Electronic Supplementary Information

Self-doping Inspired Zwitterionic Pendant Design of Radical Polymers toward a Rocking-chair-type Organic Cathode-active Material

By *Il Seok Chae, Masafumi Koyano, Kenichi Oyaizu* and *Hiroyuki Nishide**

Contents:

1. DOSY of **1**, **2** and **1**/**2** (1:1, 1:4 mol. ratio) (**Figure S1**)
2. NOESY NMR for the mixture of PTMA and TBAOH (**Figure S2**)
3. DOSY of **4** (**Figure S3**)
4. Characterization of the radical polymer: ESR and SQUID (**Figure S4, S5**)
5. Cyclic voltammograms and EQCM of PTMA (**Figure S6**)
6. Diffusion coefficient of TEMPO/poly (sodium form vinylsulfonate) aqueous (**Figure S7**)
7. Crystal data for the monomer complex (**Table S1~S8**)

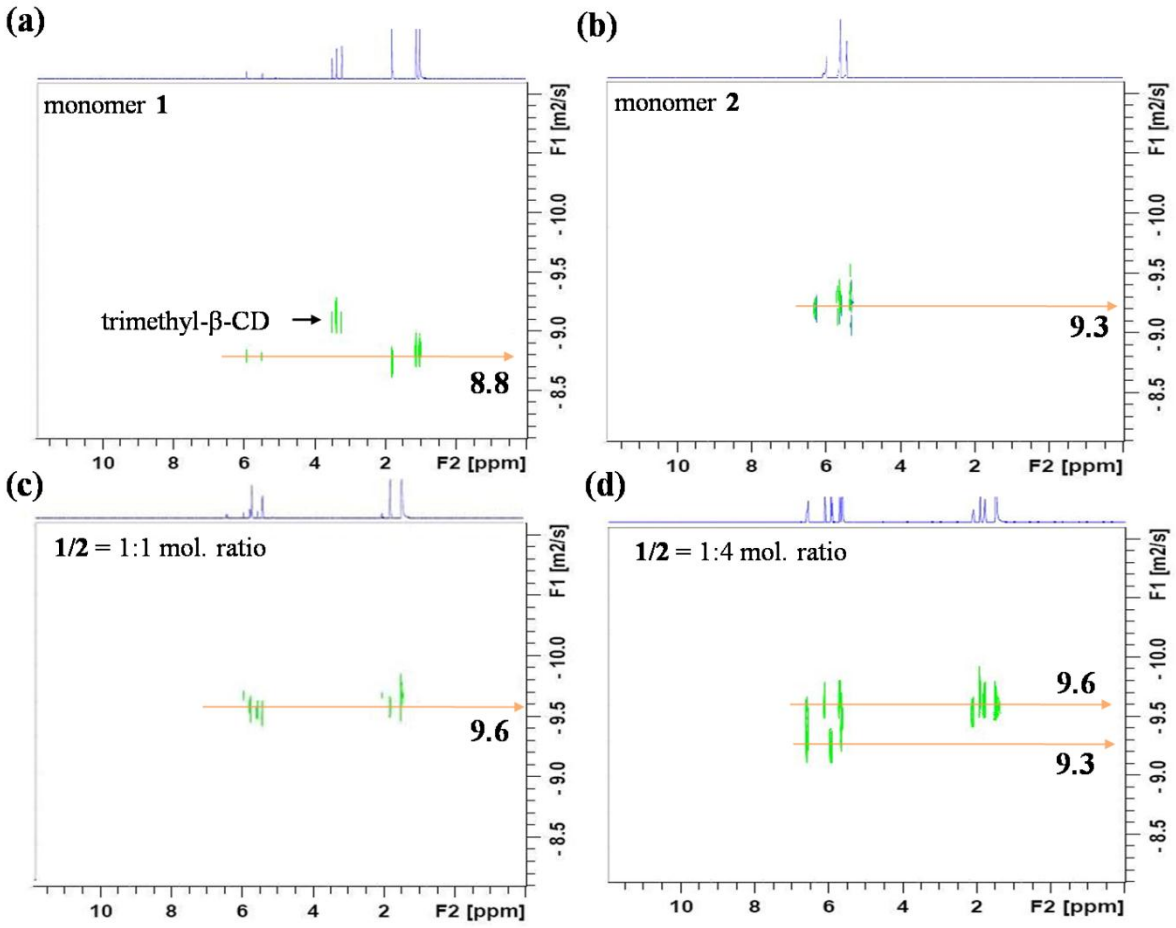

Figure S1. DOSY NMR of monomers in D_2O/MeOH-*d*4 (1/1, v/v). Since **2** could reaction with cyclodextrin compounds, trimethyl-b-cyclodextrin (reference) was only introduced to **1** as shown in (a).

The diffusion coefficient (DC) of **1** and **2** was observed 8.8 and 9.3, respectively. Although the molecular weight of **1** was larger than **2**, the DC of **2** was observed a higher value due to the ionic character ($SO3^-$). In the same mol. ratio of **1**/**2**, the diffusion coefficient of both monomers was increased and had the same DC as shown in (c). This was due to the ionic interaction of **[1^+][2^-].** In the case of 1/2=1:4 (mol. ratio), two DC were observed in (d). The reason was 3 mol ratio of **2** could not complex with **1**. Therefore, the complex form showed the same value of (c), and the others showed the (b).

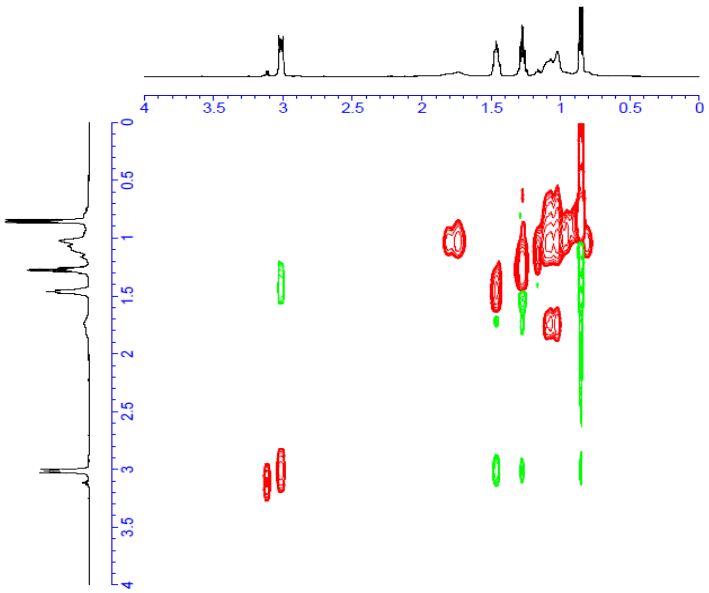

Figure S2. NOESY NMR for the mixture state of PTMA and TBAOH.

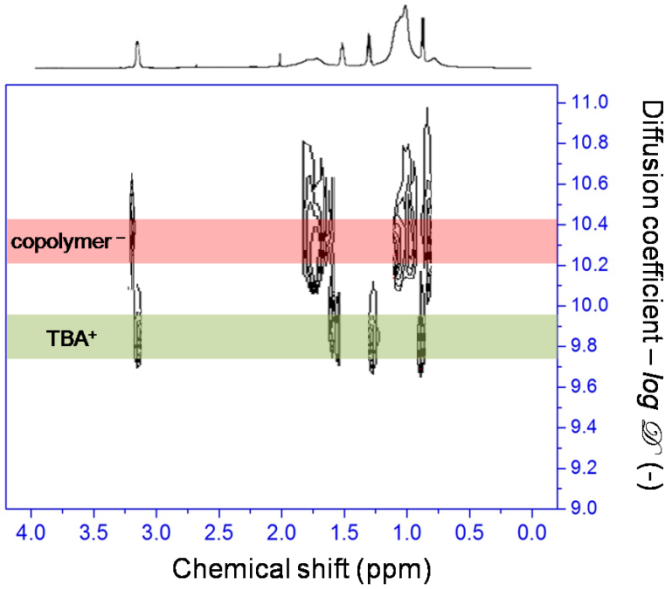

Figure S3. DOSY NMR of the poly(TEMPO-methacrylate-*stat*-TBA form vinyl sulfonate)

4. Characterization of the radical polymer

The TEMPO radical moiety of the **5** was characterized by ESR spectroscopy and SQUID magnetic measurements. The **5** gave a single broad ESR at g = 2.0070 (**Figure S4**) corresponding to that of TEMPO (2.0056). The broadening of the ESR spectrum was due to due to the spin exchange interaction between the unpaired electrons of the neighboring TEMPO radical group.

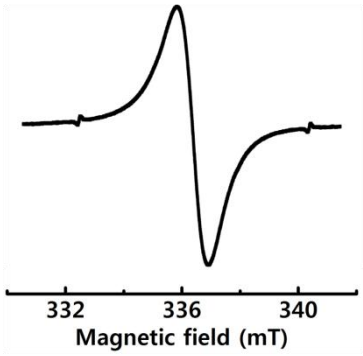

Figure S4. ESR spectrum of **5**

Magnetic susceptibilities of **5** were determined by SQUID measurements at 0.5 T and various temperatures ranging between 1.95 and 300 K. The Curie constant χT at sufficiently high temperatures (i.e. $2J << kT$) corresponded to the value of 0.375 emu K mol-1 calculated for a spin quantum number of S = 1/2, which supported the paramagnetic property of the radical polymers. The deviation of χT to lower values at low temperatures indicated a weak antiferromagnetic interaction within the polymers, as typically shown for **5** (**Figure S4**). The radical concentration was determined from the $1/\chi$ vs. T plots, based on the Curie-Weiss rule according to $1/\chi_{para} = T/C - \theta/C$ Where C is a Curie constant defined as $N_e g^2 \mu_B{}^2 S(S + 1)/(3k)$. The slope of the $1/\chi$ vs. T plots ($1/C$) gave a spin density (N_e) of 2.53 x 10^{21} spin/g for **5** (**Figure S5**), which amounted to 92.3% of the TEMPO unit in the polymer.

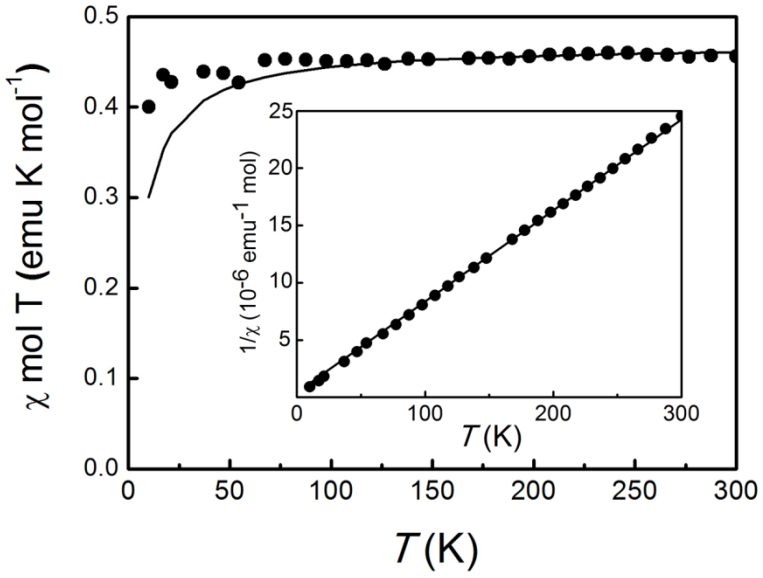

Figure S5. Plots of 1/magnetic susceptibility (22 mg) vs. temperature (Curie-Weiss plots) for **5**. Inset: SQUID measurements.

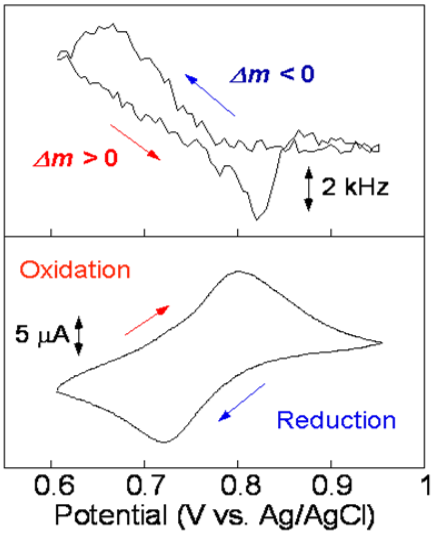

Figure S6. Cyclic voltammograms and EQCM of PTMA in water/MeCN = 1/1 (v/v) with 0.1 M $LiPF_6$.

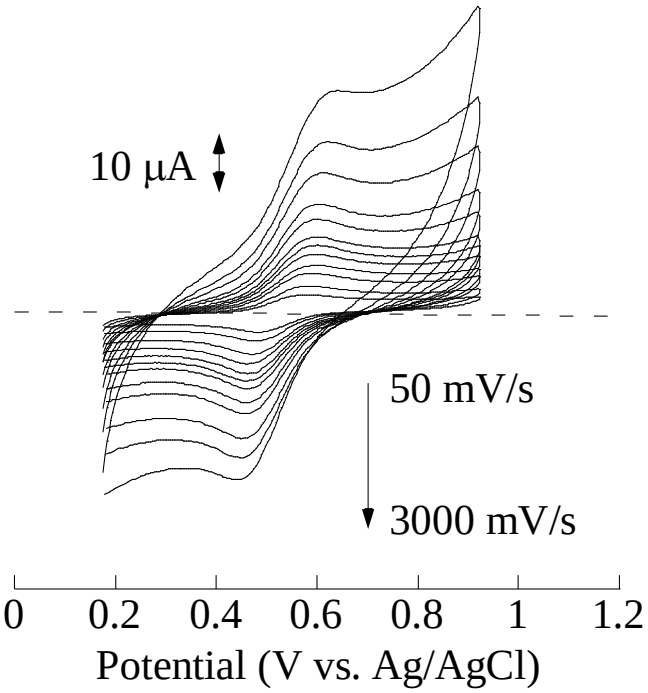

Figure S7. Cyclic voltammograms of 5 mM TEMPO in 0.1 M (unit) PVSA -Na aq at 50-3000 mV/s. Diffusion coefficient and kinetic constant was 9.48 x 10^{-6} cm^2/s and 5.46 x 10^{-3} cm/s respectively.

Table S1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
S1	0.2579(2)	0.9214(1)	1.2105(1)	2.68(4)
O2	0.2630(4)	0.8166(4)	1.1155(3)	3.11(7)
O3	0.2176(6)	0.5018(4)	0.7813(4)	4.43(9)
O4	0.1352(5)	0.9884(4)	1.1512(4)	4.08(8)
O5	0.4282(5)	1.0158(4)	1.2930(4)	4.26(8)
O6	0.1692(7)	0.4394(6)	0.5818(4)	6.8(2)
N7	0.0289(5)	0.8169(4)	0.8686(4)	2.37(7)
C8	0.3430(6)	0.3410(5)	0.7212(5)	2.67(9)
C9	0.1627(6)	0.8566(5)	0.8051(5)	2.60(8)
C10	0.2534(7)	0.7473(5)	0.8103(6)	2.98(9)
C11	0.2378(7)	0.4317(5)	0.6853(5)	3.4(1)
C12	-0.1053(6)	0.6707(5)	0.8294(5)	2.85(9)
C13	-0.2441(7)	0.6462(5)	0.7011(5)	3.4(1)
C14	0.0733(8)	0.8676(6)	0.6727(5)	3.9(1)
C15	-0.0045(8)	0.5676(6)	0.8333(6)	3.6(1)
C16	-0.1888(8)	0.6629(6)	0.9279(6)	3.6(1)
C17	0.2919(7)	1.0008(6)	0.8831(6)	3.5(1)
C18	0.1195(8)	0.5980(6)	0.7595(6)	3.8(1)
C19	0.4229(7)	0.3455(5)	0.8404(6)	3.7(1)
C20	0.1620(7)	0.8262(5)	1.3000(5)	3.5(1)
C21	0.2420(9)	0.8295(7)	1.4163(6)	4.8(2)
C22	0.356(1)	0.2482(7)	0.6167(7)	5.7(2)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}
H7	0.0847	0.8232	0.9432	3.66
H10A	0.3206	0.7494	0.8962	2.93
H10B	0.3119	0.7581	0.7615	3.58
H13A	-0.2818	0.7279	0.6964	4.06
H13B	-0.3454	0.5628	0.6872	4.06
H13C	-0.1945	0.6320	0.6371	4.06
H14A	-0.0084	0.7749	0.6216	4.64
H14B	0.1625	0.9026	0.6371	4.64
H14C	0.0084	0.9324	0.6742	4.64
H15A	0.0593	0.5728	0.9287	3.07
H15B	-0.0908	0.4716	0.8028	4.90
H16A	-0.2435	0.7244	0.9183	2.64
H16B	-0.0971	0.6875	1.0154	3.10
H16C	-0.2665	0.5783	0.9080	5.19
H17A	0.3405	0.9900	0.9667	4.18
H17B	0.3951	1.0331	0.8534	5.48
H17C	0.2335	1.0762	0.8763	3.84
H18	0.0523	0.5857	0.6662	4.63
H19A	0.3352	0.3213	0.8791	4.41
H19B	0.5071	0.4402	0.8833	4.41
H19C	0.4854	0.2783	0.8468	4.41
H20	0.0421	0.7675	1.2607	4.20
H21A	0.3620	0.8869	1.4589	5.72
H21B	0.1806	0.7744	1.4587	5.72
H22A	0.4234	0.1888	0.6344	6.81
H22B	0.2960	0.2487	0.5327	6.81

Table S3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0273(7)	0.0323(7)	0.0416(7)	0.0133(5)	0.0125(5)	-0.0005(5)
O2	0.040(2)	0.045(2)	0.039(2)	0.026(2)	0.015(2)	0.003(2)
O3	0.070(3)	0.054(3)	0.054(3)	0.043(2)	0.021(2)	0.006(2)
O4	0.058(3)	0.049(2)	0.064(3)	0.038(2)	0.025(2)	0.014(2)
O5	0.037(2)	0.054(3)	0.053(3)	0.002(2)	0.014(2)	-0.009(2)
O6	0.112(4)	0.106(4)	0.046(3)	0.089(4)	0.002(3)	-0.006(3)
N7	0.025(2)	0.027(2)	0.034(3)	0.007(2)	0.011(2)	-0.002(2)
C8	0.027(3)	0.026(3)	0.043(3)	0.009(2)	0.009(2)	0.001(2)
C9	0.031(3)	0.029(3)	0.044(3)	0.014(2)	0.020(2)	0.006(2)
C10	0.036(3)	0.042(3)	0.042(3)	0.022(3)	0.016(3)	0.006(3)
C11	0.035(3)	0.041(3)	0.048(3)	0.015(3)	0.013(3)	-0.000(3)
C12	0.031(3)	0.025(3)	0.047(3)	0.008(2)	0.012(2)	-0.002(2)
C13	0.033(3)	0.034(3)	0.048(3)	0.009(2)	0.006(3)	-0.006(2)
C14	0.058(4)	0.062(4)	0.047(3)	0.039(3)	0.028(3)	0.016(3)
C15	0.051(4)	0.029(3)	0.054(4)	0.020(3)	0.011(3)	0.000(3)
C16	0.039(3)	0.036(3)	0.056(4)	0.002(3)	0.021(3)	0.003(3)
C17	0.037(3)	0.035(3)	0.071(4)	0.014(3)	0.030(3)	0.012(3)
C18	0.058(4)	0.042(3)	0.051(4)	0.032(3)	0.020(3)	0.005(3)
C19	0.038(3)	0.033(3)	0.067(4)	0.008(3)	0.021(3)	0.009(3)
C20	0.040(3)	0.040(3)	0.049(3)	0.012(3)	0.019(3)	-0.003(3)
C21	0.067(4)	0.064(4)	0.048(4)	0.016(4)	0.029(3)	0.002(3)
C22	0.087(5)	0.081(5)	0.061(4)	0.066(4)	0.018(4)	0.001(4)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O2	1.459(4)	S1	O4	1.454(5)
S1	O5	1.433(3)	S1	C20	1.747(7)
O3	C11	1.335(8)	O3	C18	1.460(9)
O6	C11	1.185(8)	N7	C9	1.537(8)
N7	C12	1.512(5)	C8	C11	1.475(8)
C8	C19	1.326(8)	C8	C22	1.496(10)
C9	C10	1.527(8)	C9	C14	1.522(8)
C9	C17	1.524(6)	C10	C18	1.532(7)
C12	C13	1.521(7)	C12	C15	1.535(9)
C12	C16	1.528(10)	C15	C18	1.552(11)
C20	C21	1.299(8)			

Table S5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
N7	H7	0.831	C10	H10A	0.976
C10	H10B	0.864	C13	H13A	0.980
C13	H13B	0.980	C13	H13C	0.980
C14	H14A	0.980	C14	H14B	0.980
C14	H14C	0.980	C15	H15A	1.057
C15	H15B	0.986	C16	H16A	0.882
C16	H16B	1.016	C16	H16C	0.878
C17	H17A	0.964	C17	H17B	1.030
C17	H17C	1.029	C18	H18	1.027
C19	H19A	0.980	C19	H19B	0.980
C19	H19C	0.980	C20	H20	0.950
C21	H21A	0.950	C21	H21B	0.950
C22	H22A	0.950	C22	H22B	0.950

Table S6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O2	S1	O4	109.3(3)	O2	S1	O5	113.8(3)
O2	S1	C20	105.3(3)	O4	S1	O5	115.0(3)
O4	S1	C20	105.3(3)	O5	S1	C20	107.3(3)
C11	O3	C18	119.2(5)	C9	N7	C12	120.6(4)
C11	C8	C19	120.6(5)	C11	C8	C22	116.3(5)
C19	C8	C22	123.1(6)	N7	C9	C10	107.6(4)
N7	C9	C14	110.8(4)	N7	C9	C17	104.9(5)
C10	C9	C14	112.9(5)	C10	C9	C17	111.3(4)
C14	C9	C17	109.0(5)	C9	C10	C18	111.5(5)
O3	C11	O6	121.4(6)	O3	C11	C8	113.4(5)
O6	C11	C8	125.1(6)	N7	C12	C13	110.9(4)
N7	C12	C15	107.2(4)	N7	C12	C16	105.3(4)
C13	C12	C15	112.4(5)	C13	C12	C16	110.4(5)
C15	C12	C16	110.4(5)	C12	C15	C18	111.8(5)
O3	C18	C10	107.4(5)	O3	C18	C15	105.5(5)
C10	C18	C15	111.6(5)	S1	C20	C21	125.0(5)

Table S7. Bond angles involving hydrogens (º)

atom	atom	atom	angle	atom	atom	atom	angle
C9	N7	H7	107.7	C12	N7	H7	102.0
C9	C10	H10A	111.4	C9	C10	H10B	108.0
C18	C10	H10A	103.9	C18	C10	H10B	106.0
H10A	C10	H10B	115.8	C12	C13	H13A	109.5
C12	C13	H13B	109.5	C12	C13	H13C	109.5
H13A	C13	H13B	109.5	H13A	C13	H13C	109.5
H13B	C13	H13C	109.5	C9	C14	H14A	109.5
C9	C14	H14B	109.5	C9	C14	H14C	109.5
H14A	C14	H14B	109.5	H14A	C14	H14C	109.5
H14B	C14	H14C	109.5	C12	C15	H15A	106.2
C12	C15	H15B	108.2	C18	C15	H15A	114.7
C18	C15	H15B	112.9	H15A	C15	H15B	102.3
C12	C16	H16A	103.8	C12	C16	H16B	111.8
C12	C16	H16C	107.3	H16A	C16	H16B	111.5
H16A	C16	H16C	109.4	H16B	C16	H16C	112.6
C9	C17	H17A	106.2	C9	C17	H17B	111.2
C9	C17	H17C	111.8	H17A	C17	H17B	107.0
H17A	C17	H17C	114.4	H17B	C17	H17C	106.2
O3	C18	H18	112.0	C10	C18	H18	107.8
C15	C18	H18	112.6	C8	C19	H19A	109.5
C8	C19	H19B	109.5	C8	C19	H19C	109.5
H19A	C19	H19B	109.5	H19A	C19	H19C	109.5
H19B	C19	H19C	109.5	S1	C20	H20	117.5
C21	C20	H20	117.5	C20	C21	H21A	120.0
C20	C21	H21B	120.0	H21A	C21	H21B	120.0
C8	C22	H22A	120.0	C8	C22	H22B	120.0
H22A	C22	H22B	120.0				

Table S8. Torsion Angles(°)
(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O2	S1	C20	C21	113.5(5)	O4	S1	C20	C21	-131.1(5)
O5	S1	C20	C21	-8.1(6)	C11	O3	C18	C10	-105.8(5)
C11	O3	C18	C15	135.1(4)	C18	O3	C11	O6	-4.6(7)
C18	O3	C11	C8	178.6(4)	C9	N7	C12	C13	-71.3(6)
C9	N7	C12	C15	51.8(5)	C9	N7	C12	C16	169.3(4)
C12	N7	C9	C10	-52.2(5)	C12	N7	C9	C14	71.7(5)
C12	N7	C9	C17	-170.8(4)	C19	C8	C11	O3	-7.1(7)
C19	C8	C11	O6	176.2(5)	C22	C8	C11	O3	174.0(5)
C22	C8	C11	O6	-2.7(8)	N7	C9	C10	C18	51.9(5)
C14	C9	C10	C18	-70.7(6)	C17	C9	C10	C18	166.3(5)
C9	C10	C18	O3	-173.7(5)	C9	C10	C18	C15	-58.6(6)
N7	C12	C15	C18	-51.5(5)	C13	C12	C15	C18	70.6(5)
C16	C12	C15	C18	-165.7(3)	C12	C15	C18	O3	174.7(3)
C12	C15	C18	C10	58.5(5)					