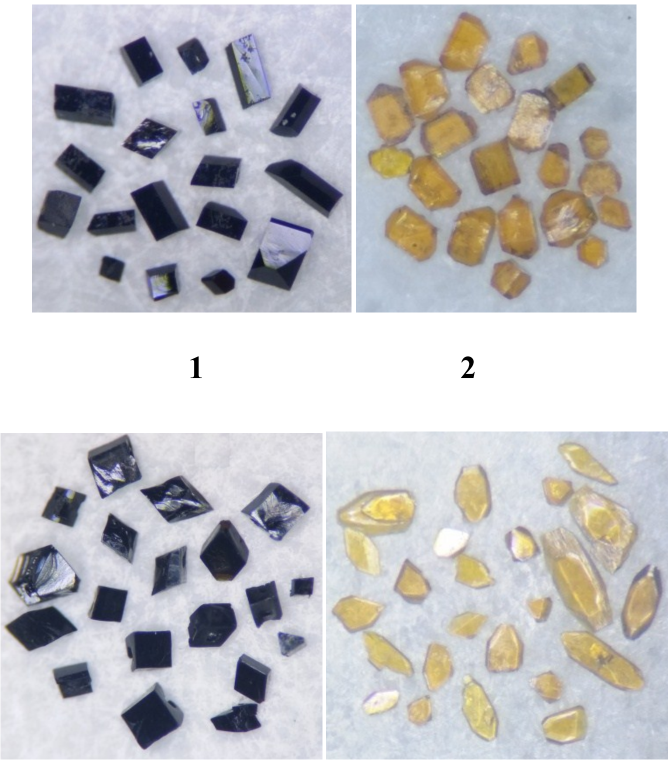
X-ray Crystallographic Study. The measurement was carried out on a Rigaku Mercury CCD diffractometer for crystals **1**, **1'**, **3**, **3'** and Bruker D8-Venture single crystal X-ray diffractometer for crystals **2** and **4**. The structure was solved by direct methods using SHELXS-16, and the refinement against all reflections of the compound was performed using SHELXL-16 for all crystals. All of the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added theoretically. The crystal data and structural refinement parameters are listed in Table S1 for crystals **1**–**4** and Table S2 for crystals **1'** and **3'**. Crystallographic data CCDC 1838004–1838009 contain the supplementary crystallographic data. The data can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

1. (a) P. Hudhomme, S. L. Moustarder, C. Durand, N. GallegoPlanas, N. Mercier, P. Blanchard, E. Levillain, M. Allain, A. Gorgues and A. Riou, *Chem. Eur. J.*, 2001, **7**, 5070–5083; (b) R. D. McCullough, M. A. Petruska and J. A. Belot, *Tetrahedron*, 1999, **55**, 9979–9998; (c) H.-H. Lin, Z.-M. Yan, J. Dai, D.-Q. Zhang, J.-L. Zuo, Q.-Y. Zhu, and D.-X. Jia, *New J. Chem.*, 2005, **29**, 509–513.

2. P. Phillps and J. Mentha, *J. Am. Chem. Soc.*, 1955, **77**, 6393−6395.

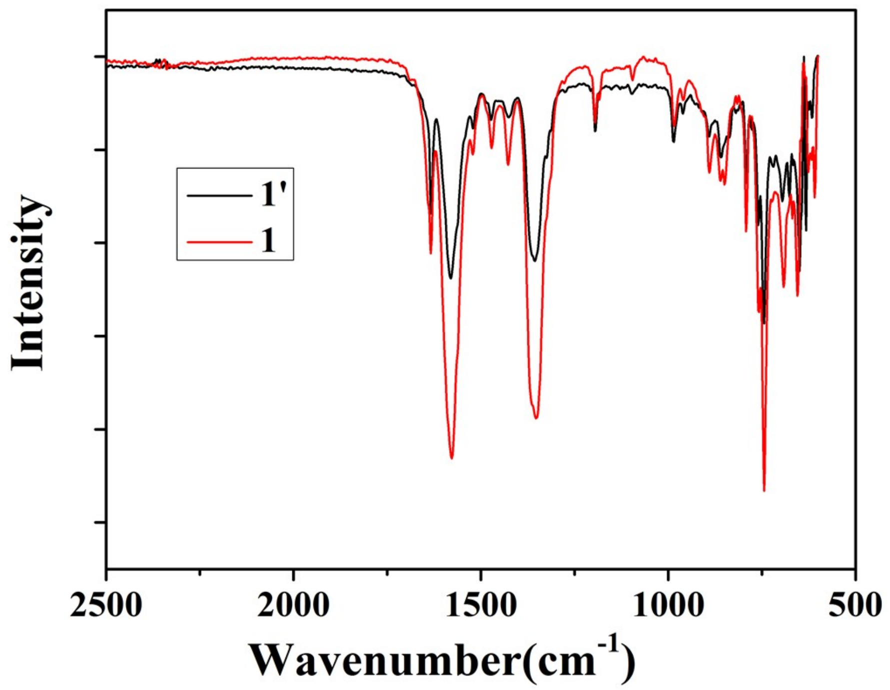
2. Figure



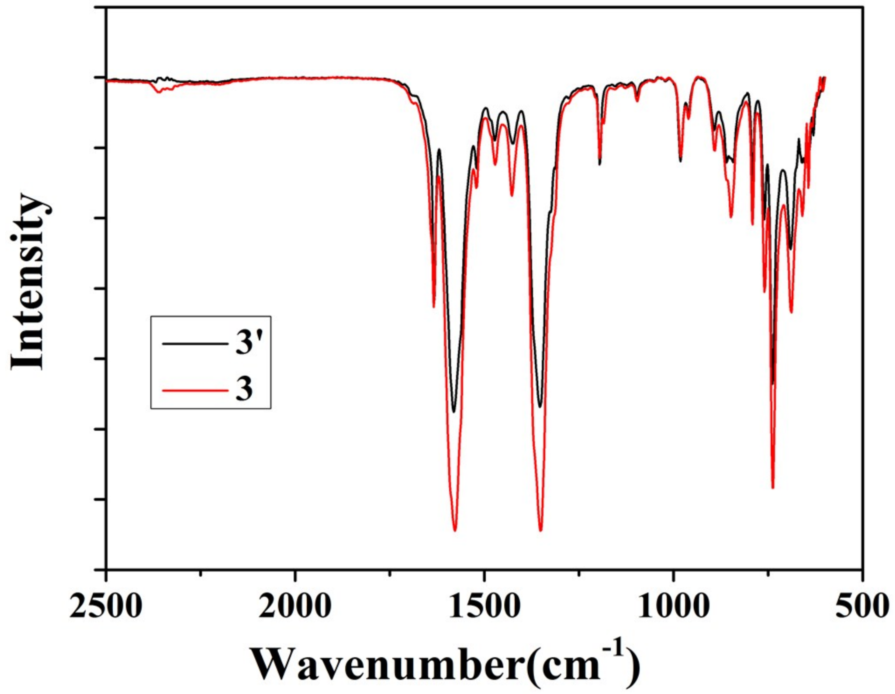
1 **2**

3 **4**

Fig. S1. Photos under a microscope of the black crystals of **1** and **3** prepared under aerobic condition and yellow crystals of **2** and **4** prepared under anaerobic condition.



(a)



(b)

Fig. S2. IR spectra of crystals **1** and **1**’ and (b) crystals **3** and **3**’, showing their identities.

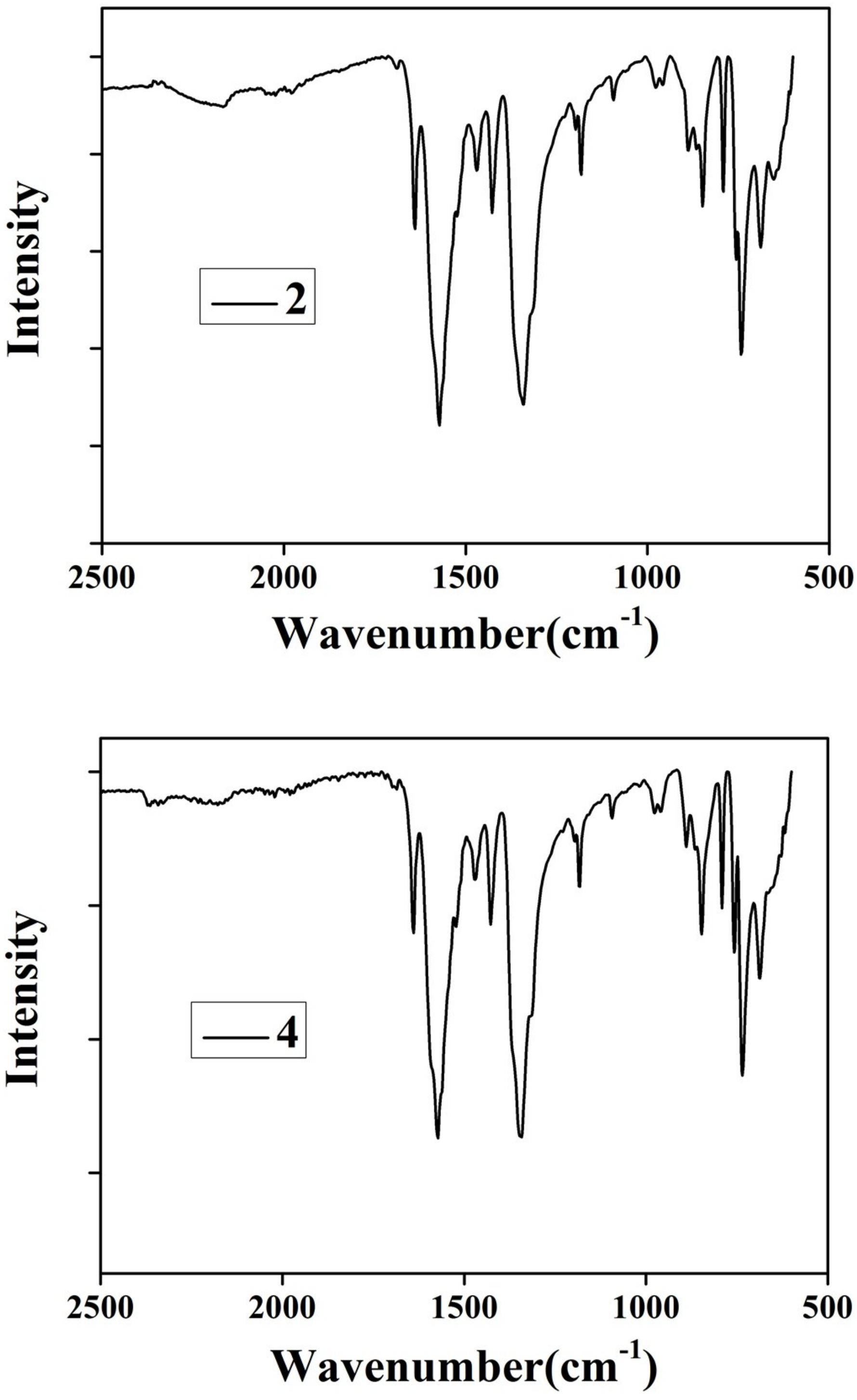
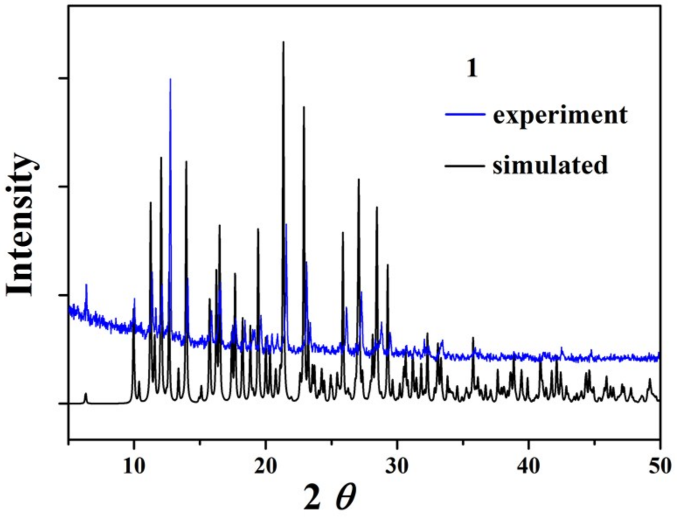
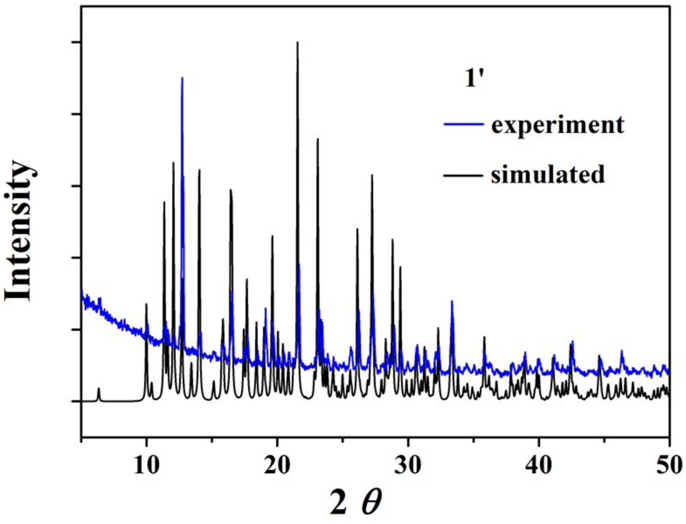
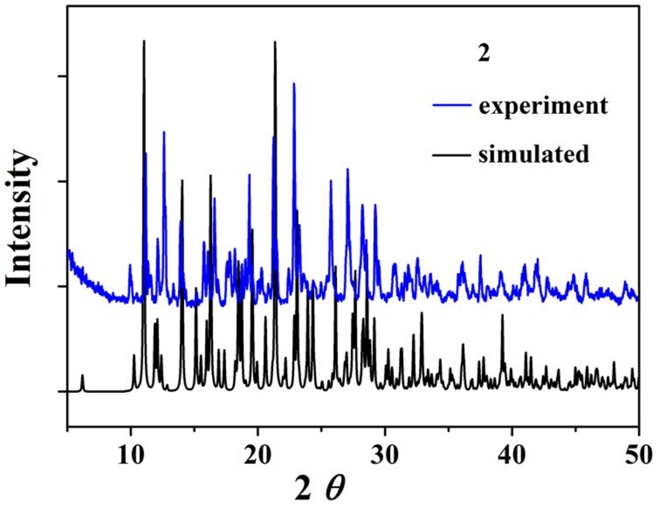


Fig. S3. IR spectra of crystals **2** and **4**.


1
experiment
simulated
Intensity
10
20
30
40
50
2 θ


1'
experiment
simulated
Intensity
10
20
30
40
50
2 θ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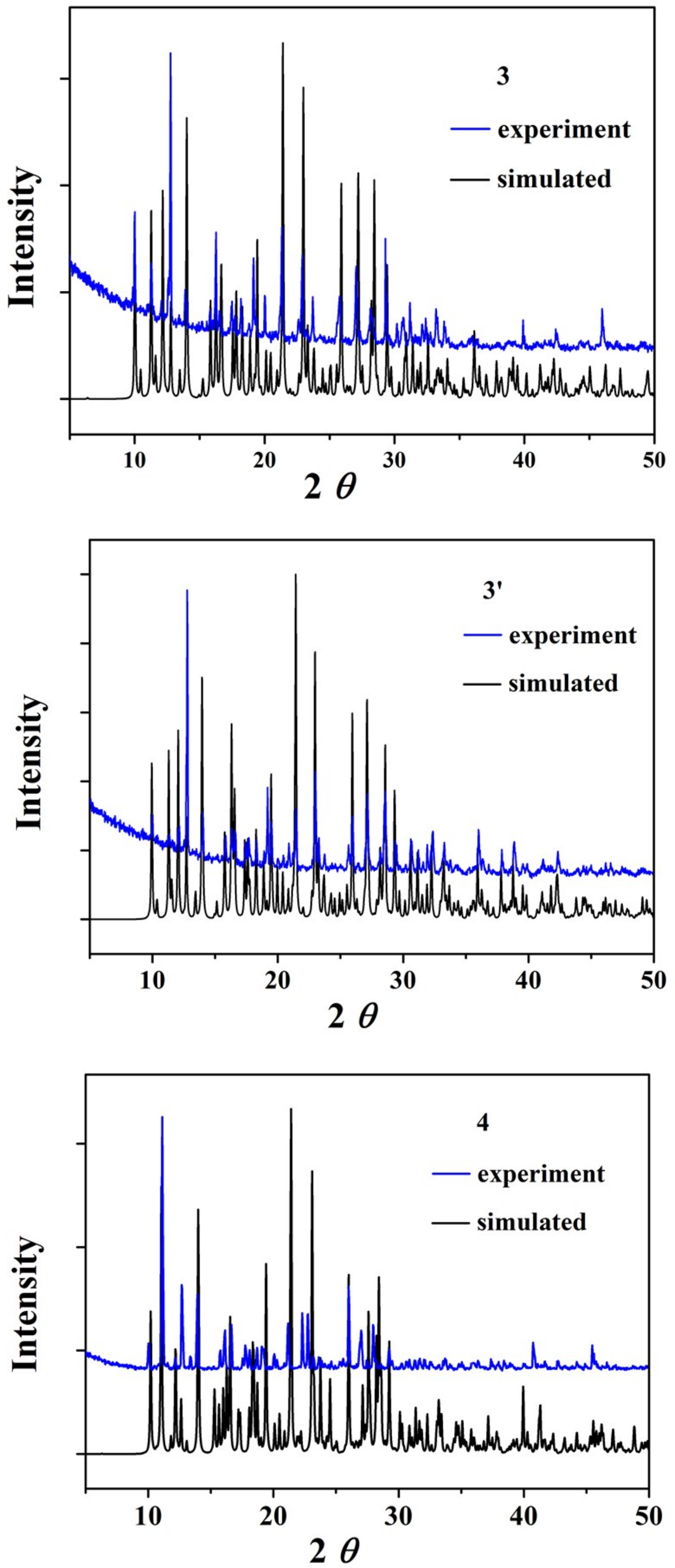

Fig. S4. The experimental powder XRD patterns and the simulated patterns from the crystal data of all six compounds.

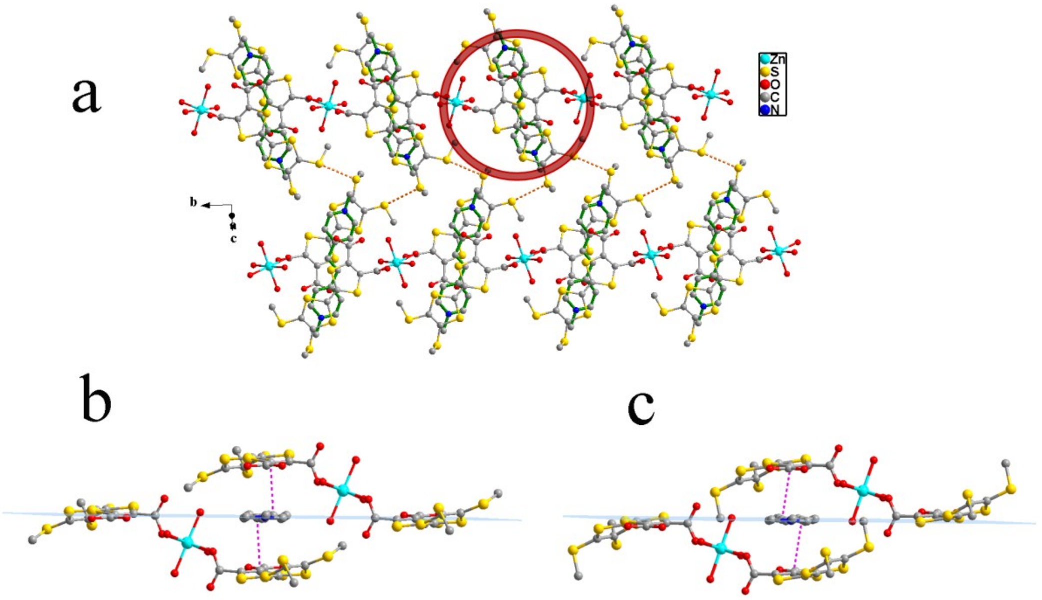

Fig. S5. (a) The supramolecular structure showing the S···S short contacts (orange dashed line) and the D···A···D subunits (red circle). (b) The host-guest diagram with short C···C contacts of MeBpe (3.250 Å for **1** and 3.371 Å for **1’**). (c) The similar diagram of **2** showing the C···C distances of 3.571 Å.

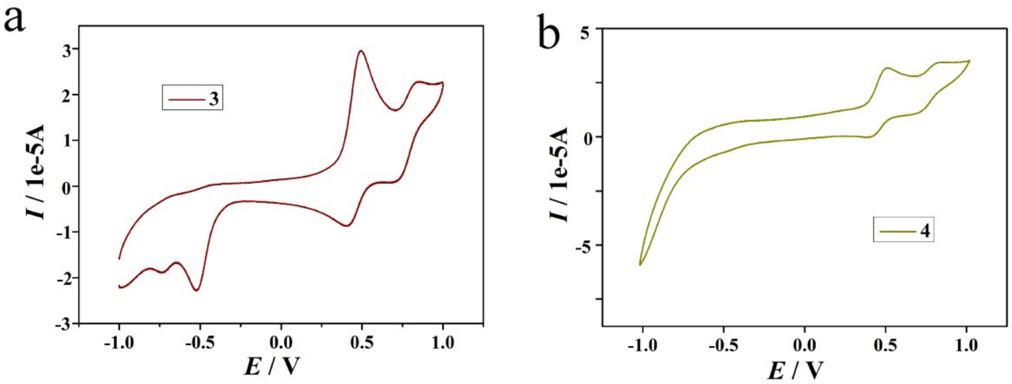

Fig. S6. Cyclic voltammogram of the solid state compounds **3** (a) and **4** (b) in CH_3CN (0.1 $mol\cdot L^{-1}$ Bu_4NClO_4, 100 mV s^{-1}, vs SEC).

3. Table

Table S1. Crystal data and structural refinement parameters for crystals **1**–**4**.

	1	**2**	**3**	**4**
formula	$C_{34}H_{40}N_2O_{14}S_{12}Zn$	$C_{34}H_{42}N_2O_{14}S_{12}Zn$	$C_{34}H_{40}MnN_2O_{14}S_{12}$	$C_{34}H_{42}MnN_2O_{14}S_{12}$
fw	1150.77	1152.89	1140.34	1142.35
cryst size (mm^3)	0.30×0.40×0.45	0.06×0.10×0.20	0.30×0.45×0.50	0.06×0.40×0.40
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	14.0234(5)	14.2765(19)	13.904(3)	14.0309(10)
b (Å)	10.7448(4)	10.2073(13)	10.668(2)	10.3024(7)
c (Å)	15.7641(7)	16.037(2)	15.757(3)	16.0378(9)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	94.765(4)	92.050(5)	95.34(3)	93.634(2)
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	2367.10(16)	2335.5(5)	2327.0(8)	2313.6(3)
Z	2	2	2	2
ρ_{calcd} (g cm^{-3})	1.615	1.636	1.627	1.640
F(000)	1184	1184	1174	1178
μ (mm^{-1})	1.111	1.126	0.886	0.892
T (K)	293(2)	293(2)	293(2)	293(2)
reflns collected	13293	18865	20837	20339
unique reflns	4162	4041	4240	4034
observed reflns	3664	3049	2896	3075
no. params	295	289	300	321
GOF on F^2	1.060	1.134	1.046	1.068
R_1 [I>2σ(I)]	0.0390	0.0872	0.1028	0.0884
$_wR_2$ [I>2σ(I)]	0.1035	0.1764	0.1512	0.1696

Table S2. Crystal data and structural refinement parameters for crystals **1'** and **3'**.

	1'	**3'**
formula	$C_{34}H_{40}N_2O_{14}S_{12}Zn$	$C_{34}H_{40}MnN_2O_{14}S_{12}$
fw	1150.77	1140.34
cryst size (mm^3)	0.20×0.35×0.45	0.10×0.30×0.40
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	13.956(3)	13.957(3)
b (Å)	10.755(3)	10.7952(19)
c (Å)	15.612(4)	15.701(3)
α (deg)	90.00	90.00
β (deg)	94.237(4)	94.815(4)
γ (deg)	90.00	90.00
V (Å^3)	2336.9(9)	2357.3(7)
Z	2	2
ρ_{calcd} (g cm^{-3})	1.635	1.607
F(000)	1184	1174
μ (mm^{-1})	1.126	0.875
T (K)	293(2)	293(2)
reflns collected	5317	5311
unique reflns	5317	5311
observed reflns	3957	3546
no. params	314	314
GOF on F^2	0.991	0.930
R_1 [$I>2\sigma(I)$]	0.0428	0.0478
$_wR_2$ [$I>2\sigma(I)$]	0.1055	0.1173