Barrierless photoisomerisation of the "simplest cyanine":
joining computational and femtosecond optical spectroscopies
to trace the full reaction path

— Supporting Information —

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1. Synthesis of 1,1’-diethyl-2,2’-pyridocyanine iodide (1122-P)

1.1 General scheme

Scheme S1: Synthesis of 1,1’-diethyl-2,2’-pyridocyanine iodide (1122-P). \( i \) EtI, \( \Delta \); \( ii \) \( n \)-propanol, 
\( \text{Et}_3\text{N} \).

The synthesis was accomplished by the following reaction sequence. \( \alpha \)-Picoline 1 and 2-iodopyridine 3 were converted to the quaternary salts (2, 4) by refluxing in the presence of ethyl iodide.\(^1\)\(^2\) The quaternary salts 2 and 4 were refluxed in \( n \)-propanol with triethylamin to obtain the dye 1,1’-diethyl-2,2’-pyridocyanine iodide 5 (1122-P).\(^3\)

1.2 Experimental details

Chloroform and ethanol were distilled. \( n \)-Propanol was dried and stored over molecular sieve (4 Å). All other reagents were used as obtained from the supplier without further purification. Purification of products was accomplished by recrystallization in ethanol/diethyl ether or by flash chromatography with silica gel 60. Thin layer chromatography was carried out with Merck Silica Gel 60 F\(_{254}\) TLC plates. HRMS were measured with LTQ-FT.

\( \alpha \)-Picoline ethyl iodide 2\(^1\)

8.0 ml (81.0 mmol) \( \alpha \)-picoline 1 and 19.5 ml (0.244 mol) ethyl iodide were refluxed for 2 hours. The remaining ethyl iodide was evaporated i. vac. and the yellow solid was recrystallised from ethanol under successive addition of diethyl ether. 16.3 g (81%) \( \alpha \)-picoline ethyl iodide 2 were obtained as a white-yellow solid.
melting point: 130°C
HRMS: calc. for [C₈H₁₂N⁺]: 122.0964 found: 122.0959

2-Iodopyridine ethyl iodide 4

5.0 g (24.4 mmol) 2-iodopyridine 3 were dissolved in 6 ml (73.2 mmol) ethyl iodide. The mixture was refluxed for 8 hours. The remaining ethyl iodide was evaporated i. vac. and the white solid was recrystallised from ethanol under successive addition of diethyl ether. 5.1 g (58%) 2-iodopyridine ethyl iodide 4 were obtained as a white solid.

melting point: 159°C
HRMS: calc. for [C₇H₉IN⁺]: 233.9774 found: 233.9765

1,1′-diethyl-2,2′-pyridocyanine iodide 5

1.0 g (4.0 mmol) α-picoline ethyl iodide 2 and 1.45 g (4.0 mmol) 2-iodopyridine ethyl iodide 4 were dissolved in 20 ml n-propanol. 1.1 ml (8 mmol) triethylamine was added and the mixture refluxed for 45 minutes. The solvent was evaporated i. vac. and the residue purified by column chromatography (ethanol:chloroform 1:4). 1,1′-Diethyl-2,2′-pyridocyanine iodide 5 was obtained as a brown oil. Purification of compound 5 by recrystallization was unsuccessful. Nevertheless the obtained optical absorption spectra of 1122-P are in excellent agreement with the results in the literature. Also we identified the product by high-resolution mass-spectroscopy.

HRMS: calc. for [C₁₅H₁₉N₂⁺]: 227.1543 found: 227.1539
2. Experimental results

**Fig. S1a** Species-associated spectra of stimulated emission (from fluorescence as in Fig. 3a) for a kinetic sequence N* → O* → 0. Black: from global analysis, red: fit by lognormal functions. Note that the second spectrum is reliable for λ ≤ 620 nm only (because the second harmonic of the gate pulse contributes a strongly fluctuating background around 650 nm). With the peak amplitudes, the intensity decay is approximated as \( I_{\text{FLUPS}}(t) = 0.897 \exp(-t/\tau_1) + 0.103 \exp(-t/\tau_2) \). The average emission time becomes \( \int_0^\infty I_{\text{FLUPS}}(t) \, dt = 0.206 \, \text{ps} \) — the same, independently, as the first time constant for the transient absorption in Fig. 2. This allows us to insert the two fixed terms \( \exp(-t/\tau_1) \) and \( \exp(-t/\tau_2) \) into the global analysis of the TA data.
Fig. S1b  Comparison of transient absorption signal (black, from excitation at 442 nm, taken from Fig. 2a) to stimulated emission (red, converted from the spontaneous fluorescence of Fig. 4). The amplitude of the latter has been scaled so that the peaks agree at 80 fs. The different TA behavior is explained by absorption from the excited state (ESA). Faint structure of stimulated emission at 80 fs (630 cm$^{-1}$ spacing) is not considered significant.
3. Computational details

The description of solvent effects on excited-state properties through continuum models is usually performed in one of two limit time-regimes, referred to as nonequilibrium (neq) and equilibrium (eq). In the neq case, only solvent electronic polarization (fast solvent degrees of freedom) is in equilibrium with the excited state electronic density of the solute, whereas nuclear degrees of freedom (slow solvent degrees of freedom) remain equilibrated with the ground state electron density. On the contrary, in the eq regime it is assumed that both fast and slow degrees of freedom are equilibrated with the excited state electron density. In the PCM formalism the solvent reaction field in the neq regime depends on the dielectric constant at optical frequency \( \varepsilon_{\text{opt}} = n^2 \) where \( n \) is the solvent refractive index; for methanol \( \varepsilon_{\text{opt}} = 1.776 \). PCM eq solvation is instead ruled by the static dielectric constant, \( \varepsilon = 32.613 \) for methanol. Neq solvation energies are more appropriate to simulate the vertical excitation and to discuss the fast part of the excited state dynamics (time after photoexcitation <200 fs), whereas the eq time regime can better model the excited state properties for the slower part of the excited state dynamics (time after excitation >1 ps).

In this work excited-state optimizations in methanol have been performed by using the “standard” LR (linear-response) implementation of PCM/TD-DFT, for which analytical gradients are available. LR-PCM/TD-DFT excitation energies are computed without using the true excited state electron density. According to our previous studies LR model provides an accurate estimate of solvent effect on bright transitions and reliable excited state equilibrium geometries. At variance, the State-Specific (SS) implementation of PCM/TD-DFT is based on a fully variational formulation of the solvent effect on the excited state properties, and it solves a different effective Schrödinger equation for each electronic state of interest. SS implementation provides a more balanced description of solvent effects than LR-PCM, especially when dealing with transitions (like the CT ones) involving large changes of the electron density.

The continuum solvent model adopted in this work cannot describe the intermolecular hydrogen bonds between methanol and 1122-P. By including explicit solvent molecules in calculations of a thiacyanine, we showed that these interactions should not affect the properties and photodynamics of the dye molecule seriously. The multi-determinantal nature of the first excited state of cyanines, is a challenge for TD-DFT calculations. In our case, it is comforting that PBE0 and B3LYP functionals provided an accurate description of the FC region of a thiacyanine and a qualitatively correct picture of its isomerization path. On the other hand, neither these functionals nor CAM-B3LYP are able to reproduce the effect of chain lengthening in cyanine derivatives. This failure, however, should not be serious for a short-bridge cyanine like 1122-P.
4. Computational results

**minS0-trans (C2 symmetry)**

\[ \phi(2-7-2'-3') = \psi(2'-7-2-3) = 24.0^\circ \]

**minS1-trans**

\[ \phi(2-7-2'-3') = \psi(2'-7-2-3) = 30.5^\circ \]

**minS1**

\[ \phi(2-7-2'-3') = 1.3^\circ ; \psi(2'-7-2-3) = 90.8^\circ \]

**Fig. S2** Minima of 1122-P in methanol at the LR-PCM//CAM-B3LYP/6-31G(d) level of theory
The results in gas phase, reported in Fig. S3, are similar to those obtained in methanol according to LR theory (and also given in Fig. 9 in the main text). The only significant difference is seen in the $C_1$ MEP: one finds a stronger tendency to remove $C_2$ symmetry. While in methanol, the $C_1$ and $C_2$ MEPs remain very close in a narrow but well-defined range of $\psi$ values ($25^\circ$–$35^\circ$), in the gas phase they come close only at $\psi=25^\circ$. Even for this value of $\psi$, the $C_1$ structure is slightly more stable. It
is also non-symmetric, as can be noticed clearly by the $S_0$ energy, which is much higher, and by the $S_1/S_0$ oscillator strength, which is much lower.

4. 1Comparison of trans, cis, and d-cis spectra according to FC|VG model

To achieve a robust and safe comparison of the spectra, not depending on discreetional choices on how to obtain representative stationary points on the excited-state PES, we resorted to the simple FC|Vertical Gradient (VG) model. It assumes that the normal modes and frequencies of the final state (of the electronic transition) are equal to those of the initial state, and geometry displacements are estimated on the ground of the final state PES gradient at the equilibrium geometry of the initial state. Furthermore, Herzberg-Teller effects are neglected (after checking that they are very weak). By theory in this model, the first moment of the spectrum, i.e the average transition energy, coincides with the vertical transition energy.

Electronic results are reported in Table 1 and 2 that compare the CAM-B3LYP results already given in Table 1 and 2 in the main text with B3LYP ones. The corresponding spectra are given in Fig. S4.
Table 1  Energies (eV) of trans, cis, and dcis isomers on S₀ PES optimized in methanol by CAM-B3LYP and B3LYP, and trans, dcis and minS₁ stationary points on S₁ PES optimized in methanol at LR-PCM// CAM-B3LYP level. S₁ energies in nonequilibrium regime. When equilibrium regime values are given, they are reported in italics.

<table>
<thead>
<tr>
<th>Structure</th>
<th>CAM-B3LYP</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6-31G(d)</td>
<td>6-311+G(2d,2p)</td>
</tr>
<tr>
<td></td>
<td>E (S₀)</td>
<td>E(S₁)</td>
</tr>
<tr>
<td>minS₀-trans</td>
<td>0.0</td>
<td>3.247</td>
</tr>
<tr>
<td>minS₁-trans</td>
<td>0.184</td>
<td>3.097</td>
</tr>
<tr>
<td>minS₀-cis</td>
<td>0.176</td>
<td>3.401</td>
</tr>
<tr>
<td>minS₀-dcis</td>
<td>0.366</td>
<td>3.527</td>
</tr>
<tr>
<td>minS₁-dcis</td>
<td>0.831</td>
<td>3.129</td>
</tr>
</tbody>
</table>

Table 2  trans, cis and dcis vertical excitation energies (eV) in nonequilibrium (neq) and equilibrium(eq) regimes

<table>
<thead>
<tr>
<th>Structure</th>
<th>CAM-B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6-31G(d)</td>
</tr>
<tr>
<td></td>
<td>LR neq</td>
</tr>
<tr>
<td></td>
<td>(0.76)</td>
</tr>
<tr>
<td></td>
<td>(0.66)</td>
</tr>
<tr>
<td></td>
<td>(0.593)</td>
</tr>
</tbody>
</table>

| B3LYP |
|       | 6-31G(d)  | 6-311+G(2d,2p) |
|       | LR neq    | LR eq | SS neq | SS eq | LR neq | LR eq | SS neq | SS eq |
| minS₀-trans | 3.049      | 2.863 | 3.111 | 3.081 | 2.991 | 2.803 | 3.043 | 3.007 |
|            | (0.55)     | (0.80) | (0.42) | (0.41) | (0.56) | (0.83) | (0.41) | (0.40) |
| minS₀-cis   | 3.022      | 2.848 | 3.074 | 2.897 | 2.960 | 2.782 | 3.043 | 3.007 |
|            | (0.50)     | (0.72) | (0.37) | (0.245) | (0.49) | (0.74) | (0.49) | (0.40) |
| minS₀-dcis  | 2.979      | 2.811 | 3.049 | 3.027 | 2.896 | 2.731 | 2.957 | 2.927 |
|            | (0.45)     | (0.67) | (0.34) | (0.34) | (0.43) | (0.67) | (0.32) | (0.31) |

Oscillator strength in parentheses.
Fig. S4  Absorption spectra of the three isomers computed with the FC|VG model. The solvent is treated in the equilibrium (eq) and nonequilibrium (neq) regimes. Geometrical displacements were estimated from excited state energy gradients computed at the LR-PCM level, with the functional and basis set indicated. For SS spectra, excitation energies and transition dipole moments (but not energy gradients) were refined at the SS-PCM level. When two sets of data (dashed and solid lines) are given, the dashed lines report eq spectra and solid lines neq spectra.
4.2 Assignments of Raman bands.

The assignment of Raman bands gives rise to interesting speculations. For the \textit{trans} species, the strongest peaks (535, 640, 1305, 1340, 1665 cm\(^{-1}\)) are all related to symmetric motions of the two pyrido rings (modes 18, 23, 52, 54, 69, sketched in \textbf{Fig S6}), which describe the motion between the two symmetric minS\(_{0\text{-}trans}\) and minS\(_{1\text{-}trans}\) structures. To the contrary, for the \textit{cis} species, the main bands calculated at 1230 and 1350 cm\(^{-1}\) correspond to vibrations with a strong component from bending of the central CH bond, coupled with ring motions. One may speculate that bands involving such CH bending are also responsible for the low-frequency peaks of the multiplet in the 1200-1300 cm\(^{-1}\) region, observed for \textit{trans} species but not reproduced by calculations. Actually, according to the latter, modes involving this bending do exist for \textit{trans} but they are dark to vRR (at VG level) since they remove the C\(_2\) symmetry. Their observation in experiment suggests either a fast overcoming of the C\(_2\) barrier along the MEP, or else the operation of the second C\(_1\) path competitive with the one depicted in \textbf{Fig 7a}, that does not pass through minS\(_{1\text{-}trans}\). Moreover, the higher-frequency mode has a localized character, showing a stronger contribution of displacements in the pyridine ring whose C-CH\(_3\) bond points in the opposite direction with respect to the central C\(_7\)-H bond (the right ring in \textbf{Fig. 6}, top left). Therefore these modes are related to the asymmetrization of the two pyrido rings which eventually leads to the minS\(_1\) structure. As such their nature is quite different from the modes of the calculated \textit{trans} spectrum in the same frequency region.

RR activity in the low-frequency region 30-400 cm\(^{-1}\) is instructive as well. The long-time transient signal of \textit{cis} species shows bands in this region which are significantly more intense and broader than those of the \textit{trans} isomer. This feature is qualitatively captured by the VG simulation and can be attributed to the fact that, while the S\(_1\) PES in the \textit{trans} isomer region shows a plateau along \(\psi\) and \(\phi\) dihedrals, and therefore no strong acceleration along twisting modes, no such plateau exists in the \textit{cis} region and the system is immediately accelerated toward the global minimum structure minS\(_1\).
Fig. S5  Franck-Condon vibrational Raman spectra of the trans isomer of Me-1122-P, upon S₀ → S₁ resonance. They were computed with different models and at different level of electronic theory. In the AH model the transition polarizability tensor is computed explicitly, taking into account Duschinsky rotation. The VG and AS models assume the same normal modes and frequencies for S₀ and S₁. They predict relative vRR intensities from the S₁ gradient (computed explicitly at the ground equilibrium geometry, VG, or estimated from the displacements obtained by S₁ geometry optimization, AS). When not stated differently, the CAM-B3LYP functional was used. “Scaled” indicates that calculated harmonic CAM-B3LYP/6-31G* frequencies have been multiplied by 0.96. Both anharmonic corrections and frequency scaling were applied by simply shifting the bands (leaving intensities unaffected).
Fig. S6  Franck-Condon VG vibrational Raman spectra in resonance with the $S_0 \rightarrow S_1$ transition of the trans isomer of Me-P. The main bands are fundamental transitions of the sketched modes.
Franck-Condon VG vibrational Raman spectra in resonance with the $S_0 \rightarrow S_1$ transition of the *cis* isomer of Me- , computed at different level of electronic theory. When not stated differently the CAM-B3LYP functional has been applied. “Scaled” indicates that calculated harmonic CAM-B3LYP/6-31G* frequencies have been multiplied by 0.96. Both anharmonic corrections and frequency scaling were applied by simply shifting the bands (leaving intensities unaffected).
Fig. S8  Franck-Condon VG vibrational Raman spectra in resonance with the $S_0 \rightarrow S_1$ transition of the cis isomer of Me-1122-P. The main bands are fundamental transitions of the sketched modes.
Fig. S9  Franck-Condon VG vibrational Raman spectra in resonance with the $S_0 \rightarrow S_1$ transition of the double-cis isomer of Me-1122-P, computed at different level of electronic theory. Conditions and labelling as in Fig. S7.
**Fig. S10** Raman spectra in resonance with the $S_0 \rightarrow S_1$ transition: comparison of experimental SAS spectra with Franck-Condon VG vibrational Raman spectra. The latter were computed for the trans, cis and d-cis isomers of Me-1122-P at harmonic CAM-B3LYP/6-31G* level, and harmonic frequencies have been multiplied by 0.96.
4.3 Assignments: mapping experimental transients to regions of the minimum energy path.

4.3.1 Simulation of the spectral evolution

$V_i^{(X)}(\psi)$ denotes the potential energy of state $i$, calculated for a fixed angle $\psi$, and with all other nuclear coordinates relaxed in state $X$. In formulas, angles are assumed to be measured in radian. But for visualisation, specific values will also be reported in degrees.

The starting distribution $P_{i=0}(\psi=\phi)$ is prepared in the electronic ground state. For the symmetrical state minS$_0$-trans, we calculate a frequency $\tilde{\nu}_{\text{torsion}} = 55 \text{ cm}^{-1}$ for the normal mode which comes closest to the conrotatory motion $\Delta\phi = \Delta\psi$. The moment-of-inertia for this torsional motion is estimated to be $m = 133.9$ amu Å$^2$. Thus we have

$$\frac{1}{\hbar c} \frac{1}{2} 3003.6 (\psi - 0.386)^2.$$

(1)

Assuming a temperature of 300 K, the corresponding Boltzmann distribution $P_{i=0}(\psi=\phi)$ is centered at 22.1° and has FWHM of 17.8° (see Fig. 7b).

After electronic excitation, evolution along the C$_2$ path (see text) leads to minS$_1$-trans which has $\phi=\psi=29.7^\circ$. From here the C$_1$ path is assumed until minS$_1$ is reached at $\psi=86.1^\circ$ (where $\phi=2.1^\circ$).

The composite potential energy curve is described as follows:

$$\frac{1}{\hbar c} \frac{1}{2} (U_A + U_B) - \frac{1}{2} \sqrt{(U_A - U_B)^2 + 4w^2}$$

(2)

$$U_A = \frac{1}{2} k_A (\psi - \psi_A)^2 + g_A$$

and

$$U_B = \frac{1}{2} k_B (\psi - \psi_A)^2 + g_B$$

(3)

where $\psi_A = 0.4701$, $k_A = 26099$, $g_A = 25458$ and $\psi_B = 1.559$, $k_B = 6807$, $g_B = 23151$, with $w=974$.

Seen from the composite path mentioned above, the potential energy $V_0^{(SI)}(\psi)$ of the ground state is described by Eqs. 2 and 3 but with the following parameters: $\psi_A' = 0.391$, $k_A' = 37699$, $g_A' = 1282$, and $\psi_B' = 1.258$, $k_B' = 3374$, $g_B' = 6215$, with $w' = 696$. 

The oscillator strength for emission, \( f(\psi) \) (Fig. 7a) is here given for regularly-spaced \( \psi \) values:

\[
\begin{array}{ccccccccccccccc}
\psi & 0.0 & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 & 0.6 & 0.7 & 0.8 & 0.9 & 1.0 & 1.1 & 1.2 & 1.3 & 1.4 & 1.5 \\
f: & 0.730 & 0.718 & 0.703 & 0.682 & 0.658 & 0.625 & 0.585 & 0.454 & 0.226 & 0.137 & 0.078 & 0.043 & 0.027 & 0.016 & 0.008 & 0.006 \\
\end{array}
\]

The Smoluchowski-equation governs diffusional motion of a distribution \( P_t \) as follows

\[
\dot{P} = -\mathcal{S} \cdot P
\]

with the Smoluchowski-Operator\(^{21}\)

\[
\mathcal{S} = -\frac{1}{\gamma m} \left\{ k_B T \frac{\partial^2}{\partial \psi^2} + \left( \frac{\partial V}{\partial \psi} \right) \frac{\partial}{\partial \psi} + \left( \frac{\partial^3 V}{\partial \psi^3} \right) \right\}
\]

Here \( \gamma \) is the friction rate constant \([s^{-1}]\) and \( m \) the effective mass. In the current case of torsional motion, the dynamical coordinate \( q \equiv \psi \) [rad] and therefore \( m \equiv \text{moment-of-inertia} \). For the minS\(_1\)-trans structure, \( m \) corresponds to 139.02 amu Å\(^2\). The potential energy becomes \( V(q) \equiv V_{0}^{S_1}(\psi) \) from above. Furthermore T=300 K is assumed also for the evolution in \( S_1 \). We find below that \( \gamma=4.42 \text{ ps}^{-1} \) describes best the observed decay and shift of the emission spectrum (Fig. 3a).

For numerical solutions we consider the range \( q_{\min} = -0.5 \ldots q_{\max} = +2.25 \) and use a virtual harmonic oscillator. This allows to cast all operators into matrix form. A basis set of \( n=200 \) vibrational wavefunctions is centered in the range, and the \( n \)th virtual vibrational state is adjusted to have classical turning points at \( q_{\min}, q_{\max} \). The coordinate \( q \) and the spatial derivative \( \partial / \partial q \) are each represented by a band matrix. At the eigenvalues \( q_i \) the potential is sampled, and with this \( V \) can be represented conveniently.\(^{22}\) Note that \( \mathcal{S} \) is non-normal because of the second term in eq. (5). Consequently its eigenvectors are not orthonormal. Even though, they may be used to express the general propagator \( \exp\{-\mathcal{S} \cdot t\} \). If this \( n \times n \) matrix is applied to the expansion coefficients of \( P_{t=0}(q) \), then the coefficients of \( P_t(q) \) are obtained.
References

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