Designing Refractive Index Fluids using the Kramers–Kronig Relations

– Supplementary Information –

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Materials and methods

Materials

The four dyes Brilliant Blue, Allura Red, Pyranine and Quinoline Yellow were purchased from fastcolours.com. Their chemical structures and IUPAC full names are given in Fig. S1. Stock solutions with concentrations of 600 mM for Brilliant Blue and 300 mM for the other dyes were prepared and subsequently diluted to lower concentrations. The absorption of those dyes in the visible range is mainly due to the resonance among the benzene rings and double bonds in the structures*.

Optical characterization

Transmittance spectra were recorded using a spectrometer (Maya Pro, Ocean Optics) with a wavelength range from 250 – 1000 nm. The dye solutions were filled into a quartz cuvette with a 1 cm light path and then placed into a Thorlabs CVH100 cuvette holder, which has two fiber adapters on opposite sides. Light from a halogen/deuterium or a xenon light source (DHL-Bal or HPX-2000, both Ocean Optics) passes through the sample and is guided into the spectrometer via optical fibres with a 200 μm diameter (QP200-2-SR-BX, Ocean Optics). A water-filled cuvette was used as reference.

Assuming a small extinction coefficient $\kappa \ll n$, the absorption coefficient α is experimentally measured through application of the Beer-Lambert law

$$\frac{I(\lambda)}{I_0(\lambda)} = e^{-i\alpha(\lambda)d}, \qquad \text{(S1)}$$

with I, I_0 the transmitted intensities of light after passing through a dye solution of thickness d and a dye-free reference, respectively. The molar absorption coefficient is then defined as

$$\varepsilon(\lambda) = \frac{\alpha(\lambda)}{c_\mathrm{d}}, \qquad \text{(S2)}$$

where c_d is the molar concentration of the dye. The relation to the extinction coefficient κ is given by eqn (4).

Refractive index measurements

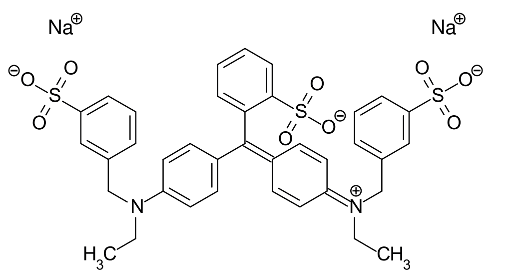
The refractive index dispersion was measured with an optical ellipsometer (alpha-se, JA Wollam). For this, the liquid was deposited onto rough, frosted glass slides (Marienfeld) and the dielectric function was extracted as described previously by Synowicki *et al.*[21].

The refractive index of the fluids was additionally assessed with an automatic refractometer (Abbemat MW, Anton-Paar) at six discrete wavelengths (455.0 nm, 488.0 nm, 513.3 nm, 533.1 nm, 589.3 nm and 644.2 nm), with a RI range of 1.30 - 1.72 nD and an accuracy of ±0.00004 nD.

dye	A	B [nm^2]
Brilliant Blue	0.064 ± 0.008	0
Allura Red	0.062 ± 0.004	511 ± 25
Pyranine	0.0143 ± 0.001	946 ± 31
Quinoline Yellow	0.0393 ± 0.003	2258 ± 69

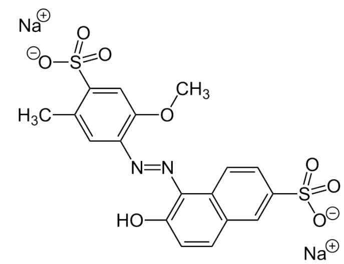
Table S1 Fit parameters A, B, determining $n_\mathrm{Cd}(\lambda)$ according to eqn (5) for the four dyes.

* A. Gürses, M. Açıkyıldız, K. Güneş, Kübra and M. S. Gürses, Dyes and Pigments, Springer, 2016, pp. 31–45.



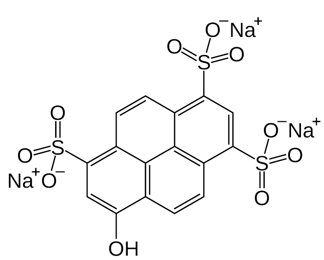
Brilliant Blue FCF

Disodium;2-[[4-[ethyl-[(3-sulfonatophenyl)methyl]amino]phenyl]-[4-[ethyl-[(3-sulfonatophenyl)methyl]azaniumylidene]cyclohexa-2,5-dien-1-ylidene]methyl]benzenesulfonate



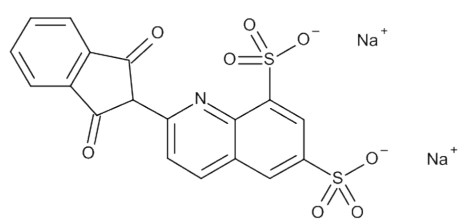
Allura Red AC

Disodium 6-hydroxy-5-[(2-methoxy-5-methyl-4-sulfonatophenyl)diazenyl]naphthalene-2-sulfonate



Pyranine

Trisodium 8-hydroxypyrene-1,3,6-trisulfonate



Quinoline Yellow WS

Sodium 2-(1,3-dioxoindan-2-yl)quinolinedisulfonate

Fig. S1 Chemical structures and IUPAC names of the dyes used in this study

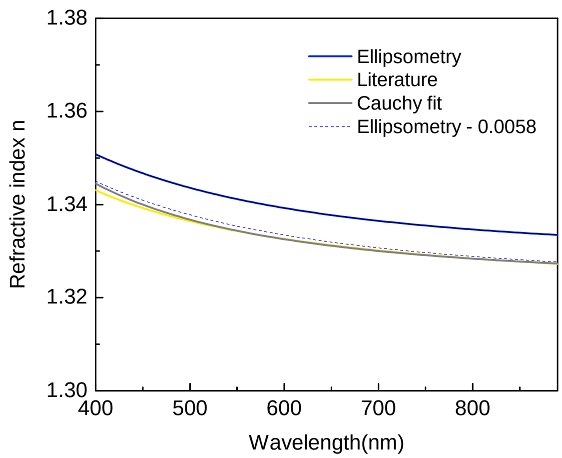


Fig. S2 Ellipsometry measurement of the refractive index of water, in comparison with literature values. In this study, a Cauchy fit (eqn (5)) was used to account for the spectral variation of the refractive index of water. Despite the close agreement of the dispersion curve from literature and the ellipsometry measurements, an offset of 0.0058 was deducted from all ellipsometry measurements to account for the discrepancy found in this measurement.

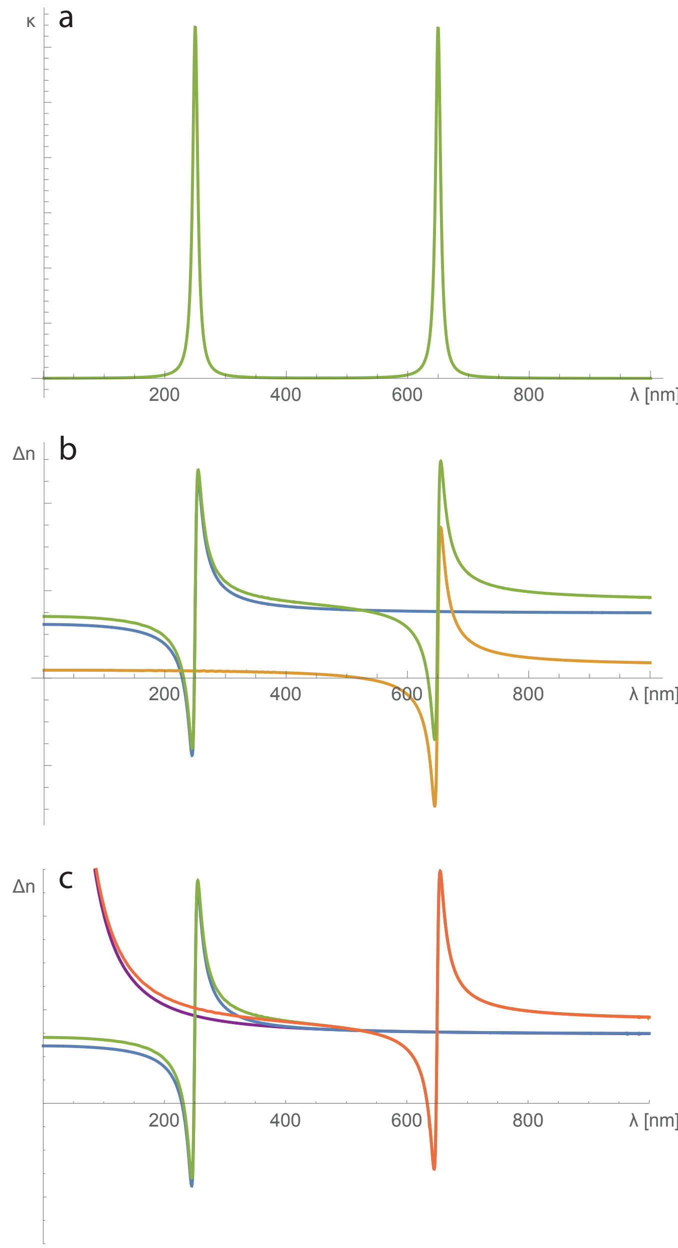


Fig. S3 Model calculations illustrating the additivity of the results of eqn (2). (a) Hypothetical extinction spectrum consisting of two Lorentz distributions centred at 250 nm and and 650 nm. (b) The integration of eqn (2) of extinction spectra containing each peak separately result in the orange and blue lines, which were added to yield the green spectrum. This resulting green spectrum is indistinguishable from the one stemming from an integration employing the double-peak spectrum. In (c) the Cauchy equation eqn (5) was fitted to the blue spectrum for wavelengths greater than 400 nm, resulting in the purple line. The addition of this Cauchy spectrum with the orange line in (b) (resulting from the Kramers-Kronig integration of only the right peak) gives rise to the red line in (c), which approximates the exact spectrum (green line) very closely for wavelengths above 400 nm.

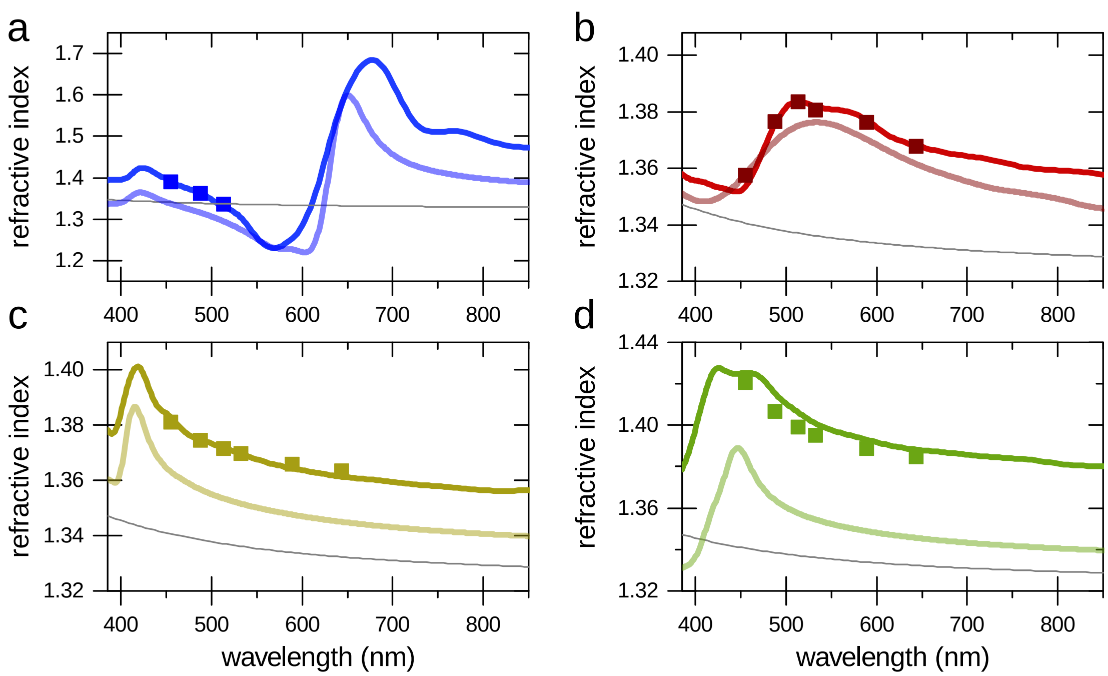


Fig. S4 Refractive index data from Fig. 2 (solid lines) and the predictions of Kramers-Kronig relation n_{KK} (light coloured lines). In the calculation of n_{KK} only the Cauchy correction for water n_{Cw} was taken into account and the final Cauchy fit was omitted ($n_{\mathrm{Cd}} = 0$, see text).