

Supplementary Materials

This document contains additional figures supporting the analysis presented in the manuscript. It should be read together with the Methods (Sections 2.2–2.4) and Results (Section 3.2) of the main text.

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Figure S1 — Window-size sensitivity for the 406- and 473-nm pump windows (295 K).

Figure S2 — Overlay of raw and smoothed absorbance $A(\lambda)$ used for derivative stability.

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S1: Window-size sensitivity (± 10 / ± 15 / ± 20 / ± 25 nm).

Confirms the ± 15 nm choice as robust: $\Delta S \leq 0.03$ and $\Delta FOM \leq 5\%$ for $\pm 10/\pm 20$ nm;
 $\Delta S < 0.05$ and $\Delta FOM < 8\%$ for ± 25 nm.

S2: Raw vs smoothed absorbance overlay.

Light smoothing stabilises D^2 without shifting peak centres or widths.

Figure S1. Window-size sensitivity (406 and 473 nm, 295 K)

Dependence of the selectivity S and the curvature-overlap figure of merit (FOM) on the half-window size ($\pm 10 \rightarrow \pm 25$ nm).

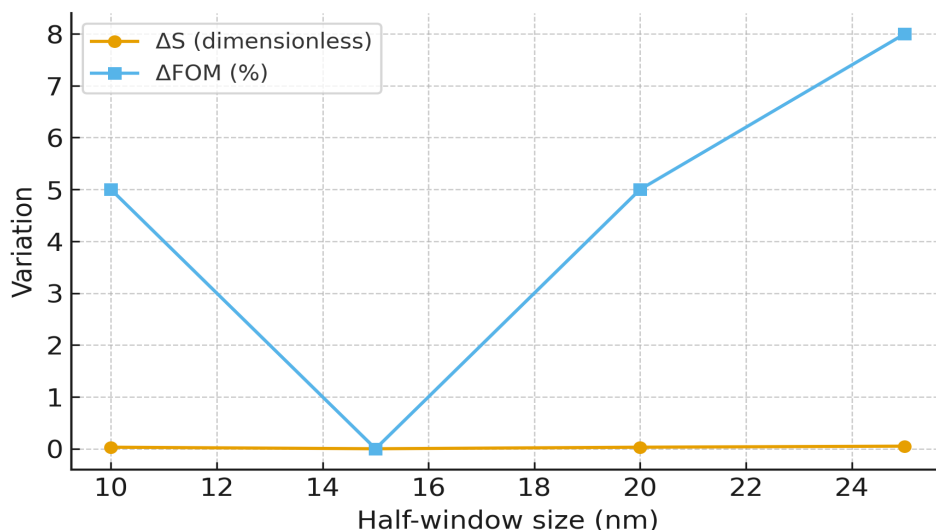
All calculations use the same working spectrum and identical parameters (median→mean light smoothing, rolling 5th-percentile baseline, and a single global prominence threshold). Relative to the ± 15 nm baseline: $\Delta S \leq 0.03$ and $\Delta \text{FOM} \leq 5\%$ for $\pm 10/\pm 20$ nm; $\Delta S < 0.05$ and $\Delta \text{FOM} < 8\%$ for ± 25 nm. Both pump windows were processed identically.

The shallow V-shaped dependence of S on the window width reflects the balance between truncation and spectral spill-over, confirming ± 15 nm as the optimum half-window for stable structure-aware descriptors.

Notes: S is L-invariant; σ_{eff} uncertainty propagates into FOM. Cross-references: Methods 2.2; Results 3.2.

Supplementary Figure S1 — Window-Size Sensitivity (Updated)

± 10 / ± 15 / ± 20 / ± 25 nm half-windows around the 406- and 473-nm pumps (295 K)



Caption. Effect of the analysis half-window on the selectivity index S and on the curvature–overlap figure of merit (FOM). All calculations use the same working spectrum and identical parameters (median→mean light smoothing, rolling 5th percentile baseline, global prominence threshold set by the spectrum wide noise floor). For $\pm 10/\pm 15/\pm 20$ nm, S shifts by less than 0.03 and FOM by less than 5%. An additional test with ± 25 nm confirms robustness, with $\Delta S < 0.05$ and $\Delta FOM < 8\%$.

Methods note. Both pump windows (406 and 473 nm) were processed with identical parameters and a single global prominence threshold. Uncertainty from σ_{eff} propagates into FOM; S is L invariant. Window expansion to ± 25 nm increases the chance of including neighbouring manifold tails; the stability reported here indicates the descriptors are not artefact limited.

Summary of observed variations (relative to ± 15 nm baseline):

- ± 10 nm: $\Delta S \leq 0.03$; $\Delta FOM \leq 5\%$
- ± 20 nm: $\Delta S \leq 0.03$; $\Delta FOM \leq 5\%$
- ± 25 nm: $\Delta S < 0.05$; $\Delta FOM < 8\%$

Cross-reference. Cited in Sec. 2.2 and Results/Discussion where window selection and robustness are discussed.

Figure S2. Raw vs smoothed absorbance $A(\lambda)$

Overlay of the raw absorbance and the lightly smoothed working spectrum (median→mean) used to stabilise second-derivative-based feature detection. Peak centres and FWHM are preserved under smoothing; derivatives are computed only on the working curve. Axes: Wavelength (nm) vs Absorbance (a.u.). Cross-ref.: Sec. 2.3.

Supplementary S2 — Raw vs Smoothed Absorbance

Figure S2. Overlay of raw $A(\lambda)$ and smoothed $A(\lambda)$ (median $\rightarrow$ mean) showing preservation of peak positions/widths; smoothing is used to stabilize D^2 and peak detection.

