Electronic Supplementary Information for:

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

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Table of Contents

1. X-ray Structure Determination ................................................................. S1
2. DFT calculations of SQM1a-b and MSQ ...................................................... S3
3. Absorption spectra of SQM1a-b immobilized on TiO2 .................................. S4
4. NMR and MS spectra ................................................................................. S5

References
1. X-ray structure determination

Crystallographic data for SQM1a: C_{39}H_{40}N_{4}O_{6}, A black prism crystal having crystal dimensions of 0.15 × 0.10 × 0.08 mm³, \( M = 660.77 \), triclinic, \( a = 10.684(8) \), \( b = 13.943(9) \), \( c = 15.095(11) \) Å, \( \alpha = 105.332(9)^\circ \), \( \beta = 110.321(6)^\circ \), \( \gamma = 93.504(11)^\circ \), \( V = 2004(2) \) Å³, space group \( P-1 \), \( Z = 2 \), \( \rho = 1.095 \) g cm⁻³, \( \mu(\text{Mo-K}\alpha) = 0.744 \) cm⁻¹, \( F(000) = 700.0 \). Reflection data (\( 2\theta < 62.1^\circ \)) were collected on a Rigaku Mercury CCD area detector at 296 K with a graphite monochromated Mo-K\( \alpha \) radiation (\( \lambda = 0.71070 \) Å). Of the 18394 reflections that were collected, 10774 were unique (\( R_{\text{int}} = 0.046 \)); 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 Calculation 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). 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 the B3LYP/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 oscillator strength ($f = 1.5$) characterized to HOMO-LUMO excitation.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$E$ (eV)</th>
<th>$f$</th>
<th>Composition$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQM1a</td>
<td>1.83</td>
<td>0.56</td>
<td>H–1 → L (16%), H → L (69%)</td>
</tr>
<tr>
<td></td>
<td>2.79</td>
<td>1.06</td>
<td>H–1 → L (69%)</td>
</tr>
<tr>
<td>SQM1b</td>
<td>1.88</td>
<td>0.55</td>
<td>H–1 → L (17%), H → L (69%)</td>
</tr>
<tr>
<td></td>
<td>2.83</td>
<td>0.99</td>
<td>H–1 → L (68%)</td>
</tr>
<tr>
<td>MSQ</td>
<td>2.27</td>
<td>1.47</td>
<td>H → L (71%)</td>
</tr>
</tbody>
</table>

$^a$ $n$ is the ordering number of the calculated excited state. $^b$ H = HOMO, L = LUMO.
3. Absorption spectra of SQM1a-b immobilized on TiO$_2$

Absorption spectra of the dyes immobilized 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 °C) spectrum (A), and $^{13}$C-NMR (400 MHz, 25 °C) spectrum (B) of SQM1a in CDCl$_3$-CD$_3$OD (16/1(v/v)).
**Fig. S4** $^1$H-NMR [400 MHz, 25 °C, CDCl$_3$] spectrum (A) and $^{13}$C-NMR [400 MHz, 25 °C, CDCl$_3$-CD$_3$OD (16/1(v/v))] spectrum (B) of SQM1b.
Fig. S5 $^1$H-NMR [400 MHz, 25 °C, DMSO-$d_6$] spectrum (A) and $^{13}$C-NMR [400 MHz, 25 °C, CDCl$_3$-CD$_3$OD (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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