Electronic Supplementary Information for

Effects of Alkyl Chain Substitution on Crystal Structure of Benzothiazole-derived Squarylium Dyes

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Outline

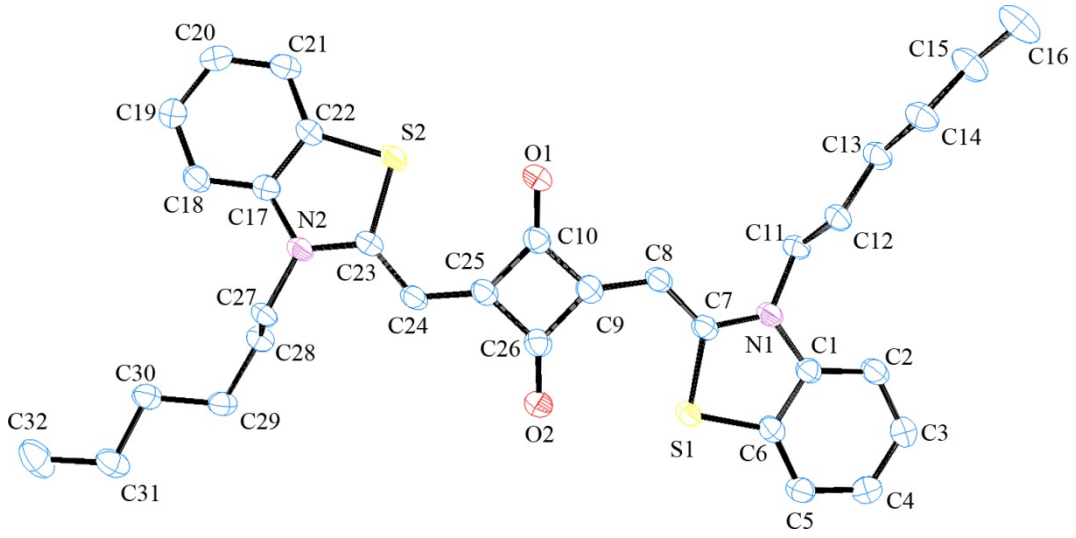

Figure S1. ORTEP view of SQ6 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity).

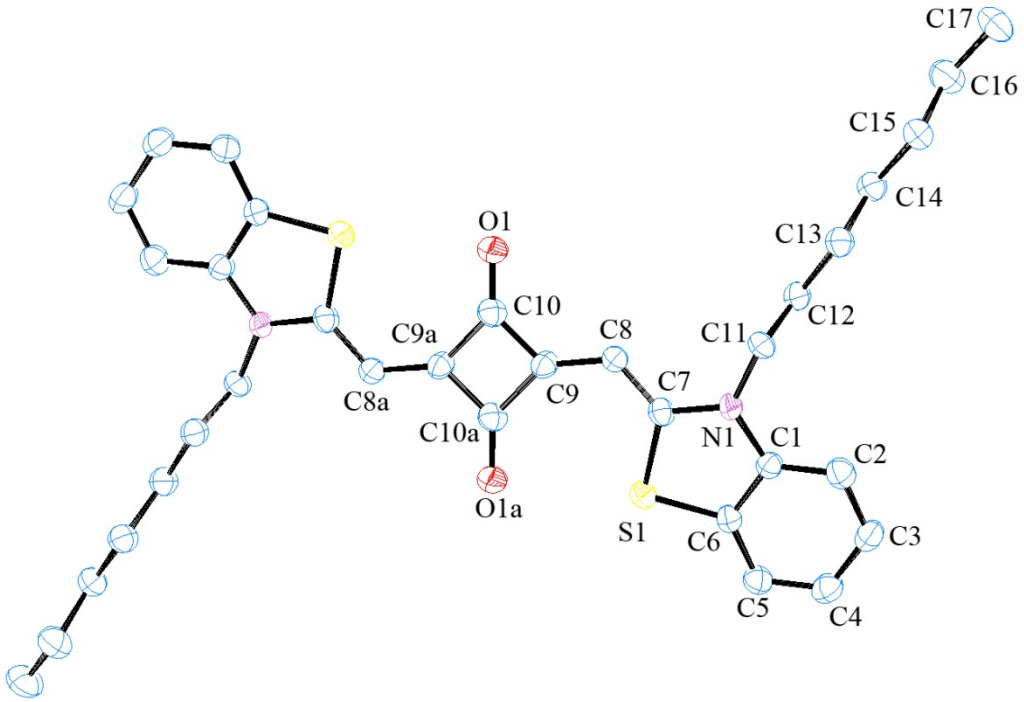

Figure S2. ORTEP view of SQ7 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity).Symmetry code; a = 2 − *x*, 1 − *y*, −*z*

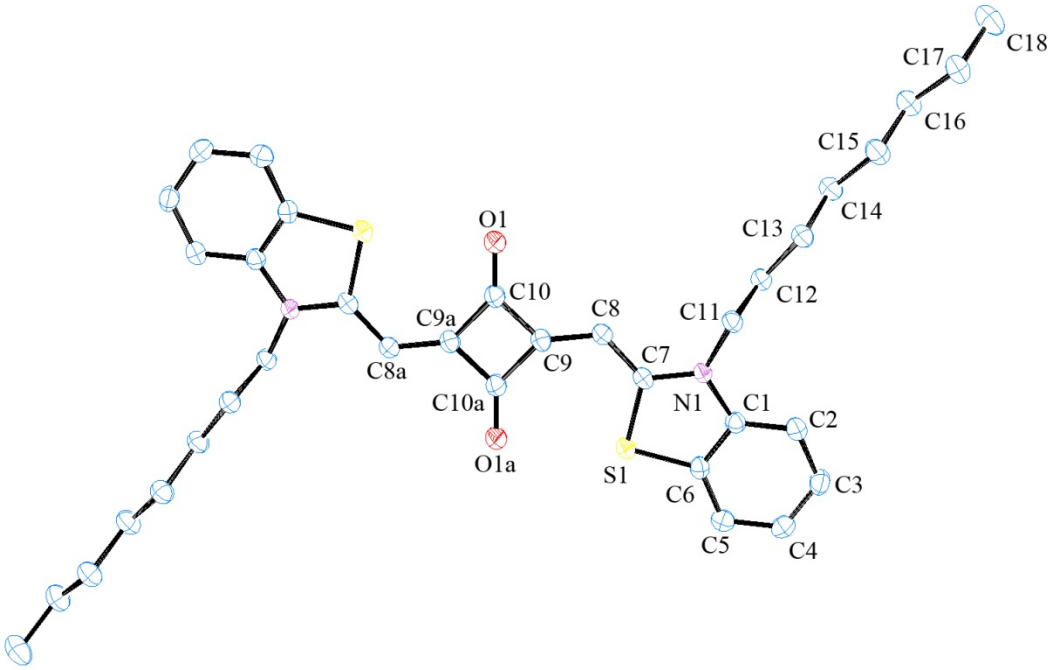

Figure S3. ORTEP view of SQ8 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity).Symmetry code; a = 2 − *x*, 1 − *y*, −*z*

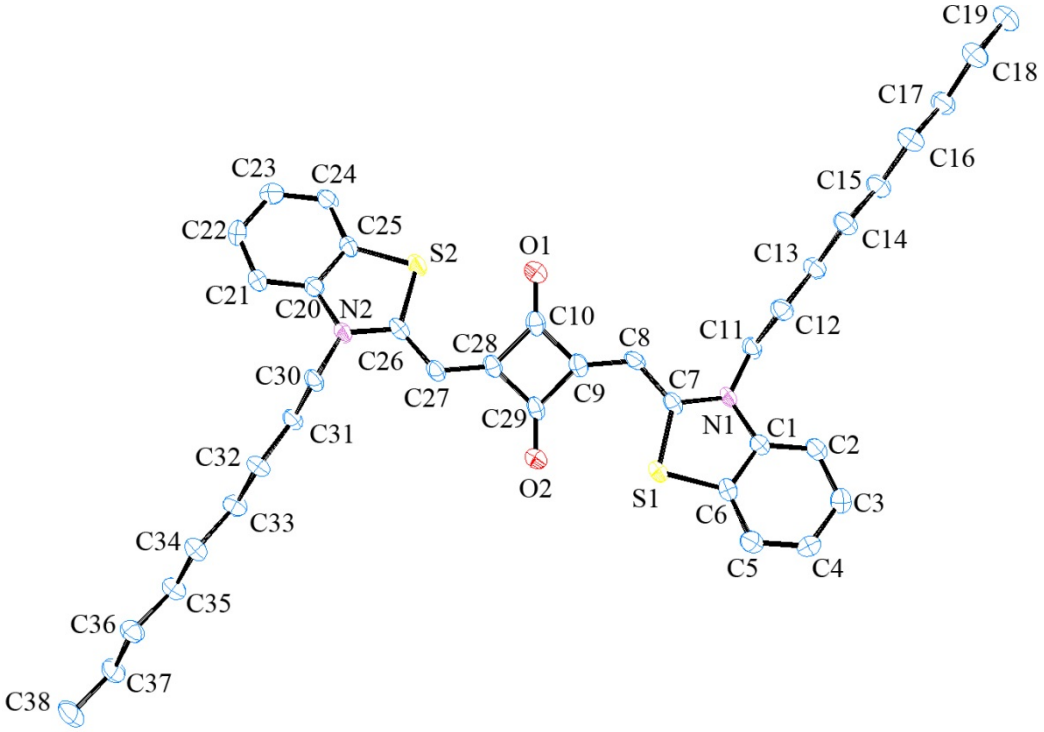

Figure S4. ORTEP view of SQ9 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity).

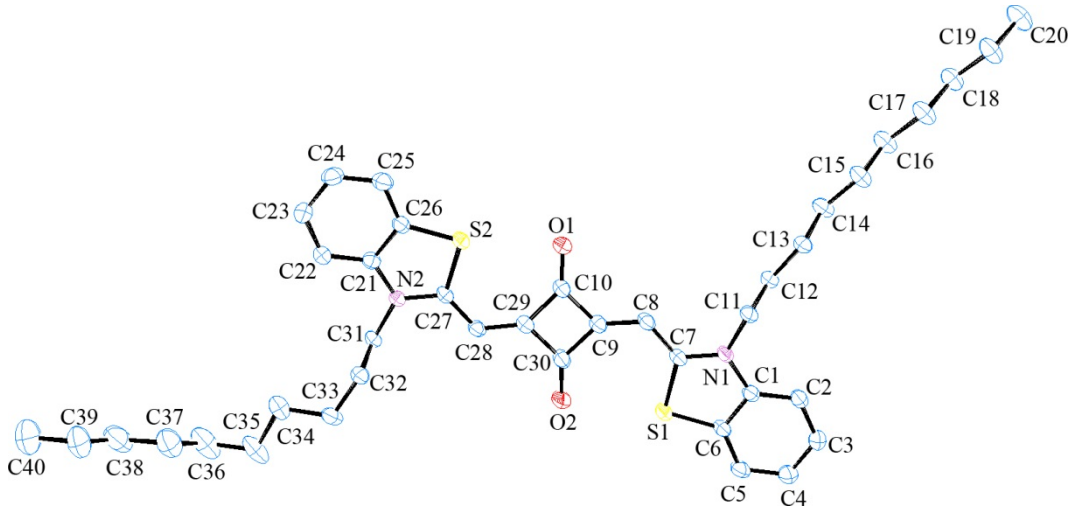

Figure S5. ORTEP view of SQ10 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity).

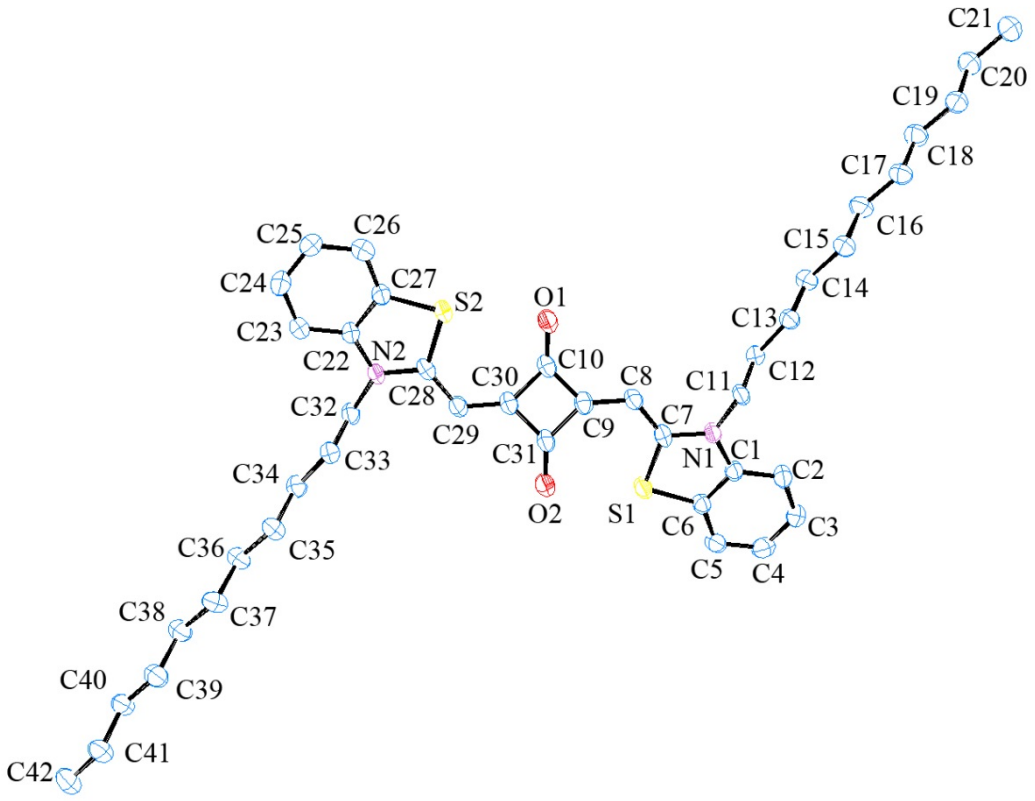

Figure S6. ORTEP view of SQ11 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity).

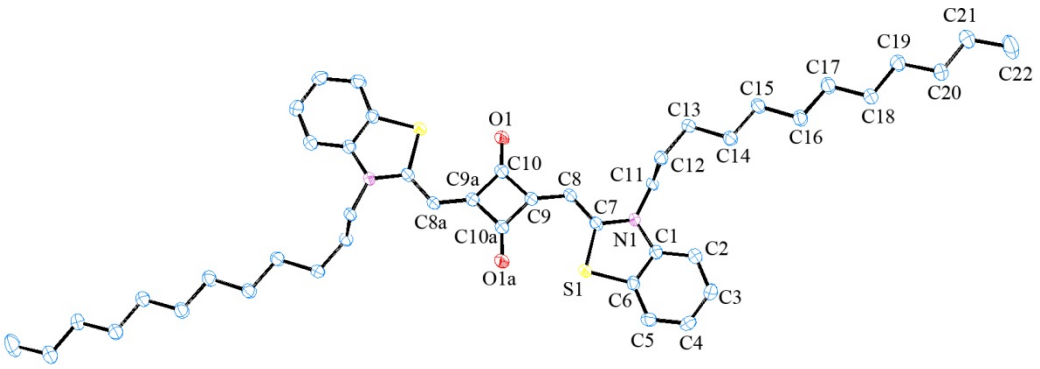

Figure S7. ORTEP view of SQ12 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity). Symmetry code; a = −1 − *x*, 3 − *y*, −*z*

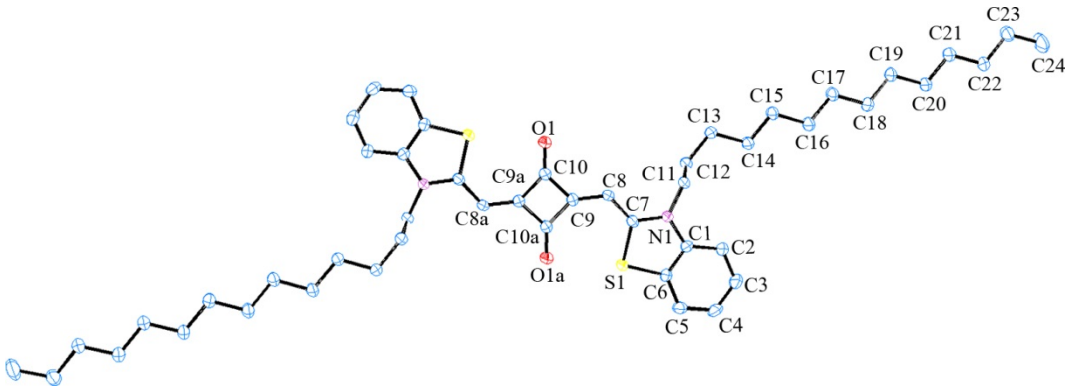

Figure S8. ORTEP view of SQ14 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity). Symmetry code; a = 3 − *x*, 3 − *y*, 1 – *z*

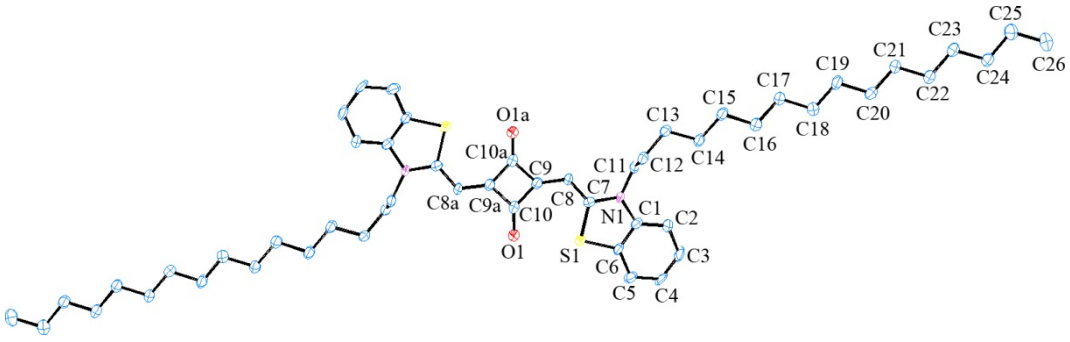

Figure S9. ORTEP view of SQ16 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity). Symmetry code; a = 4 − *x*, −1 − *y*, 1 – *z*

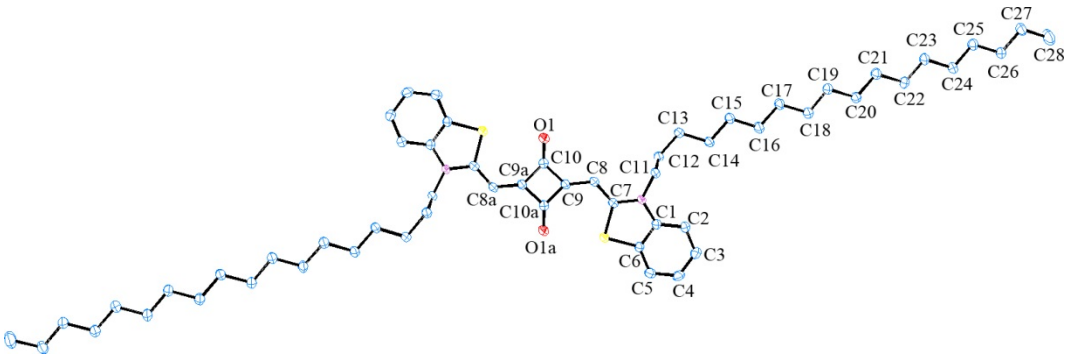

Figure S10. ORTEP view of SQ18 showing 50% probability ellipsoids and the atom-numbering scheme (H atoms were omitted for clarity). Symmetry code; a = −2 − *x*, −1 − *y*, 1 – *z*

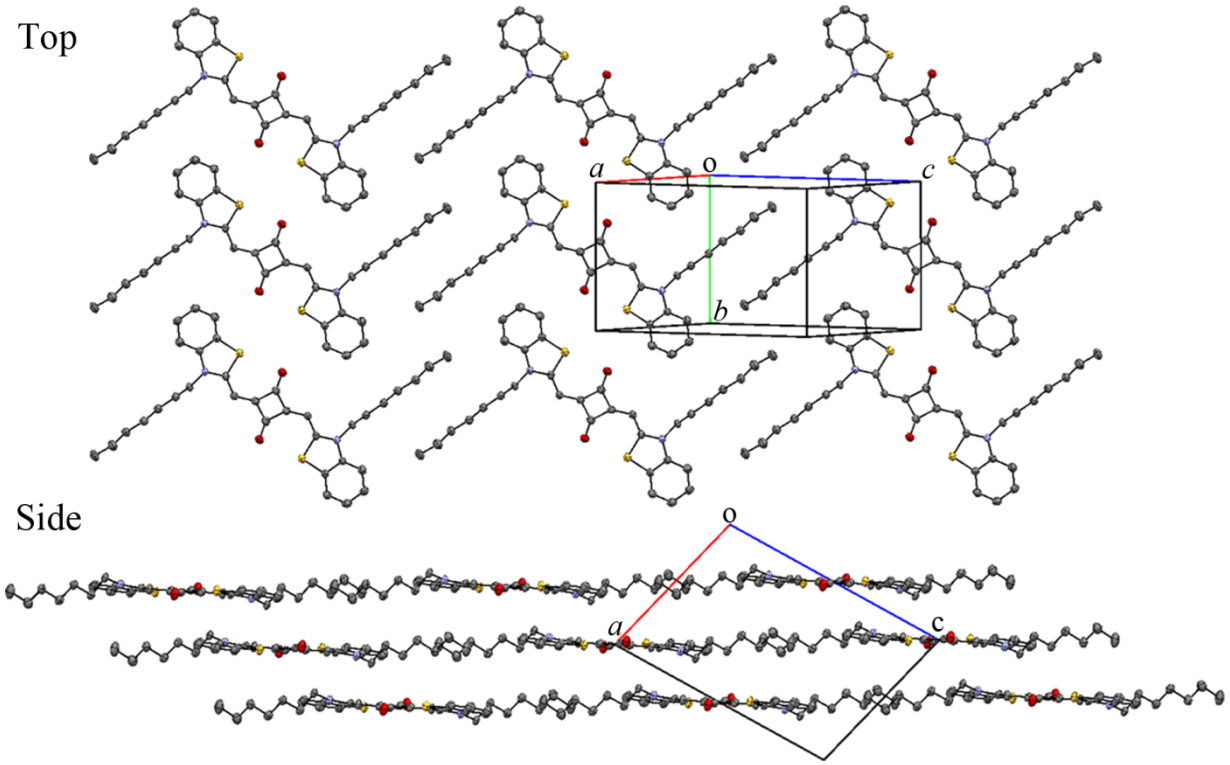

Figure S11. Monolayer and side views of packing structure in SQ07 (type II). The nearest Miller index is (101) for the monolayer. Hydrogen atoms were omitted for clarity.

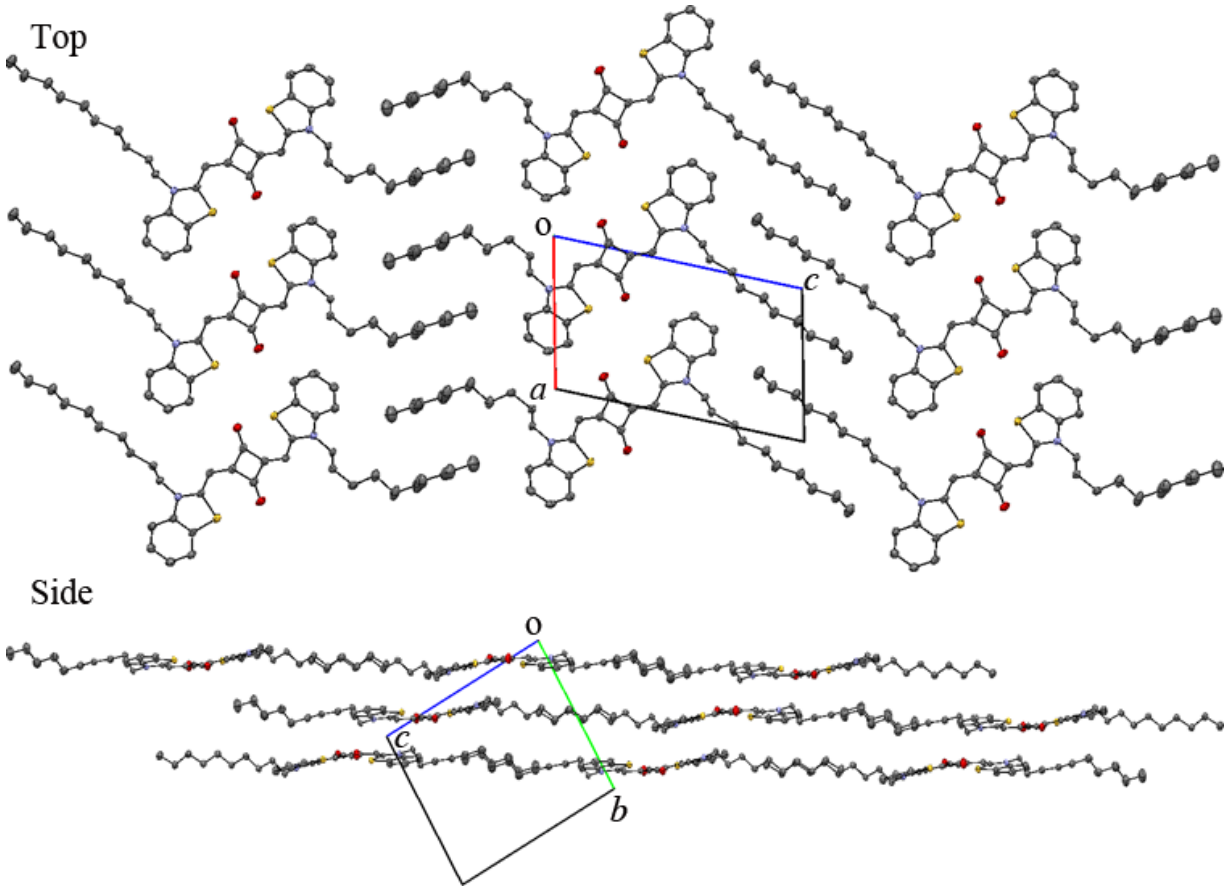

Figure S12. Monolayer and side views of packing structure in SQ10 (type III). The nearest Miller index is (064) for the monolayer. Hydrogen atoms were omitted for clarity.

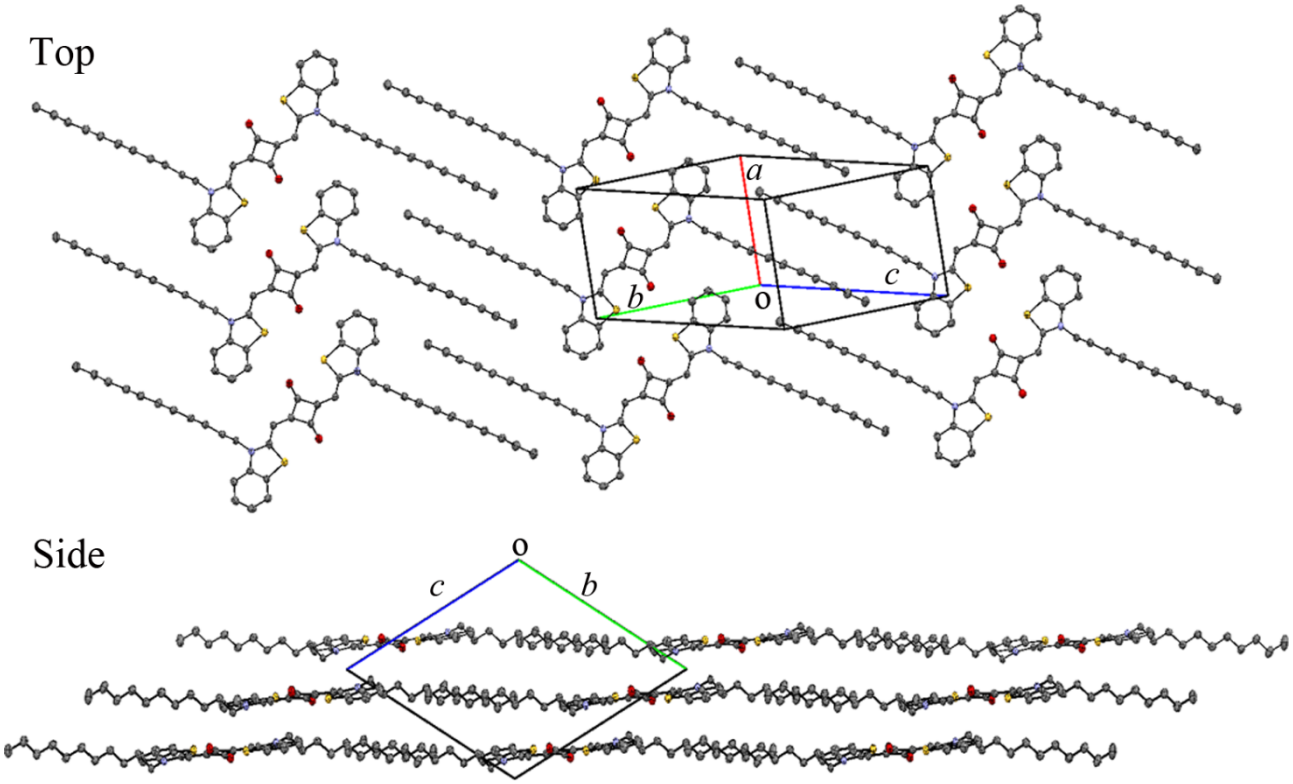

Figure S13. Monolayer and side views of packing structure in SQ11 (type III). The nearest Miller index is (044) for the monolayer. Hydrogen atoms were omitted for clarity.

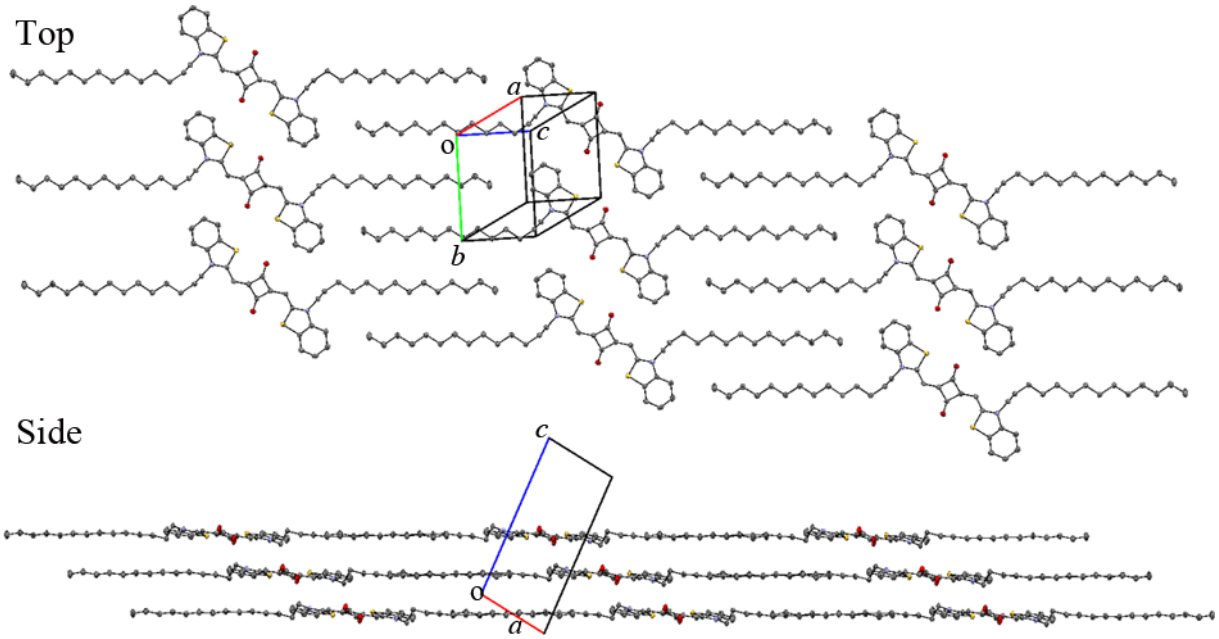

Figure S14. Monolayer and side views of packing structure in SQ14 (type IV). The nearest Miller index is (-208) for the monolayer. Hydrogen atoms were omitted for clarity.

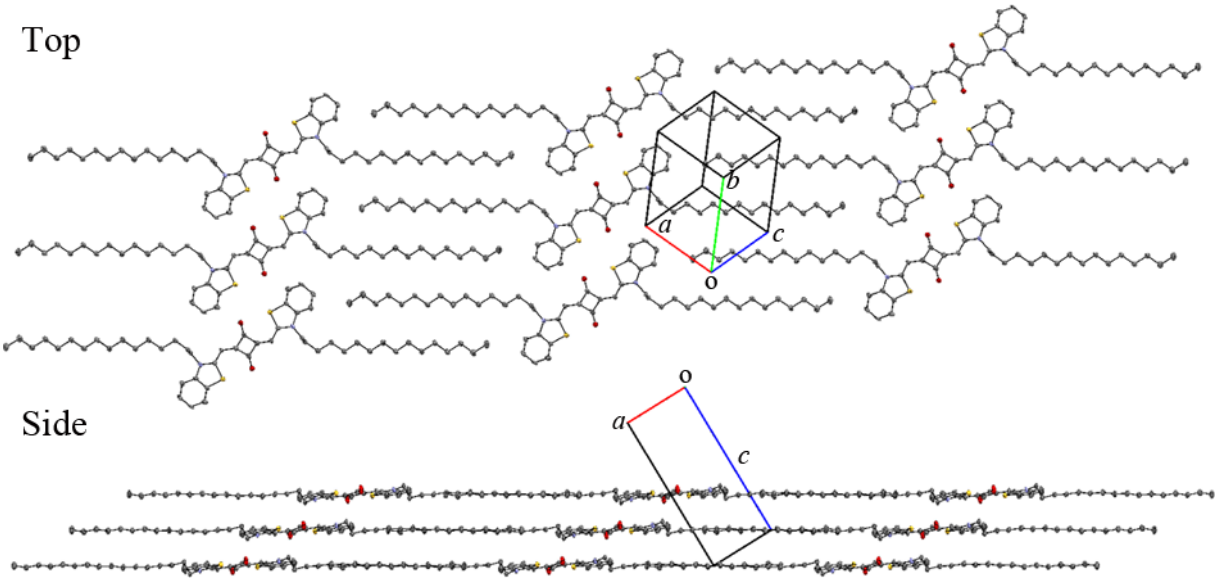

Figure S15. Monolayer and side views of packing structure in SQ16 (type IV). The nearest Miller index is (104) for the monolayer. Hydrogen atoms were omitted for clarity.

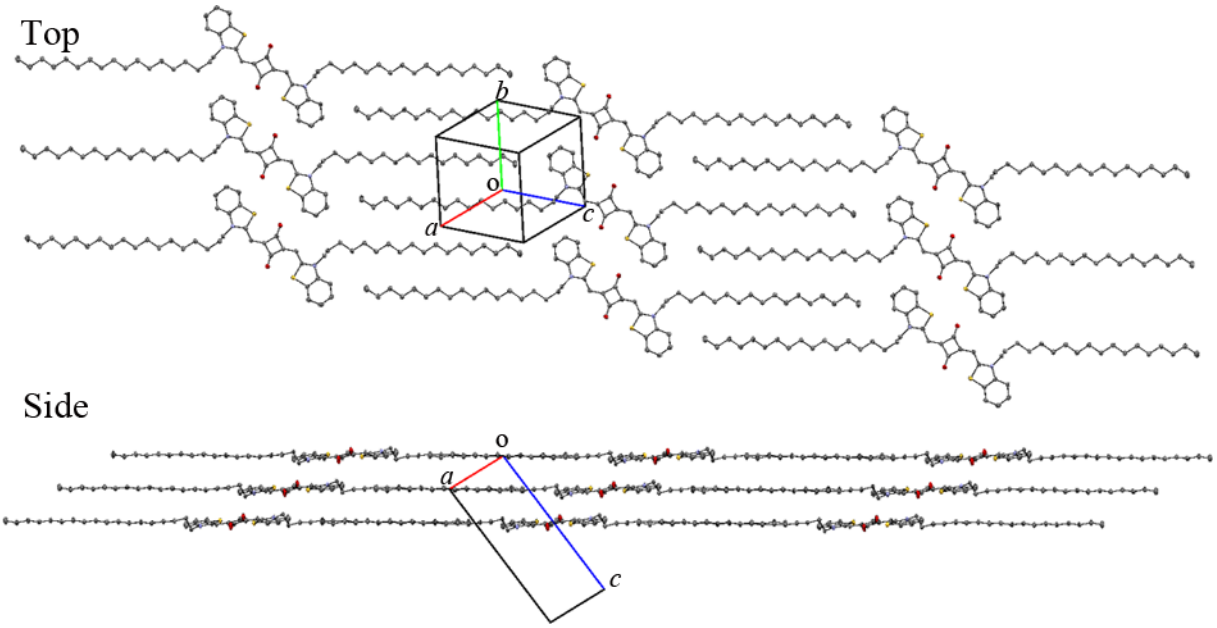

Figure S16. Monolayer and side views of packing structure in SQ18 (type IV). The nearest Miller index is (104) for the monolayer. Hydrogen atoms were omitted for clarity.

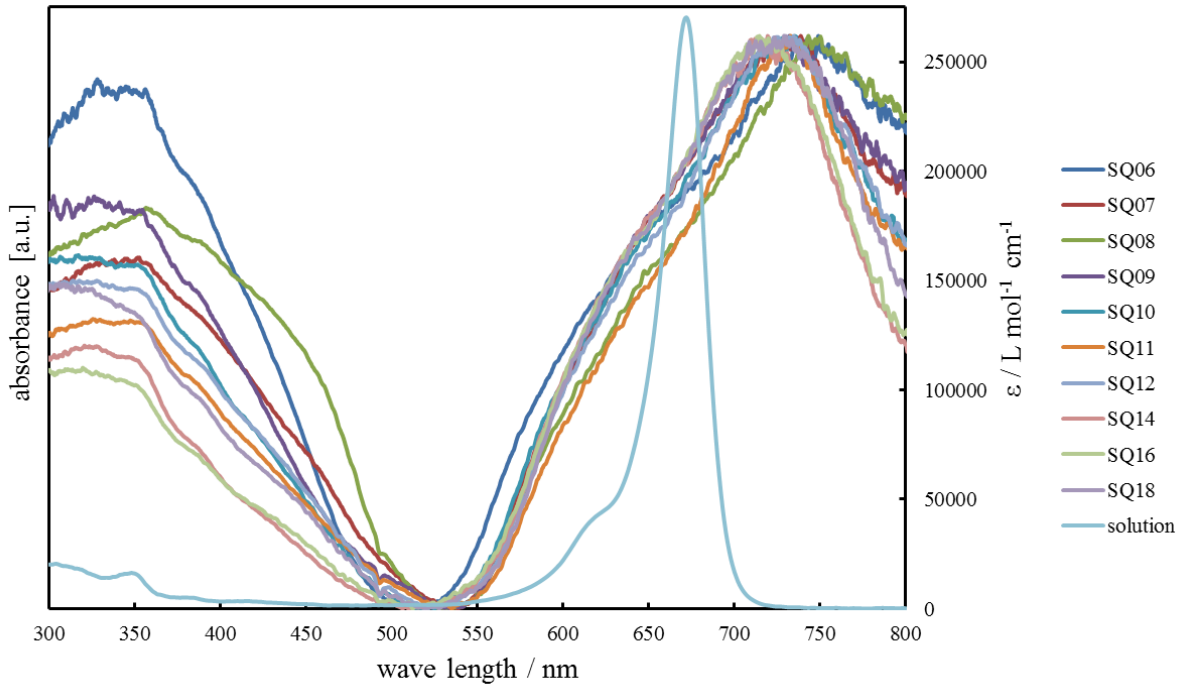

Figure S17. Optical waveguide spectra of all single crystals and UV-Vis absorption spectra of CH_2Cl_2 solution.

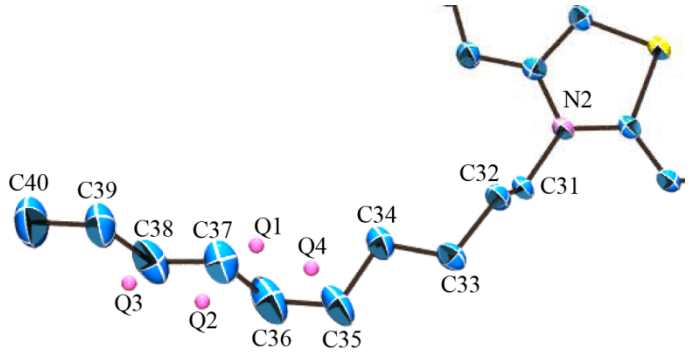

Figure S18. ORTEP view of the C31–C40 alkyl chain of SQ10 showing 50% probability ellipsoids (H atoms were omitted for clarity). Fourier synthesis peaks Q1–Q4 presented heights of 0.91, 0.82, 0.51 and 0.45 eÅ^{-3}, respectively.

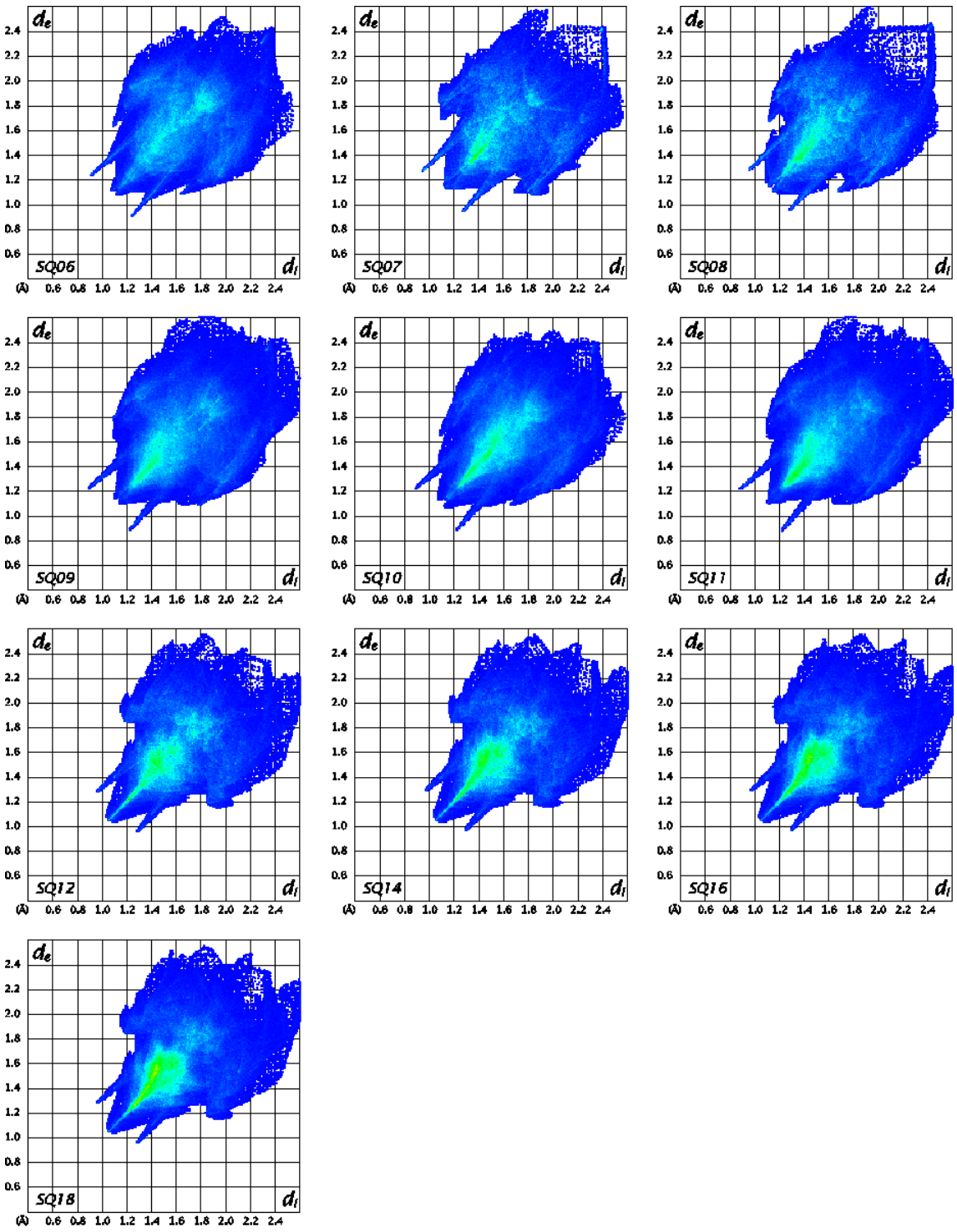

Figure S19. Fingerprint plot in Hirshfeld surface for SQ06-12, 14, 16, 18

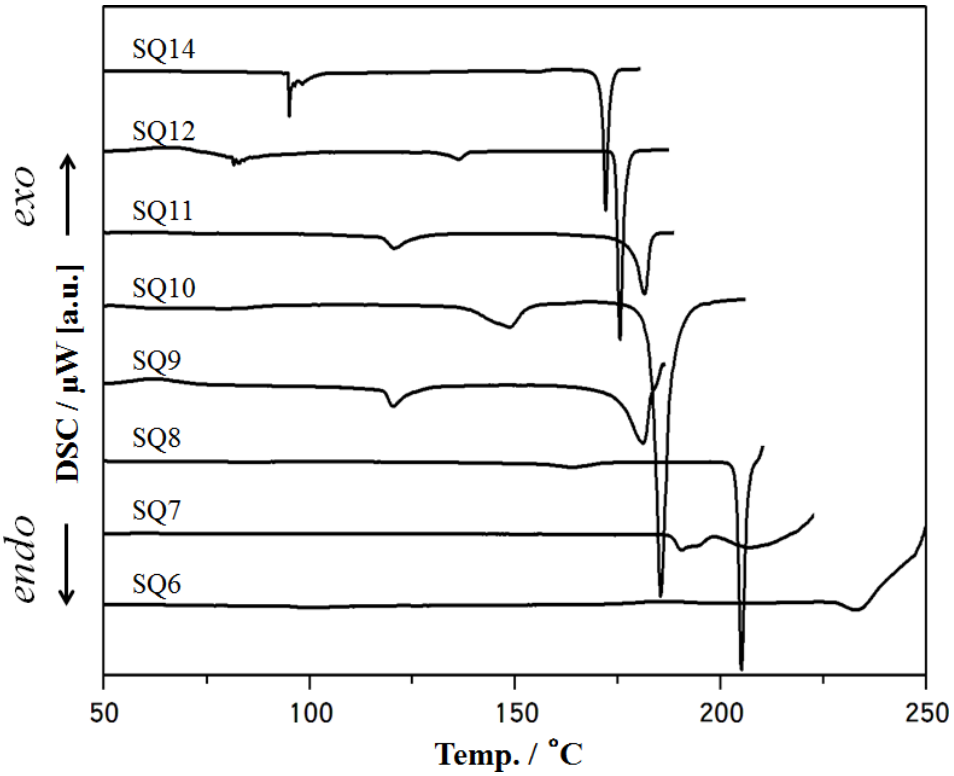

Figure S20. DSC curves of various squarylium dyes obtained for virgin samples.

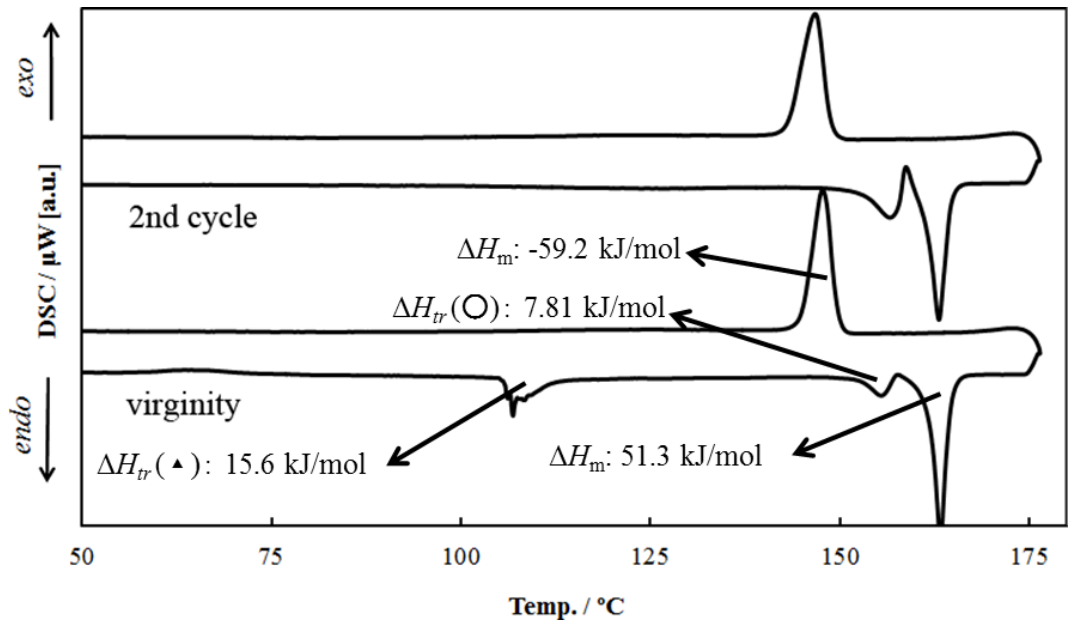

Figure S21. DSC curves of SQ16. Arrows indicate the enthalpies of each transition.

Table S1. Selected geometry parameters of the hydrogen bond and the S…O interaction

Compound	D-H…A	D…A /Å	DHA /°	S…O	S…O /Å
SQ06	C5-H5…O1a	3.203(3)	166.4	S1…O2	3.0348
	C21-H21…O2b	3.179(3)	134.7	S2…O1	2.9458
SQ07	C5-H5…O1b	3.282(4)	165.4	S1…O1a	2.9895
SQ08	C5-H5…O1b	3.2733(19)	159.1	S1…O1a	2.9951
SQ09	C5-H5…O1a	3.169(4)	168.8	S1…O2	2.9993
	C24-H24…O2b	3.164(4)	150.7	S2…O1	3.0454
SQ10	C5-H5…O1a	3.179(3)	166.3	S1…O2	2.9866
	C25-H25…O2b	3.142(3)	144.0	S2…O1	2.9714
SQ11	C5-H5…O1a	3.145(3)	153.1	S1…O2	3.0412
	C26-H26…O2b	3.168(3)	169.8	S2…O1	3.0001
SQ12	C5-H5…O1b	3.199(3)	147.4	S1…O1a	2.9583
SQ14	C5-H5…O1b	3.199(3)	146.6	S1…O1a	2.9586
SQ16	C5-H5…O1b	3.202(7)	147.0	S1…O1	2.9708
SQ18	C5-H5…O1b	3.197(4)	147.9	S1…O1a	2.9607

Symmetry codes: SQ06: a = −1 + *x*, *y*, *z*, b = 1 + *x*, *y*, *z*, SQ07: a = 2 − *x*,1 − *y*, −*z*, b = *x*, 1 + *y*, *z*. SQ09: a = 1 + *x*, *y*, *z*, b = −1 + *x*, *y*, *z*, SQ10: a = −1 + *x*, *y*, *z*, b = 1 + *x*, *y*, *z*, SQ11: a = −1 + *x*, *y*, *z*, b = 1 + *x*, *y*, *z*, SQ12: a = −1 − *x*, 3 − *y*, −*z*, b = *x*, −1 + *y*, *z*, SQ14: a = 3 − *x*, 3 − *y*, 1 − *z*, b = *x*, −1 + *y*, *z*, SQ16: b = 4 − *x*, −*y*, 1 − *z*, SQ18: a = −2 − *x*, −1 − *y*, 1 − *z*, b = *x*, 1 + *y*, *z*

Least-squares planes calculated by SHELX-97

Least-squares planes (x, y, z in crystal coordinates) and maximum deviations from them in 26 atoms of the π-conjugated moiety are shown below. (Symmetry codes are the same about the atom-numbering scheme)

SQ06

1.1794 (31) x + 8.8970 (31) y − 4.8828 (61) z = 1.4498 (76): 0.8738 Å (O1)

SQ07

8.2883 (35) x + 0.4304 (37) y + 6.1705 (59) z = 8.5035 (49): ±0.3284 Å (O1 and O1a)

SQ08

8.4515 (21) x + 0.4968 (24) y + 6.0686 (41) z = 8.4515 (21): ±0.1980 Å (O1 and O1a)

SQ09

0.5462 (31) x + 9.1532 (28) y + 5.9263 (58) z = 6.6028 (29): −0.6869 Å (O1)

SQ10

−0.8272 (27) x + 12.3752 (10) y + 5.3399 (51) z = 1.2705 (15): −0.7937 Å (O1)

SQ11

0.5297 (29) x + 9.7063 (45) y + 5.9778 (56) z = 11.4639 (49): −0.6702 Å (O2)

SQ12

−2.1152 (34) x + 1.2639 (31) y + 13.0732 (32) z = 2.9534 (30): ±0.0552 Å (O1 and O1a)

SQ14

−2.1031 (37) x − 1.2862 (34) y + 15.7572 (17) z = 2.7946 (21): ±0.0509 Å (O1 and O1a)

SQ16

2.1096 (99) x − 1.2939 (89) y + 16.2559 (66) z = 12.9941 (139): ±0.0584 Å (O1 and O1a)

SQ18

2.1230 (52) x + 1.2678 (47) y + 16.6361 (41) z = 5.5611 (48): ±0.0477 Å (O1 and O1a)