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Conformational effect of symmetrical squaraine dyes on the performance of dye-sensitized solar cells

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1. X-ray structure determination

Crystallographic data for **SQM1a**: $C_{39}H_{40}N_4O_6$, A black prism crystal having crystal dimensions of 0.15 × 0.10 × 0.08 mm^3, M = 660.77, triclinic, a = 10.684(8), b = 13.943(9), c = 15.095(11) Å, α = 105.332(9)°, β = 110.321(6)°, γ = 93.504(11)°, V = 2004(2) Å^3, space group P-1, Z = 2, ρ = 1.095 g cm^{-3}, μ(Mo-Kα) = 0.744 cm^{-1}, F(000) = 700.0. Reflection data ($2\theta < 62.1°$) were collected on a Rigaku Mercury CCD area detecter at 296 K with a graphite monochromated Mo-Kα radiation (λ = 0.71070 Å). Of the 18394 reflections that were collected, 10774 were unique (R_{int} = 0.046); equivalent reflections were merged. A numerical absorption correction was applied which resulted in transmission factors ranging from 0.989 to 0.994. Lorentz and polarization corrections were applied. The structure was solved by a direct methods using the SIR92 program,[1] expanded using the DIRDIF99 program.[2] The final cycle of full-matrix least-squares refinement on F was based on 3587 observed reflections ($I > 1.50\sigma(I)$) and 480 variable parameters and converged to R_1 = 0.1127, wR_2 = 0.0980 and GOF = 1.202. One oxygen atom (O6) was found from the Fourier synthesis and may correspond to a water molecule from the solvent or environment used in the preparation of single crystals. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All the calculations were performed using the CrystalStructure 3.8 software package of the Molecular Structure Corporation.[3] Full crystallographic details excluding structure factors have been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC-901550 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

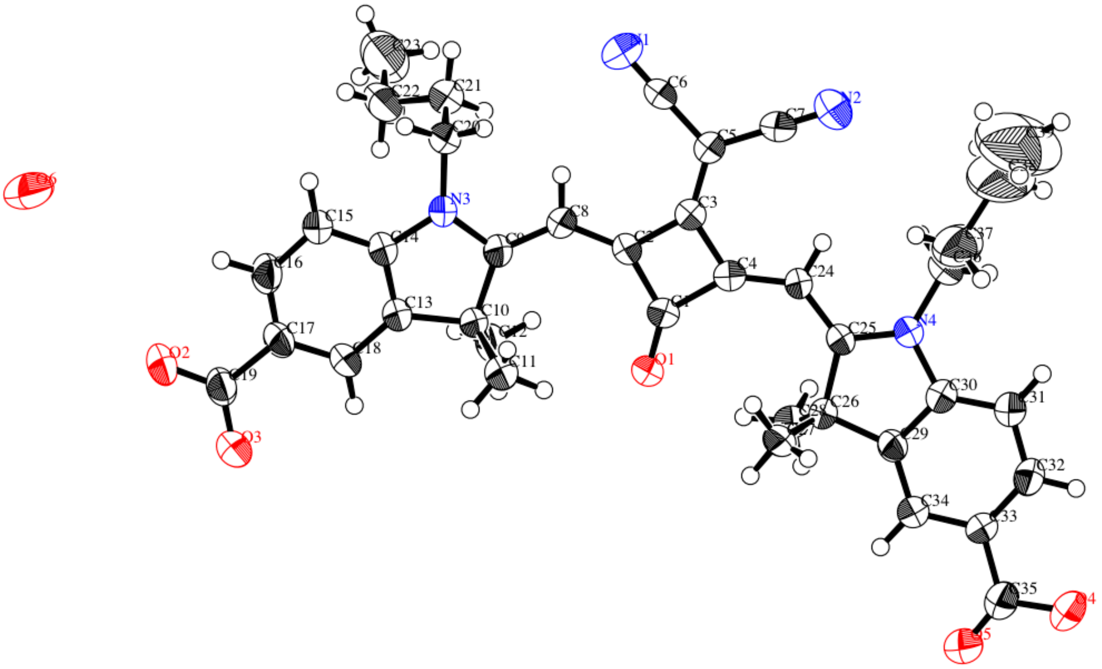

Fig. S1 An ORTEP drawing of **SQM1a**. Thermal ellipsoids are set at the 50% probability level.

2. DFT Calculationd of SQM1a-b and MSQ

The ground-state geometries of **SQM1a-b** and **MSQ** were optimized in the gas phase by DFT calculations with the Gaussian 09 program (**Fig. 6**).[4] The calculations were performed on the models in which the butyl substituents have been replaced by methyl groups with the B3LYP exchange-correlation functional under a 6-31G(d) basis set. The time-dependent DFT (TD-DFT) calculations were performed to calculate the compositions in terms of molecular orbital contributions based on their corresponding optimized geometries calculated at theB3LYP/6-31G(d) level. In TDDFT calculations, the lowest 4 singlet-singlet excitations were calculated (**Table S1**). The calculation for **MSQ** showed only a transition with higher ocillator strength (f = 1.5) characterized to HOMO-LUMO excitation.

Table S1. Calculated lowest exited energies (E), oscillator strengths (f), and composition in terms of molecular orbital contributions.

Dye	E (eV)	f	Composition[b]
SQM1a	1.83	0.56	H–1 → L (16%), H → L (69%)
	2.79	1.06	H–1 → L (69%)
SQM1b	1.88	0.55	H–1 → L (17%), H → L (69%)
	2.83	0.99	H–1 → L (68%)
MSQ	2.27	1.47	H → L (71%)

[a] n is the ordering number of the calculated excited state. [b] H = HOMO, L = LUMO

3. Absroption spectra of SQM1a-b immobilized on TiO_2

Absorption spectra of the dyes imobilized on TiO_2 were measured using TiO_2 thin films (5 μm-thickness) prepared from a nanocrystalline TiO_2 paste (PST-18NR) (**Fig. S2**). The TiO_2 films were immersed in the dye bath including dyes (0.12 mM) and chenodeoxycholic acid (6.0 mM) in *t*-BuOH/acetonitril (1/1 (v/v)) and then kept for given time at room temperature. The resulting films were washed with acetonitrile to remove non-adsorbed dyes.

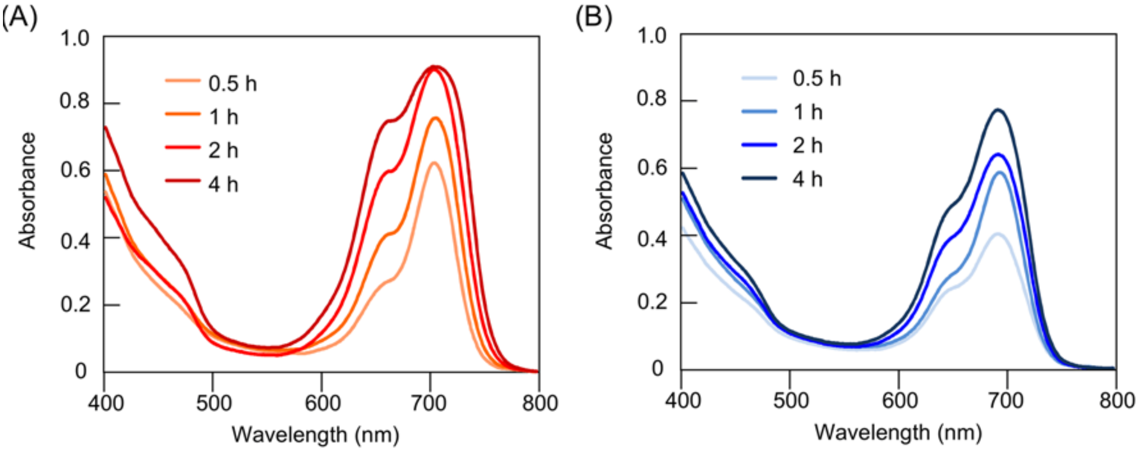

Fig. S2 Absorption spectra of **SQM1a** (A) and **SQM1b** (B) immobilized on TiO_2 (5 μm-thickness) with the change of immersion time.

4. NMR and MS Spectra

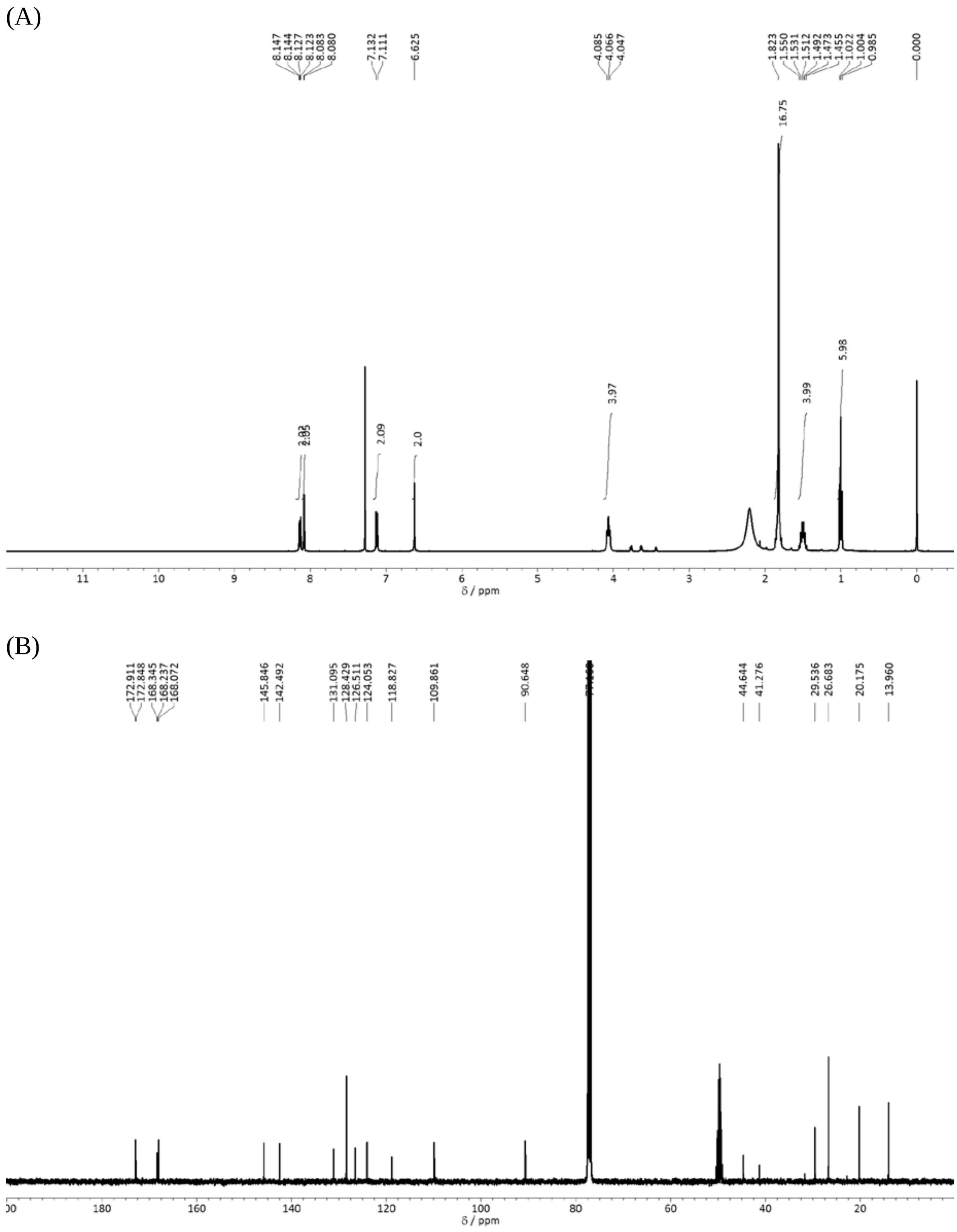

Fig. S3 ^{1}H-NMR (400 MHz, 25 ºC) spectrum (A), and ^{13}C-NMR (400 MHz, 25 ºC) spectrum (B) of **SQM1a** in $CDCl_3$-CD_3OD (16/1(v/v)).

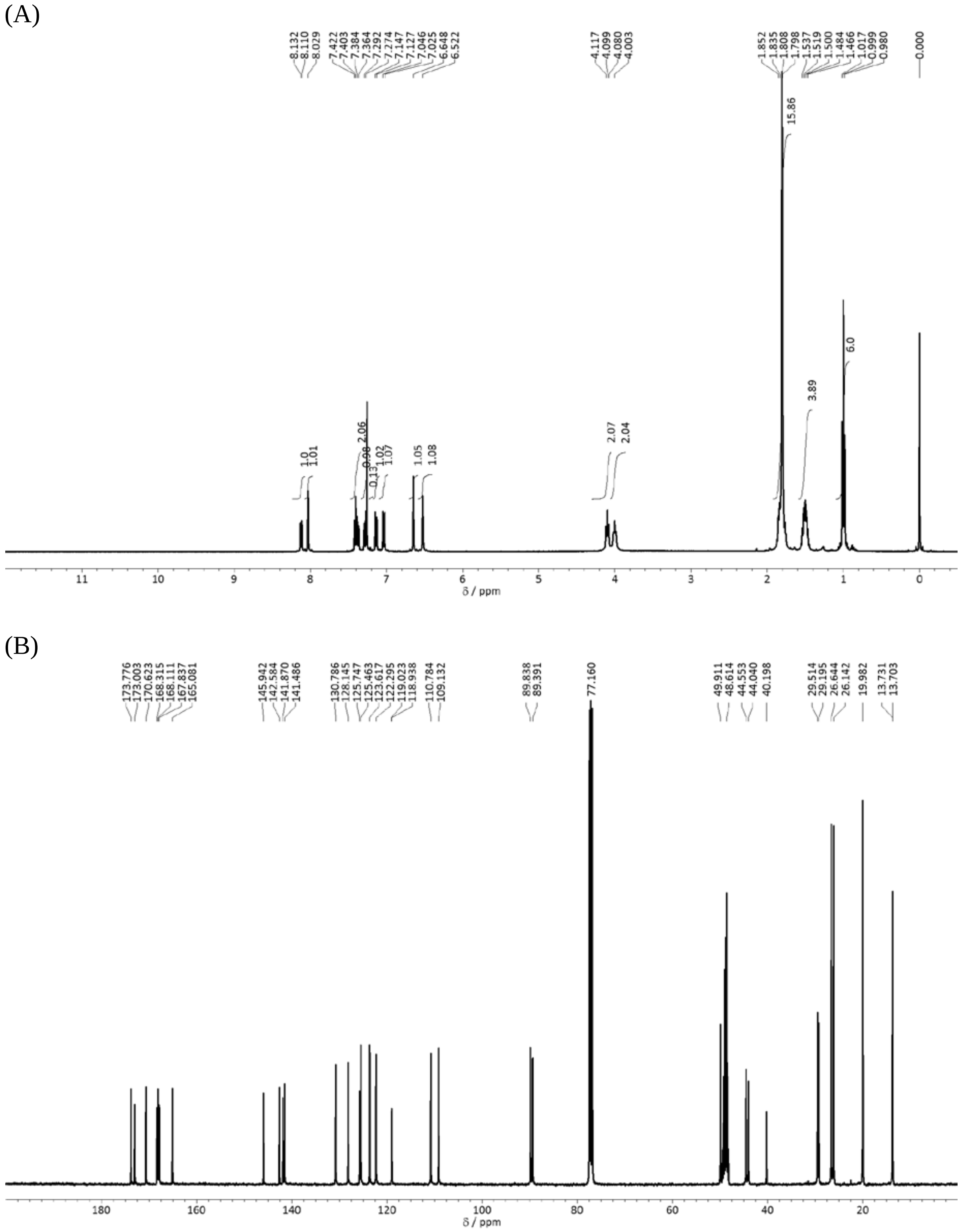

Fig. S4 ^{1}H-NMR [400 MHz, 25 ºC, $CDCl_3$] spectrum (A) and ^{13}C-NMR [400 MHz, 25 ºC, $CDCl_3$-CD_3OD (16/1(v/v))] spectrum (B) of **SQM1b**.

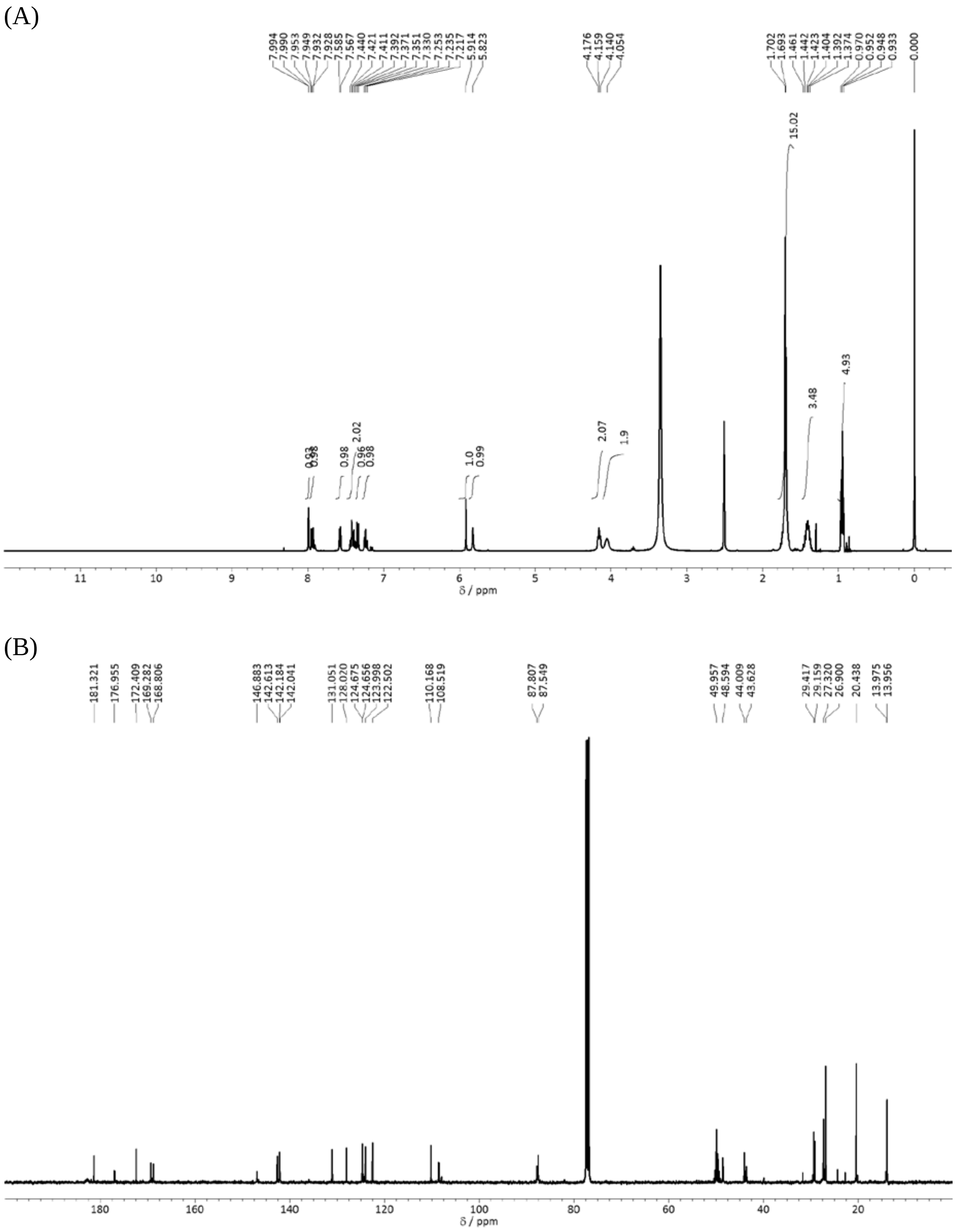

Fig. S5 ^{1}H-NMR [400 MHz, 25 ºC, DMSO-d_6] spectrum (A) and ^{13}C-NMR [400 MHz, 25 ºC, $CDCl_3$-CD_3OD (16/1(v/v))] spectrum (B) of **MSQ**.

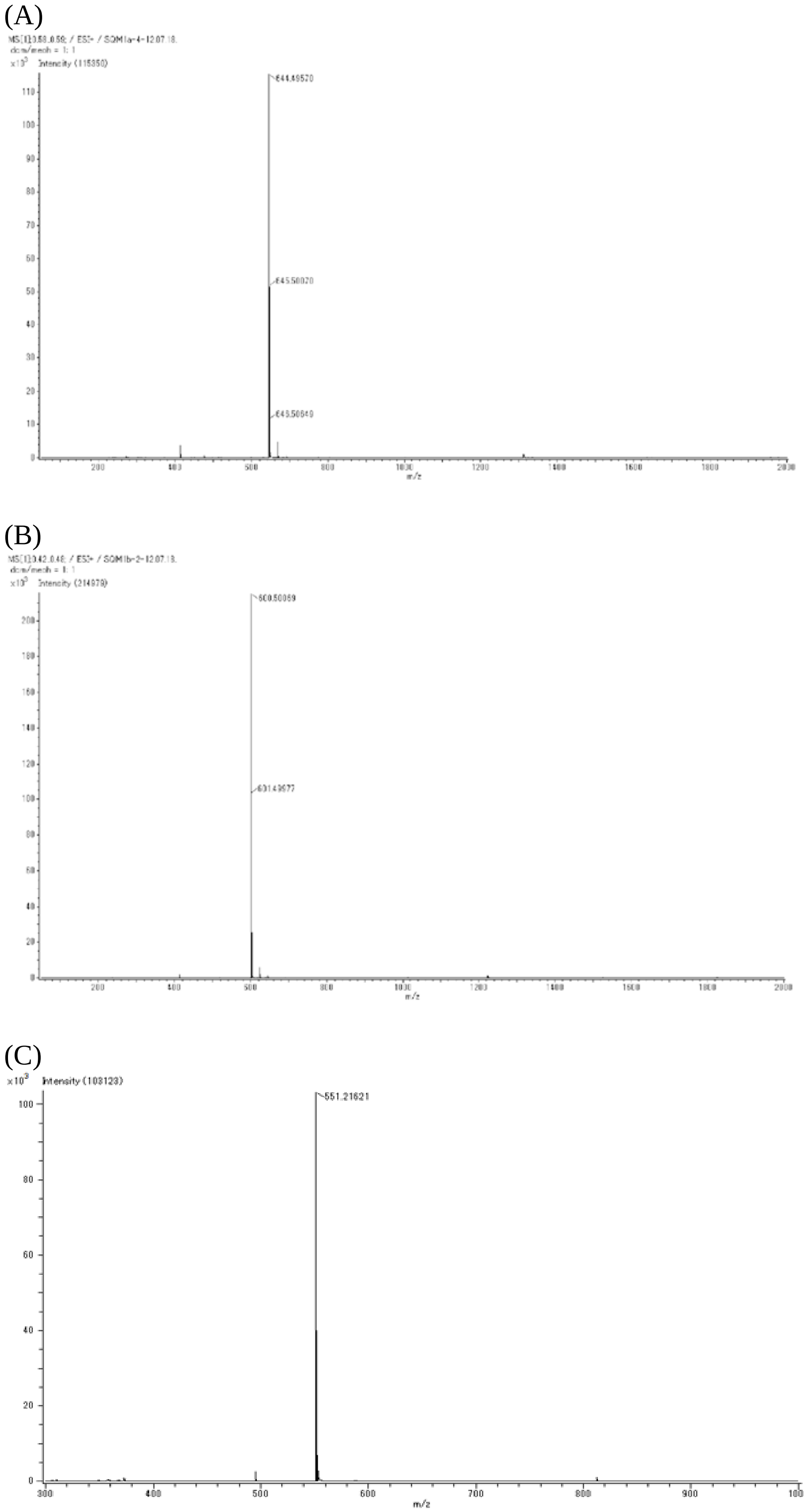

Fig. S6 ESI-Mass spectra of **SQM1a** (A), **SQM1b** (B), and **MSQ** (C).

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