Supporting Information for

Cyclic Kinetics during Thermal Equilibration of an Axially Chiral Bis-Spiropyran

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1. General methods

$^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker 300 MHz and 500 MHz spectrometers. Chemical shifts (δ) are reported in ppm; multiplicities are indicated as “s” (singlet), “d” (doublet), “t” (triplet), “q” (quartet), “m” (multiplet), or “br” (broad). Coupling constants (J) are reported in Hz. The spectra were referenced to residual dichloromethane ($^1$H: δ = 5.32 ppm; $^{13}$C: δ = 53.84 ppm), chloroform ($^1$H: δ = 7.26 ppm; $^{13}$C: δ = 77.00 ppm), or dimethyl sulfoxide ($^1$H: δ = 2.50 ppm). High-resolution mass spectra were recorded at 60-70 eV on a Waters Micromass Q-TOF spectrometer (ESI, Ar). UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Analytical thin layer chromatography (TLC) was performed using silica gel 60 F254-coated aluminum sheets (Merck 1.05554.0001).

2. Synthesis of 4′-Bromo-7′-[4′-bromo-1′,3′,3′-trimethyl-6-nitro-1′,3′-dihydrospiro[chromene-2,2′-indole]-7′-yl]-1′,3′,3′-trimethyl-6-nitro-1′,3′-dihydrospiro[chromene-2,2′-indole] (I).

1 was synthesized according to a previously published procedure.$^{S1}$

Scheme S1. Synthesis of 1.
2A. Preparation of the $\text{1}_{\text{in-in}}$ diastereoisomer ($R,S_a,R + \text{enantiomer}$).

A solution of $6$ (1.00 g, 2.0 mmol) and 2-hydroxy-5-nitrobenzaldehyde (0.87 g; 5.2 mmol) in ethanol (70 mL) was refluxed under a nitrogen atmosphere for 15 h. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The solid residue was dissolved in 150 mL of dichloromethane and washed with an aqueous NaOH solution (100 mL; three times). The organic phase was dried over MgSO$_4$ and the solvent was evaporated under reduced pressure. The residue was dissolved in a minute amount of dichloromethane and the product was precipitated using hexane. Repeated precipitation with hexane from chloroform afforded $1$ (1.25 g; 1.57 mmol; 78%) as an amorphous solid. The product was obtained as a single diastereomer $\text{1}_{\text{in-in}}$ ($R,S_a,R + \text{enantiomer}$).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.97$ (d, 2H, $J = 2.7$ Hz), 7.51 (dd, 2H, $J = 9$, 2.7 Hz), 6.98 (d, 2H, $J = 10.4$ Hz), 6.93 (d, 2H, $J = 8.2$ Hz), 6.83 (d, 2H, $J = 8.2$ Hz), 6.18 (d, 2H, $J = 9$ Hz), 5.79 (d, 2H, $J = 10.4$ Hz), 2.50 (s, 6H), 1.42 (s, 6H), 1.28 (s, 6H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 159.76$ (2C), 147.37 (2C), 141.15 (2C), 133.53 (2C), 133.13 (2C), 129.93 (2C), 125.71 (2C), 123.51 (2C), 123.08 (2C), 120.69 (2C), 119.48 (2C), 118.61 (2C), 118.14 (2C), 114.80 (2C), 107.68 (2C), 53.73 (2C), 31.32 (2C), 22.32 (2C), 20.12 (2C).

HR MS (ESI) m/z: exact mass calculated for C$_{38}$H$_{32}$N$_4$O$_6$Br$_7$Na$^{81}$ [M+Na]$^+$ = 823.0566; found = 823.0570.

$R_f$(3:2 hexane-diethyl ether) = 0.36.

Single crystals for X-ray diffraction analysis were prepared by crystallization from CH$_2$Cl$_2$ (3°C, 2 days).

![Fig. S1. $^1$H NMR spectrum of $\text{1}_{\text{in-in}}$ (300 MHz, CD$_2$Cl$_2$).](image-url)
Fig. S2. $^{13}$C NMR spectrum of $\mathbf{1}_{\text{in-in}}$ (300 MHz, CD$_2$Cl$_2$).

2B. Preparation of the $\mathbf{1}_{\text{out-out}}$ diastereomer ($S,S_a,S +$ enantiomer).

A solution of diastereomer $\mathbf{1}_{\text{in-in}}$ in CH$_2$Cl$_2$ was kept at 3°C for approximately six weeks. The resulting colorless crystals of $\mathbf{1}_{\text{out-out}}$ were filtered and washed with cold chloroform.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 8.0$ (dd, 2H, $J = 8.8, 2.7$ Hz), 7.97 (d, 2H, $J = 2.7$ Hz), 6.98 (d, 2H, $J = 8.3$ Hz), 6.96 (d, 2H, $J = 10.4$ Hz), 6.95 (d, 2H, $J = 8.3$ Hz), 6.80 (d, 2H, $J = 8.8$ Hz), 5.81 (d, 2H, $J = 10.4$ Hz), 2.28 (s, 6H), 1.48 (s, 6H), 1.22 (s, 6H).

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta = 160.02$ (2C), 147.90 (2C), 141.41 (2C), 133.41 (2C), 133.18 (2C), 129.63 (2C), 126.23 (2C), 123.97 (2C), 123.12 (2C), 121.22 (2C), 120.49 (2C), 118.72 (2C), 118.10 (2C), 115.68 (2C), 107.54 (2C), 53.90 (2C), 31.38 (2C), 22.05 (2C), 20.39 (2C).

$R_f$ (3:2 hexane-diethyl ether) = 0.31.
Fig. S3. $^1$H NMR spectrum of I$_{out-out}$ (300 MHz, CD$_2$Cl$_2$).

Fig. S4. $^{13}$C NMR spectrum of I$_{out-out}$ (500 MHz, CD$_2$Cl$_2$).
2C. Preparation of 1_{in-out} diastereomer (R,S_a,S + enantiomer).

Diastereomer 1_{in-in} in CH₂Cl₂ was kept at room temperature under ambient light for ten days to allow for the generation of an equilibrated mixture of all diastereomers. 1_{in-out} was isolated by column chromatography on silica using a diethyl ether-hexane-triethylamine (20:80:0.1) mixture as the eluent (attempts to isolate the desired diastereomer in the absence of the base failed because spiropyran rapidly isomerizes under acidic conditions 

\(^{1}\)H NMR (300 MHz, CD₂Cl₂): \(\delta = 8.06-8.00 \text{ (m, 4H), 6.99-6.78 \text{ (m, 7H), 6.70 \text{ (d, 1H, } J = 8.8 \text{ Hz), 5.77 \text{ (d, 1H, } J = 10.4 \text{ Hz), 5.63 \text{ (d, 1H, } J = 10.4 \text{ Hz), 2.51 \text{ (s, 3H), 2.37 \text{ (s, 3H), 1.47 \text{ (s, 3H), 1.46 \text{ (s, 3H), 1.27 \text{ (s, 3H), 1.10 \text{ (s, 3H).}}}})} \)

\(^{13}\)C NMR (125 MHz, CD₂Cl₂): \(\delta = 160.23, 160.13, 148.04, 147.73, 141.48, 141.45, 133.69, 133.45, 133.41, 133.36, 129.76 \text{ (2C), 126.27, 126.20, 124.15, 123.54, 123.29, 123.19, 121.16, 121.06, 120.65, 119.68, 118.96, 118.80, 118.20 \text{ (2C), 115.73, 115.40, 107.79, 107.43, 53.99, 53.92, 32.09, 29.90, 22.21, 21.94, 20.28, 20.20.}} \)

\(R_f \) (3:2 hexane-diethyl ether) = 0.52.

Single crystals for X-ray diffraction analysis were prepared by crystallization from a mixture of CH₂Cl₂ and hexane at 3°C (1.5 days).

![Fig. S5. \(^{1}\)H NMR spectrum of 1_{in-out} (300 MHz, CD₂Cl₂).](image-url)
3. X-ray crystal structure analysis for 1_{in-in}, 1_{out-out} and 1_{in-out}.

3A. X-ray crystal structure analysis for 1_{in-in}.

Crystal data: \( \text{C}_{40}\text{H}_{36}\text{N}_{4}\text{O}_6\text{Cl}_4\text{Br}_2 (\text{C}_{38}\text{H}_{32}\text{N}_4\text{O}_6\text{Br}_2 + 2\text{Cl}_2\text{H}_2\text{Cl}_2) \) colorless, 0.12 \times 0.04 \times 0.04 \text{mm}^3, monoclinic, \( P2_1/c \) (N14), \( a = 12.973(3), b = 26.717(5), c = 11.882(2) \text{Å}, \beta = 105.30(3)° \) from 20 degrees of data, \( T = 100(2) \text{K}, V = 3972.3(14) \text{Å}^3, Z = 4, F_w = 970.35, D_c = 1.623 \text{Mg} \cdot \text{m}^{-3}, \mu = 2.363 \text{mm}^{-1}. \)

Data collection and processing: Bruker Appex2 KappaCCD diffractometer, MoKa (\( \lambda = 0.71073 \text{Å} \)), graphite monochromator, 76795 reflections collected, \(-16 \leq h \leq 16, -34 \leq k \leq 34, -15 \leq l \leq 15, \) frame scan width = 0.5°, scan speed 1.0° per 40 sec, typical peak mosaici 0.67°, 9068 independent reflections (R-int = 0.0516). The data were processed with Denzo-Scalepack.

Solution and refinement: The structure was solved by direct methods with SHELXS-97; full-matrix least-squares refinement based on \( F^2 \) with SHELXL-97. 539 parameters with 12 restraints, final R1 = 0.0442 (based on \( F^2 \)) for data with \( I > 2 \sigma(I) \) and R1 = 0.0597 on 9068 reflections, goodness-of-fit on \( F^2 = 1.030 \), the largest electron density peak = 1.172 \text{Å}^{-3}, the deepest hole = -1.237 \text{Å}^{-3}.

Crystallographic information file for 1_{in-in} is attached as “in-in.cif”.

Fig. S6. \(^{13}\text{C} \) NMR spectrum of 1_{in-out} (500 MHz, CD\_2\Cl).
3B. X-ray crystal structure analysis for $1_{\text{out-out}}$.

Crystal data: $\text{C}_{39}\text{H}_{34}\text{N}_4\text{O}_6\text{Cl}_2\text{Br}_2$ (C$_{38}$H$_{32}$N$_4$O$_6$Br$_2$ + C$_1$H$_2$Cl$_2$) colorless, 0.16 × 0.04 × 0.02 mm$^3$, monoclinic, Cc (N9), $a = 14.5120(5)$, $b = 22.9160(4)$, $c = 12.0150(4)$ Å, $\beta = 113.674(9)^\circ$ from 20 degrees of data, $T = 120(2)$ K, $V = 3659.4(4)$ Å$^3$, $Z = 4$, $F_w = 885.42$, $D_c = 1.602$ Mg·m$^{-3}$, $\mu = 2.416$ mm$^{-1}$.

Data collection and processing: Nonius KappaCCD diffractometer, MoK$\alpha$ ($\lambda = 0.71073$ Å), graphite monochromator, 9397 reflections collected, $-17 \leq h \leq 17$, $-27 \leq k \leq 27$, $-14 \leq l \leq 14$, frame scan width = 1°, scan speed 1.0° per 120 sec, typical peak mosaicity 0.83°, 6837 independent reflections (R-int = 0.0168). The data were processed with Denzo-Scalepack.

Solution and refinement: The structure was solved by direct methods with SHELXS-97; full-matrix least-squares refinement based on $F^2$ with SHELXL-97. 485 parameters with 2 restraints, final $R_1 = 0.0336$ (based on $F^2$) for data with $I > 2\sigma(I)$ and $R_1 = 0.0378$ on 6837 reflections, goodness-of-fit on $F^2 = 1.050$, the largest electron density peak = 0.454 Å$^{-3}$, the deepest hole = −0.421 Å$^{-3}$.

Crystallographic information file for $1_{\text{out-out}}$ is attached as “out-out.cif”.

3C. X-ray crystal structure analysis for $1_{\text{in-out}}$.

Crystal data: $\text{C}_{39}\text{H}_{34}\text{N}_4\text{O}_6\text{Cl}_2\text{Br}_2$ (C$_{38}$H$_{32}$N$_4$O$_6$Br$_2$ + C$_1$H$_2$Cl$_2$) yellow, 0.10 × 0.08 × 0.07 mm$^3$, triclinic, P-1 (N2), $a = 11.4948(4)$, $b = 13.0509(5)$, $c = 14.1702(5)$ Å, $\alpha = 94.897(3)^\circ$, $\beta = 98.175(2)^\circ$, $\gamma = 114.503(2)^\circ$ from 20 degrees of data, $T = 100(2)$ K, $V = 1889.93(12)$ Å$^3$, $Z = 2$, $F_w = 885.42$, $D_c = 1.556$ Mg·m$^{-3}$, $\mu = 2.339$ mm$^{-1}$.

Data collection and processing: Bruker Apex2 KappaCCD diffractometer, MoK$\alpha$ ($\lambda = 0.71073$ Å), graphite monochromator, 13151 reflections collected, $-14 \leq h \leq 14$, $-13 \leq k \leq 16$, $-17 \leq l \leq 16$, frame scan width = 0.5°, scan speed 1.0° per 240 sec, typical peak mosaicity 0.83°, 7378 independent reflections (R-int = 0.0249). The data were processed with Denzo-Scalepack.

Solution and refinement: The structure solved by direct methods with SHELXS-97; full-matrix least-squares refinement based on $F^2$ with SHELXL-97. 484 parameters with 0 restraints, final $R_1 = 0.0353$ (based on $F^2$) for data with $I > 2\sigma(I)$ and $R_1 = 0.0555$ on 7378 reflections, goodness-of-fit on $F^2 = 1.025$, the largest electron density peak = 0.995 Å$^{-3}$, the deepest hole = −0.845 Å$^{-3}$.

Crystallographic information file for $1_{\text{in-out}}$ is attached as “in-out.cif”.
4. Derivation of rate constants from NMR data

The figure below shows a typical stack of full $^1$H NMR spectra recorded at different time intervals ($t = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10$ days) (in this case, $1_{in-in}$ in CD$_2$Cl$_2$ at room temperature).

Fig. S7. Time-resolved $^1$H NMR spectra of $1_{in-in}$ (300 MHz, CD$_2$Cl$_2$).

Among all protons in $1$, those of N-bound CH$_3$ groups were best separated (2.51-2.28 ppm range) and provided unique signatures of all diastereomers (see Fig. S8).

Fig. S8. Partial $^1$H NMR spectrum of an equilibrated mixture of $1_{in-in}$, $1_{out-out}$, and $1_{in-out}$ (300 MHz, CD$_2$Cl$_2$). Although the 2.51 ppm and the 2.50 ppm signals partially overlap, they can still be integrated accurately because the intensities of the 2.51 ppm and the 2.37 ppm signals (due to $1_{in-out}$’s diastereotopic methyl groups) are identical.
We fitted the equations for the rate constants:

\[
\frac{\partial c_{\text{in-in}}}{\partial t} = -k_1 c_{\text{in-in}} - k_{-3} c_{\text{in-in}} + k_{-1} c_{\text{in-out}} + k_3 c_{\text{out-out}} ,
\]

\[
\frac{\partial c_{\text{in-out}}}{\partial t} = -k_1 c_{\text{in-out}} - k_2 c_{\text{in-out}} + k_1 c_{\text{in-in}} + k_{-2} c_{\text{out-out}} ,
\]

\[
\frac{\partial c_{\text{out-out}}}{\partial t} = -k_3 c_{\text{out-out}} - k_{-2} c_{\text{out-out}} + k_{-3} c_{\text{in-in}} + k_2 c_{\text{in-out}}
\]

to the experimental data (i.e. the concentration of each isomer after a given time) by employing an approximation algorithm based on the MatLab functions fminsearch (which finds the minimum of unconstrained multivariable functions using a derivative-free method) and ode45 (which solves non-stiff differential equations). Initially, first-guess values of rate constants were used to calculate the concentrations at different times; the deviation between the data points and the calculated points was calculated and a new set of \( k_i \) values was selected by the algorithm; this procedure was repeated until convergence between the calculated and the experimental values was reached. For all experiments, first-guess values were \( k_i = k_1 = k_{-1} = k_2 = k_{-2} = k_3 = k_{-3} = 0.1 \text{ day}^{-1} \).

Using the above procedure, we obtained the following results:

<table>
<thead>
<tr>
<th></th>
<th>( k_1 )</th>
<th>( k_{-1} )</th>
<th>( k_2 )</th>
<th>( k_{-2} )</th>
<th>( k_3 )</th>
<th>( k_{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CD}_2\text{Cl}_2 \text{ (rt) } )</td>
<td>0.194</td>
<td>0.122</td>
<td>0.259</td>
<td>0.410</td>
<td>0.493</td>
<td>0.493</td>
</tr>
<tr>
<td>( \text{CDCl}_3 \text{ (rt) } )</td>
<td>0.159</td>
<td>0.0637</td>
<td>0.418</td>
<td>0.697</td>
<td>0.480</td>
<td>0.720</td>
</tr>
<tr>
<td>( \text{DMSO-d}_6 \text{ (rt) } )</td>
<td>0.506</td>
<td>0.493</td>
<td>0.552</td>
<td>1.052</td>
<td>0.246</td>
<td>0.132</td>
</tr>
<tr>
<td>( \text{Acetone-d}_6 \text{ (rt) } )</td>
<td>0.257</td>
<td>0.198</td>
<td>0.485</td>
<td>0.970</td>
<td>0.790</td>
<td>0.511</td>
</tr>
<tr>
<td>( \text{THF-d}_8 \text{ (rt) } )</td>
<td>0.110</td>
<td>0.0507</td>
<td>0.120</td>
<td>0.308</td>
<td>0.818</td>
<td>0.687</td>
</tr>
<tr>
<td>( \text{CD}_2\text{Cl}_2 \text{ (276 K) } )</td>
<td>0.00934</td>
<td>0.0105</td>
<td>0.0257</td>
<td>0.0257</td>
<td>0.0319</td>
<td>0.0283</td>
</tr>
</tbody>
</table>

(All values in day\(^{-1}\); rt = room temperature, ca. 295 K)

To check the validity of our algorithm, we then chose different initial guesses; for example, for equilibration in \( \text{CD}_2\text{Cl}_2 \) at 295 K, we chose the following sets of initial guesses:

\( k_1 = k_2 = k_3 = 0.1 \text{ day}^{-1} \),
\( k_1 = k_2 = k_3 = 0.01 \text{ day}^{-1} \),
\( k_1 = k_2 = k_3 = 1 \text{ day}^{-1} \), and
\( k_1 = 0.5 \text{ day}^{-1}; k_2 = 0.4 \text{ day}^{-1}; k_3 = 0.3 \text{ day}^{-1} \)

This yielded identical final values of the rate constants down to the third decimal place (the numbers of the function evaluations were 134, 213, 282, and 139, respectively).

To further verify our method, we used the derived rate constants to model the concentration profiles. Figure S9 compares the experimental results (circles) with the equilibration profiles (lines) calculated by plugging \( k_1 \) through \( k_{-3} \) into the rate equation.
Fig. S9. Experimental (circles) and calculated (lines) equilibration profiles for the equilibration of 
a) $1_{in}$ in CD$_2$Cl$_2$, b) $1_{out}$ in CD$_2$Cl$_2$, c) $1_{in}$ in CD$_2$Cl$_2$, d) $1_{in}$ in CDCl$_3$, and e) $1_{in}$ in DMSO-$d_6$. Equilibration profiles in b) and c) were calculated from the rate constants found in a) (not enough data points were collected in experiments b) and c) for the algorithm to work). RMSEs (root-mean-square errors) quantify the convergence between the experimental and the calculated data points. All equilibration experiments were carried out at room temperature ($T = 295$ K).

Fig. S10. Equilibration profiles (top panel) and free energy diagrams for a) $1_{in}$ in CD$_2$Cl$_2$ at $T = 276$ K, b) $1_{in}$ in acetone-$d_6$ at $T = 295$ K, and c) $1_{in}$ in THF-$d_8$ at $T = 295$ K. All values in the free energy diagrams are in kJ·mol$^{-1}$. 

S10
5. Low stability of open-ring 1.

The spectra below show that the SP → MC isomerization is significantly hampered in 1. Moreover, the small amount of open-ring form of 2 faded (ring closing) much more rapidly than open-ring 1.
6. Considerations regarding solid-state photoisomerization of \( \text{I}_{\text{out-out}} \).

We report here on an unexpected finding concerning reversible photoisomerization of \( \text{I}_{\text{out-out}} \) in the solid (crystalline) state. When the dark-adapted, transparent crystals of \( \text{I}_{\text{out-out}} \) (e.g. Fig. S13a, left) were exposed to ambient light conditions (laboratory’s fluorescent light), they turned pale blue. The effect was more pronounced when the same crystals were exposed to several minutes of low-intensity UV (\( \lambda \approx 365 \text{ nm} \)) radiation (Fig. S13a), indicating that some of the SP units isomerized to the open-ring MC forms. In both cases, the reaction was reversible: when placed in the dark, the crystals become transparent within several hours. Notably, neither \( \text{I}_{\text{in-in}} \) nor \( \text{I}_{\text{in-out}} \) showed any signs of photochromism in the crystalline state: the transparent crystals of both of these diastereomers were not affected by any wavelength in the near-UV or visible regions.

The successful photoisomerization within crystalline \( \text{I}_{\text{out-out}} \) cannot be accounted for by the void space in the crystals, which is lowest for \( \text{I}_{\text{out-out}} \) (6.1%, compared with 6.7% and 9.8% for \( \text{I}_{\text{in-in}} \) and \( \text{I}_{\text{in-outs}} \), respectively; see Fig. S14). We note, however, that the benzopyran moieties in the crystal structures of \( \text{I}_{\text{in-in}} \) and \( \text{I}_{\text{in-out}} \) are all oriented parallel to one another, thus forming extended stacks, whereas no such stabilization is found in \( \text{I}_{\text{out-out}} \) (Fig. S14). Interestingly, subsequent cycles of UV irradiation resulted in a progressively more intense color of the UV-adapted crystals (Fig. S13a), whereas fading in the dark was in each case complete. The increasing coloration occurs concomitantly with the gradual formation of cracks (Fig. S13b), which can provide additional free space required to accommodate the large structural changes accompanying the SP \( \rightarrow \) MC isomerization. Overall, the observation that molecules as similar as the three diastereomers exhibit such contrasting behaviors in the crystalline state highlights the challenges of rationally designing reversibly photoswitching solids.

Fig. S13 shows visual changes to a small crystal of \( \text{I}_{\text{out-out}} \) upon exposure to UV light and dark adaptation. We devoted significant efforts to show the presence of the open-ring isomer of 1 by X-ray crystallography; unfortunately, the structures of all \( \text{I}_{\text{out-out}} \) crystals, including the deep-blue ones pre-exposed to intense UV light for long periods of time, were identical to those of pristine \( \text{I}_{\text{out-out}} \). These results indicate that despite the deep blue color of the UV-adapted crystalline \( \text{I}_{\text{out-outs}} \), the vast majority of molecules remained in the SP form (see also previous studies on photoinduced coloration of crystalline spiropyrans, which are not supported by crystal structures\(^{55, 56}\)).

![Fig. S13.](image)

\( \text{Fig. S13.} \) \( \text{a) Optical micrographs of crystalline } \text{I}_{\text{out-out}} \text{ undergoing reversible color changes upon UV irradiation and dark adaptation. b) Cracks that appear in the crystals of } \text{I}_{\text{out-out}} \text{ as a result of prolonged exposure to UV light.} \)
Fig. S14. Molecular packing in the crystals of 1_{in-in}, 1_{out-out}, and 1_{in-out} (all crystals comprise both enantiomers of each diastereomer). 1_{in-in}: unit cell: 3972.3 Å\(^3\); 1: 3108.2 Å\(^3\); solvent: 598.7 Å\(^3\); unoccupied volume: 265.4 Å\(^3\) (6.68%). 1_{out-out}: unit cell: 3659.4 Å\(^3\); 1: 3188.9 Å\(^3\); solvent: 246.8 Å\(^3\); unoccupied volume: 223.7 Å\(^3\) (6.11%). 1_{in-out}: unit cell: 1889.9 Å\(^3\); 1: 1581.1 Å\(^3\); solvent: 122.7 Å\(^3\); unoccupied volume: 186.1 Å\(^3\) (9.85%).

7. Supporting references

(S2) Roxburgh, C. J.; Sammes, P. G. Dyes Pigments 1995, 27, 63.