ELECTRONIC SUPPLEMENTARY INFORMATION:

Femtosecond to Microsecond Observation of the Photochemical Reaction of 1,2di(quinolin-2-yl)disulfide with Methyl Methacrylate

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1. Additional Experimental Details

Methanol, chloroform, acetonitrile, *n*-hexane, ethyl acetate (all Analytical Grade, Sigma Aldrich), 2-quinolinethiol (97%, Sigma Aldrich), iodine (Fluka, \geq 99.8%), sodium thiosulfate pentahydrate (\geq 99.5%, Sigma Aldrich) and deuterated chloroform (99.8 atom % D, Sigma Aldrich) were used as received. Styrene (\geq 99%, Sigma Aldrich) was passed through a basic aluminum oxide column prior to use to remove the inhibitor, 4-*tert*-butylcatechol. The transient electronic and vibrational absorption spectroscopy of QSSQ in styrene solution were performed using the same experimental setups described in the main text.

2. Synthesis of 1,2-di(quinolin-2-yl)disulfide QSSQ¹

To a solution of 2-quinolinethiol (5.0 mmol, 0.81 g) in 1/5 (v/v) of water/acetonitrile solution (400 ml), iodine (2.5 mmol, 0.63 g) was added. The solution was stirred for 10 min at room temperature, then 1% aqueous sodium thiosulfate (50 ml) and water (200 ml) were added to the solution. The solution was thereafter extracted with chloroform (200 ml × 3) and the organic solvent was removed under reduced pressure. Recrystallization from methanol/chloroform gave pale yellow crystals (0.74 g, 92% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.03 (m, 4H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.72 (m, 4H), 7.49 (t, *J* = 7.5 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 159.29, 147.92, 137.45, 130.37, 128.36, 127.73, 126.40, 126.37, 117.20 ppm.

 Identification of Methyl 2-hydroxy-2-methyl-3-(quinolin-2-ylthio)propanoate QS-MMA-OH

A long-time (final) main photoproduct formed from a reaction of quinoline-2-thiyl (QS) radical with MMA was photochemically synthesized using the same experimental set-up described in the main text (Section 2.2) except for using defocused 1800 nJ/pulse UV laser pulses (diameter of the irradiation area ~ 10 mm). Concentrations of QSSQ and MMA were the same as the TVAS experiment described in Section 3.2 (3.8 mM for QSSQ and 100 mM for MMA in 50 ml CHCl₃), but CHCl₃ was used as a solvent instead of CDCl₃. The photoreaction was carried out for 48 h, then excess MMA and CHCl₃ were removed in *vacuo*. Column chromatography of the crude reaction mixture using silica gel (Sigma Aldrich, pore size 60 Å, 230-400 mesh) and *n*-hexane/ethyl acetate = 1/4 (v/v) as eluent gave QS-MMA-OH as a pale yellow liquid (38.6 mg, 37% yield) and 46% recovery of QSSQ based on isolated yield (i.e. 68% yield of the reacted QSSQ). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.94$ (d, J=8.6 Hz, 4H), 7.73 (d, J = 8.6 Hz, 2H), 7.66 (t, J = 7.5 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 3.76 (s, 6H), 3.72 (d, J = 14.6 Hz, 2H), 3.62 (d, J = 14.6 Hz, 2H), 1.63 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 175.64, 159.48, 147.23, 136.34, 130.28, 127.61, 127.08, 126.09, 125.99, 120.85, 76.04, 52.54, 41.17, 26.36 ppm. HRMS (ESI): calculated for [M+Na]⁺ C₁₄H₁₅NNaO₃S, 300.0670; found 300.0665.



4. Time-Resolved Vibrational Absorption Spectroscopy of W(CO)₆ in Cyclohexane Solution

Figure S1: Left panel: transient vibrational absorption spectra of 0.60 mM W(CO)₆ in cyclohexane solution following 267-nm excitation. Right panel: time-dependence of $W(CO)_6$ ground state bleach band at 1984 cm⁻¹. The bleach recovery over the microsecond range is not a signature of recovery of ground state molecules by relaxation, but instead derives from the sample flow. All of the band intensities in the longer-time TVA spectra presented in the main text were corrected using the gradient represented by the red line, which was obtained using the integrated band intensities from 1 µs to 87 µs.

5. Steady State FT-IR spectra of QSSQ



Figure S2: Upper panel: steady state FTIR spectra of 100 mM MMA in CDCl₃ (black) and 31 mM QSSQ / 100 mM MMA in CDCl₃ (red). Lower panel: difference spectrum obtained by taking the difference between spectra measured after and before adding QSSQ. Each spectrum was obtained in a Harrick cell with a 50 μ m thick spacer and CaF₂ windows.

6. Linear Correction for Computed Infrared Frequencies



Figure S3: Linear correlation between experimental infrared frequencies of QSSQ in $CDCl_3$ solution and computed infrared band positions for QSSQ obtained at the B3LYP/6-311++G(3df,3pd) level.

7. Transient Electronic Absorption Spectra of Pure MMA



Figure S4: Transient absorption spectra of pure MMA following 330-nm excitation (left), and time-dependence of band intensity at 380 nm (right). MMA does not absorb 330-nm light, and therefore the transient signals seen in the figure are most likely derived from multiphoton absorption.

8. Computed Potential Energy Curves for QSSQ

The calculation of potential energy curves (PECs) followed a similar procedure to that described in our previous report,² and used the Molpro package.³ The computation of PECs for the relatively large molecule QSSQ was performed using the state averaged complete active space self-consistent field (SA-CASSCF) method with a 6-31G(d) basis set. The geometries at each S-S bond distance were frozen at their ground state equilibrium geometry obtained with the Gaussian 09 package,⁴ at the B3LYP/6-311++G(3df,3pd) level of theory (rigid PECs scan). This treatment was necessary to avoid formation of QS radical dimer π -complexes.² Using these structures, complete active space with second-order perturbation theory (CASPT2) energies were calculated using the SA-CASSCF result as a reference wavefunction. An imaginary level shift of 0.4 a.u. was used for all of the CASPT2 calculations to avoid intruder state problems. These calculations included ten electrons in ten active orbitals (10/10) comprising the S-S σ bond, the corresponding S-S anti-bonding σ^* , the four π and the four corresponding π^* orbitals.



Figure S5: Potential energy curves along the S-S bond distance (R_{S-S}) for QSSQ calculated at the CASPT2(10/10)/6-31G(d) level. The lowest bound excited singlet potential curve and the lowest two dissociative singlet $\pi\sigma^*$ states are illustrated.

9. Fitting of the Decay Kinetics of QS Radical in Methanol Solution to a Diffusion Model

The model we used to fit the decay kinetics of QS radical in methanol solution is the same as our previous report of the benzothiazole-2-thiyl radical,² and was proposed by Smoluchowski.⁵ The survival probability $\Phi(t)$ of a QS radical is described by:

$$\Phi(t) = 1 - \frac{R}{r_0} \left\{ \frac{k_{rev}}{k_{rev} + 4\pi R D N_A} \right\} \left[erfc \left\{ \frac{r_0 - R}{2\sqrt{Dt}} \right\} - exp \left\{ P^2 D t + P(r_0 - R) \right\} erfc \left\{ P\sqrt{Dt} + (1) \right\} \right]$$

In this expression,

$$P = \frac{1}{R} \left\{ \frac{k_{rev} + 4\pi R D N_A}{4\pi R D N_A} \right\}$$
(2)

and erfc is the complementary error function. A radical pair is initially separated by a distance r_0 , but diffusion to within a contact (reactive) distance *R* enables reaction with a second-order rate coefficient k_{rev} . *D* is a diffusion coefficient represented by the Stokes-Einstein equation:

$$D = k_B T / 6\pi \eta a \tag{3}$$

and N_A denotes the Avogadro constant, k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent and a is the hydrodynamic radius. We estimated a value for the hydrodynamic radius of a = 3.21 Å using the van der Waals volume of a QS radical, and by treating the molecule as a sphere. R was fixed to 9.26 Å for the data fitting. This value corresponds to twice the distance from the center of one quinoline ring to the center of the sulfur-sulfur bond of the parent QSSQ, as deduced from the equilibrium geometries obtained from DFT calculations. Kinetic data from 0.6 - 200 ps were incorporated into the fits. The shortest time delay corresponds to when the intensity of the QS band at 527 nm reaches its

maximum. Figure S6 illustrates the results of this fitting. We only used the first 200 ps of the normalized integrated band intensity because solvation stabilizes the radicals and suppresses recombination, and therefore the model underestimates their survival probabilities at longer time delays.⁶



Figure S6: Fitting of the intensity of the band centered at 527 nm to the diffusion model of Eqn 1 for time delays from 0.6 – 200 ps. The fit gives an initial separation distance $r_0 = 9.6 \pm 0.2$ Å and a cage recombination rate coefficient of $k_{rev} = (3.4 \pm 0.2) \times 10^{10}$ M⁻¹ s⁻¹.

10. Spectral Decomposition for Transient Electronic Absorption Spectra of QSSQ in Methanol Solution



Figure S7: Example of decomposition of TEA spectra for 1.0 mM QSSQ in MeOH solution following 330-nm excitation, at time delays of (a) 10 ps; (b) 20 ps; (c) 30 ps; (d) 50 ps; (e) 100 ps. The different color spectra represent QS (red), QS radical dimer (green), the total fit (black) and the TEA spectrum (blue). The spectral decomposition was carried out using a basis spectrum for the QS radical matching the absorption spectrum at 5 ps, where peak shifts of QS radical bands were complete, and a Gaussian function of fixed width and center for the dimer band. This method assumes that the spectral band shape for the QS radical did not

change further with time.

11. Exponential Fittings for Observed Bands in TVA Spectra of QSSQ in CDCl₃ Solution

Table S1: Exponential time constants τ and long-time residual amplitudes (expressed as percentages of peak band intensities) from fits to time-dependent band intensities for the representative bands observed in TVAS measurements.

Band position / cm ⁻¹	τ / ps	Long-time residual / %	
QSSQ bleach (with some product band overlap)			
1091	24 ± 2	15 ± 1	
1141	26 ± 1	22 ± 1	
1293	32 ± 2	31 ± 1	
1421	27 ± 1	24 ± 1	
1557	30 ± 2	24 ± 1	
1585	27 ± 1	20 ± 1	
QS radical			
1367	55 ± 3	57 ± 1	
1415	47 ± 6	25 ± 2	
1548	28 ± 1	1 ± 1	
1575	26 ± 1	2 ± 1	



12. Temporal Band Position Shift for the QS Radical Band in TVAS

Figure S8: Time-dependence of the position of a QS radical IR absorption band in deuterated chloroform solutions following 330-nm excitation. The chosen band is the one observed at 1367 cm⁻¹ after equilibration with the solvent. The solid line represents a fit of the band positions to a single exponential function.

13. Computed Vertical Excitation Wavelengths, Oscillator Strengths and Extinction Coefficients for the QS-MMA Radical



Figure S9: Computed oscillator strengths and simulated UV/vis absorption spectra for the QS-MMA radical obtained at the TD-DFT/6-311++G(3df,3pd) level of theory. The simulated spectra use a Gaussian function (with standard deviation of 0.4 eV) for the band shapes.

14. Spectral Decomposition for Transient Electronic Absorption Spectra of QSSQ in MMA Solution



Figure S10: Example of decomposition of TEA spectra for 1.0 mM QSSQ in MMA solution following 330-nm excitation, at time delays of (a) 30 ps; (b) 100 ps; (c) 200 ps; (d) 400 ps; (e) 800 ps. The different color spectra represent QS (red), QS-MMA (green), the total fit (black) and the TEA spectrum (blue). The spectral decomposition was carried out using the absorption spectrum at 10 ps as the signature of the QS radical, and at 1300 ps for the QS-MMA radical.



15. Transient Vibrational Absorption Spectra of QSSQ in CDCl₃ Solution

Figure S11: Transient vibrational absorption spectra of 3.8 mM QSSQ in $CDCl_3$ solution following 330-nm excitation. The arrows correspond to the band positions indicated in the main text (1088, 1168, 1595 and 1653 cm⁻¹). Note the absence of these features in the QSSQ / CDCl₃ solutions without added MMA (compare Fig. 6 of the main article).

16. Transient Vibrational Absorption Spectra of QSSQ in MMA/CDCl₃ Solution under Oxygen-Purged Conditions



Figure S12: Transient vibrational absorption spectra of 3.8 mM QSSQ / 100 mM MMA in N₂-bubbled CDCl₃ solution following 330-nm excitation.



17. Spectral Decomposition for Transient Vibrational Absorption Spectra of QSSQ in MMA/CDCl₃ Solution

Figure S13: Examples of spectral decompositions of TVA spectra for 3.8 mM QSSQ / 100 mM MMA in CDCl₃ solution following 330-nm excitation, at time delays of (a) 10 ns; (b) 50 ns; (c) 150 ns; (d) 500 ns; (e) 2000 ns. The different color spectra represent QS-MMA (red, dark blue and pink), QSSQ bleach (green), the total fit (black) and the TVA spectrum (blue). The spectral decomposition was carried out using the absorption spectrum at 10 ps as representative of the QSSQ bleach band, and Gaussian functions of fixed width and center for the QS-MMA bands.

18. Photo-induced reactions of QSSQ in styrene solution

Figure S14 shows TEA spectra of QSSQ in styrene following 330-nm excitation, as well as the time-dependences of integrated band intensities. The spectral shapes at early time delays resemble those seen in MeOH solution (Fig. 3 in the main text), except for a shift of the strong visible band peak assigned to the QS radical to a higher wavelength of 532 nm. However, the kinetic behavior of the QS radical in styrene solution is significantly different from what was seen in the MeOH solution: the QS radical band completely disappears with time constants of $\tau_1 = 6.6 \pm 0.3$ ps and $\tau_2 = 104 \pm 2$ ps if biexponential fitting is employed. The slower decay component is attributed to reaction of QS radical with styrene, but as we discussed in Section 3.2 in the main text, we could not reliably extract the kinetics corresponding to the reaction with styrene from the measured decay of QS radical absorption in TEA spectra.



Figure S14: (a) Transient electronic absorption spectra of 1.0 mM QSSQ in styrene following 330-nm excitation. (b) Integrated band intensities for the QS radical band (black), and the QS-St band (red) obtained by spectral decomposition with the KOALA program.⁷ The integrated intensity for the QS-St radical has been multiplied by a factor of 5 for clarity. The decomposition was carried out with the same method as Figure 5 in the main text (see Figure S15 for an example). The solid lines represent biexponential fitting for the QS radical band intensities and single exponential fitting for the QS-St radical band.

At later time delays, a broad band is observed that is centered at around 375 nm and extends to \sim 550 nm. This feature is not seen in TEA spectra of QSSQ in MeOH solution (see Figure S14(a)). The time dependence of the band intensity was obtained by spectral decomposition with the KOALA program, an example of which is provided in Figure S15, and is shown in Figure S14(b). A fit of this time-dependence to a single exponential function gives a time constant of 83 ± 5 ps for the rise of the broad band. We assigned this feature to a carbon centered radical (denoted as QS-St) formed via the following addition reaction of the QS radical with styrene, on the basis of the kinetic behavior and the computed electronic absorption spectrum for the QS-St radical plotted in Figure S16:



This assignment is further confirmed by the results of TVAS measurements discussed below.



Figure S15: Example of decomposition of TEA spectra for 1.0 mM QSSQ in styrene solution following 330-nm excitation, at time delays of (a) 20 ps; (b) 30 ps; (c) 50 ps; (d) 100 ps; (e) 200 ps. The different color spectra represent QS (red), QS-St (green), the total fit (black) and the TEA spectrum (blue). The spectral decomposition was carried out using the same procedure as for Figure S10 except for the use of the TEA spectrum at 1300 ps to represent the QS-St radical band.



Figure S16: Computed oscillator strengths and simulated UV/vis absorption spectra for the QS-St radical obtained at the TD-DFT/6-311++G(3df,3pd) level of theory.

Figure S17 shows TVA spectra of 3.8 mM QSSQ in styrene solution following 330-nm excitation, and time-dependent integrated band intensities of selected features. As was mentioned in Section 3.1.2 in the main text, the three negative bands at 1091, 1141, 1293 cm⁻¹ are ascribed to QSSQ depletion by the excitation laser, and five relatively small bands at 1156, 1182, 1202, 1319 and 1335 cm⁻¹ observed at later time delays correspond to consumption of styrene, which is confirmed by comparison with the steady state FTIR spectrum of pure The product band at 1367 cm⁻¹ is assigned to the QS radical, as we discussed in styrene. Section 3.1.2 for QSSQ in CDCl₃ solution. In contrast to the CDCl₃ solution, the QS radical band completely disappears after a time delay of ~400 ps, and a fit of the integrated band intensity to a biexponential function gives time constants of $\tau_1 = 9.1 \pm 0.2$ ps and $\tau_2 = 93 \pm 3$ This decay behavior is in accord with the TEAS measurements for the ps for the decay. styrene solution, and the deduced time constants are in reasonable agreement from the two sets of measurements.



Figure S17: (a) Transient vibrational absorption spectra of 3.8 mM QSSQ in styrene solution following 330-nm excitation. Strong absorptions by styrene interfere with the TVA spectra over the probe region above 1400 cm⁻¹, and this region is therefore shaded and not considered further. (b) Expanded view of TVA spectra for the 1125 cm⁻¹ – 1165 cm⁻¹ region to highlight QS-St radical bands, and the 1340 cm⁻¹ – 1385 cm⁻¹ region for the QS radical. The arrows in the figure correspond to the infrared positions mentioned in the text. (c) Integrated band intensity for the bands at 1137 cm⁻¹, 1202 cm⁻¹, 1148 cm⁻¹ and 1367 cm⁻¹. The kinetic traces for the bands at 1137 cm⁻¹ and 1148 cm⁻¹ were obtained with the same method as Figure 6 in the main text (see Figure S18 for an example). The solid lines represent biexponential fitting for the intensity of the QS radical bands at 1137 cm⁻¹ and 1148 cm⁻¹ and 1148 cm⁻¹, and the styrene band at 1202 cm⁻¹.

We now focus on the appearance of product bands. On top of the bleach band at 1141 cm⁻¹, the growths of two product bands at 1137 cm⁻¹ and 1148 cm⁻¹ are evident at later time delays. There may also be a product band at 1097 cm⁻¹, but its formation is less clear-cut. Hence, we concentrate on the analysis of the former two product bands. Spectral decomposition with the KOALA program (as illustrated in Figure S18) suggests that the 1137 and 1148 cm⁻¹ bands grow with time constants of 84 ± 11 ps and 74 ± 15 ps which agree within the 2 SD uncertainties. These deduced time constants also agree with the time constant for the rise of the broad band observed in TEA spectra, and in addition, they are consistent with a time constant of 76 ± 9 ps for the development of the styrene bleach band at 1202 cm⁻¹. Moreover, the observed band positions are in excellent agreement with the computed fundamental infrared frequencies presented in Table S2. Consequently, we assigned these product bands to the QS-St radical formed via the anti-Markovnikov addition reaction of the QS radical to the terminal (β) C-atom in styrene, as shown in reaction scheme (4). A similar addition reaction of the QS radical at the α -position of styrene is possible (i.e. the Markovnikov type addition), and our DFT calculations predict that both the anti-Markovnikov and Markovnikov addition products have almost the same infrared band positions and intensities.² However, our computed enthalpy of activation for the Markovnikov pathway is 18.6 kJ/mol higher than for the anti-Markovnikov addition. Furthermore, addition of a thivl radical to an alkene or alkyne is known to favor the anti-Markovnikov pathway.^{8, 9} Consequently, we ruled out the Markovnikov type addition product.

The following equation can be employed to extract kinetic information based on scheme (4):

$$\frac{d[QS-St]}{dt} = k_4[QS][styrene] = k_4[QS]$$
(5)

The concentration of styrene is in considerable excess over the concentration of QS radical, so a pseudo first-order kinetic analysis is appropriate, in which we denote $k_4[styrene] = k'_4$.

Accordingly, a bimolecular reaction rate coefficient for the addition reaction of the QS radical and styrene of $k_4 = (1.4 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is estimated, using a concentration of neat styrene of 8.7 M, and a value for k'_4 as the reciprocal of an average value of the three deduced time constants from TEAS and TVAS measurements. The estimated rate coefficient is the highest yet reported for addition of an aromatic thiyl radical to an alkene, and is comparable with the highest known rate coefficients for reactions of alkyl thiyl radicals with styrene.^{8, 10}

Table S2: Calculated fundamental infrared frequencies and intensities, and observed infrared band positions for the QS-St radical, obtained at the B3LYP / 6-311++G(3df,3pd) level of theory. Calculated infrared frequencies over our experimental probe region (1080 cm⁻¹ – 1400 cm⁻¹) with band intensities greater than 10 km mol⁻¹ are shown.

Calculation		Experiment
Frequency /	Intensity / km	Frequency /
cm ⁻¹	mol ⁻¹	cm ⁻¹
1084	34	_a
1086	92	1097 ^a
1137	65	1137
1152	14	1148
1297	30	_a
1337	15	_a
1362	19	_a

^{*a*} Not observed or uncertain due to spectral overlap with a QSSQ, styrene bleach or QS radical band.



Figure S18: Example of spectral decomposition of TVA spectra for 3.8 mM QSSQ in styrene solution following 330-nm excitation, at time delays of (a) 50 ps; (b) 80 ps; (c) 150 ps; (d) 500 ps; (e) 1200 ps. The different color spectra represent QS-St (red and dark blue), QSSQ bleach (green), the total fit (black) and the TVA spectrum (blue solid line). The spectral decomposition was carried out using the same procedure as for Figure S13.

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